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Modification of Ntezi Bentonite Structure by Hydrochloric Acid: Process Kinetics and Structural Properties of the Modified Samples

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Abstract. Bentonite from Ntezi was modified by reacting it with different concentrations of hydrochloric acid solutions. The modified samples were analysed by x-ray fluorescence. The kinetics of the modification reaction was studied by performing the experiment at different temperatures and times. Results of the analysis of the modified samples showed that the octahedral cations were removed which altered the chemical composition of the bentonite. The surface area and adsorptive capacity of the bentonite were improved after the modification. The kinetic studies showed that the acid modification reaction is controlled by the product layer diffusion and can be represented by $[1\text{-}(1\text{-}X)^{1/3}]^2 = k\ t$; where, X is the fraction of the bentonite dissolved at time t. The activation energy was determined to be 24.98 kJ/mol.

Keywords: adsorption, bleaching, activation, kinetic model, chemical treatment, bentonite

Introduction

Natural clays are acquiring prominence as low-cost adsorbent over the past few decades due to their local and abundant availability and capability to undergo modification. The use of these natural clays is hampered by the presence of net negative charge on the surface and small surface area and these factors have led to the need for research and development in the field of modification of clay surfaces to enhance their adsorptive properties.

Clay minerals vary in their chemical composition and this leads to varying mineralogical properties that include: layer charge, cation exchange capacity, adsorption capacity and morphology (Steudel *et al*., 2009). Due to the large chemical composition variability, clay minerals are used in different industrial applications such as ceramics, food, chemical and paper industries. Sometimes, the clay minerals are used in their natural state and at other times after some specific modification (Komadel, 2003). One of such modification methods is acid treatment. Acid activation of clay mineral has been studied for years by many researchers (Steudel *et al*., 2009; Vicente-Rodriguez *et al*., 1994a; Suarez *et al*., 1992; Cetisli and Gedikbey, 1990; Bonilla *et al*., 1981; Rodriguez-Reinoso *et al*., 1981; Abdul-Latif and Weaver, 1969). Different types of acid treatment have been described in the literature, varying from each other by the nature of the acid used, temperature, and intensity and time of the attack. Acid treatment of clay minerals, namely fibrous clays (Myriam *et al*., 1998; Suarez-Barrios *et al*., 1995; Vincente Rodriguez *et al*., 1995, 1994a), smectites (Suarez *et al*., 2001; Prieto *et al*., 1999; Vincente Rodriguez *et al*., 1994b) and Kaolinite (Belver *et al*., 2002) is widely applied in order to optimise their physicochemical behaviour, aiming better industrial properties. Xianzhen and Chuyi (1990) have done acid treatments with sepiolite, concluding that the silica obtained could be competitive in different industrial ways, with that obtained by precipitation. The acid treatment of clay minerals is usually referred to as acid activation, because it increases the specific surface area and the number of active sites of the solids. This treatment modifies the surfaces of clays by disaggregations of particles, possible elimination of mineral impurities and removal of metal-exchange cations. The common commercial use of acid-treated clay minerals is bleaching or decolourations of oils (Christidis *et al*., 1997; Srasra *et al*., 1989; Taylor *et al*., 1989; Kheok and Lim, 1982) and in general in the fields of adsorption and catalysis (Mokaya and Jones, 1995; Fahn and Fenderl, 1983).

Two types of octahedral sheets occur in clay minerals: dioctahedral, where two-thirds of the octahedral sites are occupied by trivalent cations, such as Al^{3+} or Fe^{3+}; and the trioctahedral type, mostly occupied by divalent cations, such as Mg^{2+}; the negative charge of the layers is balanced by hydrated exchangeable cations in the

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interlayers, mostly Ca^{2+}, Mg^{2+}, and Na^+ (Tomic *et al*., 2011; Tyagi *et al*., 2006). Acid modified natural bentonite are the subject of many researchers (Amari *et al*., 2010; Madejova *et al*., 2009; Steudel *et al*., 2009; Venaruzzo *et al*., 2002; Bergaya and Lagaly, 2001). The first step in modifying the clay mineral structure with acid is a separation of exchangeable cations from protons. The second step is flushing Al, Mg, and Fe from octahedral and tetrahedral sheets, in a way that SiO_4 groups of tetrahedral sheets remain mostly intact.

In this work, hydrochloric acid modification of bentonite from Ntezi was carried out to increase the surface area and adsorption capacity and also to investigate the structural changes that occurred in the modified samples. Special emphasis was paid to the kinetics of the modification process to study its mechanism.

Materials and Methods

Bentonite samples were mined from the site, dried and grinded to 0.212 mm particle size. These samples were reacted with different concentrations (2, 4, 6, 8, 10, and 12 mol/L) of hydrochloric acid solution. Ten grams of the sized fraction was reacted with already determined volume of the acid solution in a 250 mL bottomed flask and heated to a fixed temperature of 70 °C, while, on a magnetic stirring plate stirring was continued throughout the reaction duration. After completion of the reaction time, the suspension was immediately filtered to separate undissolved materials, washed three times with distilled water. The resulting solutions were analysed for aluminum, magnesium and iron ions using MS atomic absorption spectrophotometer (AAS 4000 Perkin Elmer). The residue was washed to neutrality with distilled water, air dried and oven dried at 80 °C and labeled as NZ0, NZ2, NZ4, NZ6, NZ8, NZ10, and NZ12, where, the numbers denote the acid concentration used in the activation process. To study the kinetics of the dissolution process of the octahedral ions-aluminum, magnesium and iron, the activation was repeated at different times (1 to 6 h) and at different temperatures (70 to 120 °C).

The chemical compositions and intensity change of absorption bands of the solid residues were determined by x-ray fluorescence (XRF, Philips PW 2400) and fourier transforms infrared (FTIR, Shimadzu S8400) spectroscopy, respectively. The surface area of the natural and treated samples were determined using the method of ethylene glycol monoethyl-ether (EGME) as developed by Carter *et al*. (1986; 1965), while, the cation exchange capacity (CEC) was determined using the method of Inglethorpe *et al*. (1993) which involves centrifuging a mixture of few grams of clay with solution of buffered barium chloride for hours and discarding the supernatant, adding distilled water and solution of magnesium sulphate, then titrating the mixture with EDTA.

The bleaching capacity of the natural and acid activated clay samples was investigated by using them to bleach palm oil. About 5 g of each sample was reacted with refined palm oil and heated to 80 °C for 30 min. At the completion of the reaction time, the oil was filtered and the bleaching efficiency was determined by measuring the colour of the bleached oils using a uv-vis spectrophotometer (Shimadzu UV mini 1240) at wavelength of 450 nm.

Results and Discussion

Chemical composition of bentonite samples. The chemical composition of the natural and treated bentonite samples are shown in Table 1. The content of SiO_2 was observed to increase as the acid concentration increased up to 10 mol/L and decreased with further increase in acid concentration. This could be due to the formation of mullite which protects the clay layers from further acid attack. The contents of the octahedral cations (Al_2O_3, Fe_2O_3 and MgO) decreased intensely as the acid concentration increased and they were increased with further attack after 10 mol/L concentration (Table 1). The behaviour shown by the Al_2O_3, Fe_2O_3, and MgO contents with progressive acid treatment is related to the progressive dissolution of the clay mineral. The octahedral sheet destruction passes the cations into the solution, while, the silica generated by the tetrahedral sheet remains in the solid phase due to its insolubility (Dias *et al*., 2003). Pesquera *et al*. (1992) suggest that this free silica generated by the initial destruction of the tetrahedral sheet, is polymerised by the effect of such high acid concentration and is deposited on the undestroyed silicate fractions, thereby protecting it from further acid attack (Vicente-Rodriguez *et al*., 1994a; Srasra *et al*., 1989).

Surface area of the activated bentonite. The acid activation was carried out with hydrochloric acid concentration range from 2 mol/L to 12 mol/L. Pushpaletha *et al*. (2005) reported that the surface area of acid activated bentonite generally increases with increase in acid concentration until a maximum surface area is reached after which it gradually decreases. In this study, the surface area was observed to increase with increase

Table 1. Chemical composition and Si/(Al + Fe + Mg) of natural and HCl modified bentonite from Ntezi

Chemical composition	Clay samples						
	NZ0	NZ2	NZ4	NZ6	NZ8	NZ10	NZ12
Al_2O_3	16.54	13.87	10.23	7.09	5.94	2.41	2.88
SiO_2	54.72	59.93	65.84	69.75	72.53	75.61	75.09
Fe_2O_3	13.23	10.14	8.06	5.04	3.78	2.17	2.23
CaO	0.41	0.35	0.21	0.12	0.04	0.01	0.01
MgO	7.10	5.36	3.19	2.16	1.49	0.52	0.54
K_2O	0.35	0.16	0.09	0.03	0.01	0.01	0.01
TiO_2	1.24	0.93	0.68	0.48	0.27	0.14	0.06
Na_2O	0.04	0.02	0.01	0.01	0.01	0.001	0.001
ZnO	0.89	0.57	0.38	0.19	0.11	0.04	0.02
LOI	5.28	3.85	3.16	2.42	1.94	1.65	1.11
Total	99.80	95.18	91.85	87.29	86.12	82.561	81.951
Si/(Al + Fe + Mg)	1.48	2.04	3.07	4.88	6.47	14.83	13.29
Bleaching efficiency (%)	38.9	54.97	62.87	69.82	77.45	91.64	84.06
Surface area (m^2/g)	97	136	169	197	245	297	275

in acid concentration from 2 mol/L to 10 mol/L. A maximum surface area was obtained with 10 mol/L HCl as shown in Fig. 1. This increase in surface area with rise in acid concentration is attributed to the removal of impurities, replacement of exchangeable cations such as K^+, Na^+ and Ca^{2+}, with hydrogen ions and leaching out of Al^{3+}, Fe^{3+} and Mg^{2+} from the octahedral and tetrahedral sheets which expose the edges of the platelets (Tsai *et al*., 2007). The decrease in the surface area with further increase in acid concentration could be attributed to the deeper penetration of the acid into the voids and excessive leaching of Al^{3+}, Fe^{3+} and Mg^{2+}, resulting in the collapse of the crystalline structure (Pesquera *et al*., 1992).

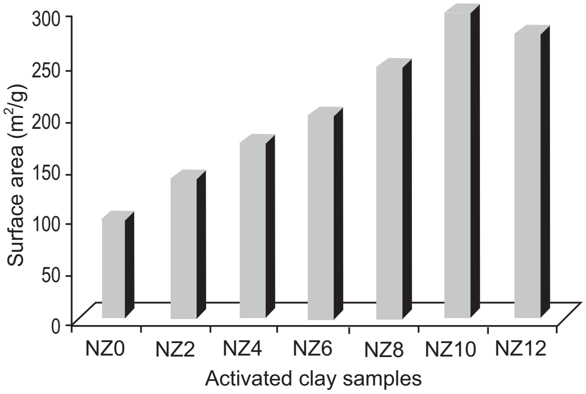

Fig. 1. Surface area of bentonite modified with different acid concentrations.

Cation exchange capacity of the activated samples. The results of the cation exchange capacity of the activated samples showed that the exchange ability of the activated samples decreased as the concentration of the acid used in the activation increased (Fig. 2). With the increase of concentration of hydrochloric acid, the bentonite showed a gradual decrease of the CEC until dissolving with 10 mol/L acid. In treatment with 12 mol/L HCl acid, as the SiO_2 content decreased, an increase of CEC was observed in comparison with the CEC observed with the sample treated with 10 mol/L. This is due to the removal of the exchangeable ions from the lattice of the clay samples by the acid hydrogen ion which occupies the vacant sites.

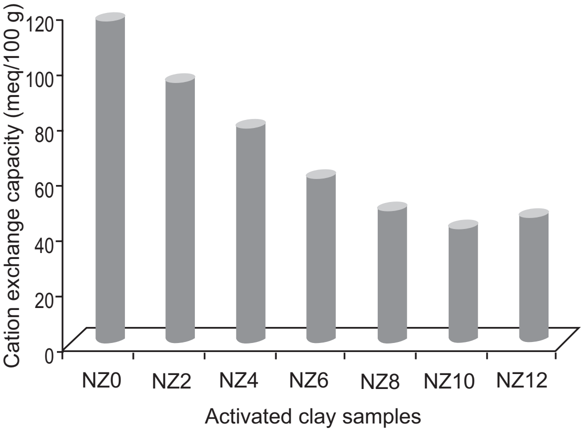

Fig. 2. Cation exchange capacity of the clay samples modified with different acid concentrations.

Effect of time on the modification of bentonites. Results of the activation process at different times showed that there is a linear relationship between the fraction of the octahedral ions removed and time. This is shown in Figs. 3-5 for the removal of Al^{3+}, Fe^{3+} and Mg^{2+} ions, respectively. Comparison of the rate of removal of these three cations, showed that the removal is in the following order, $Mg^{2+} > Fe^{3+} > Al^{3+}$ as shown in Figs. 3-5.

Effect of temperature on the modification of bentonite. The effect of temperature on the bentonite modification was studied in the range of 70-120 °C. The experimental results are presented in Fig. 6. Data in the figure shows that the dissolution rate of the cations in the acid medium increased as the leaching temperature increases up to the maximum temperature used in this study. The increase in removal rate of the cations could be as a result of high kinetic energy in the system which speeds up the rate of reaction on the surface of the clay. The same trend was reported by others (Numluk and Chaisena, 2012; Xu *et al*., 2012; Philips and Wills, 1982).

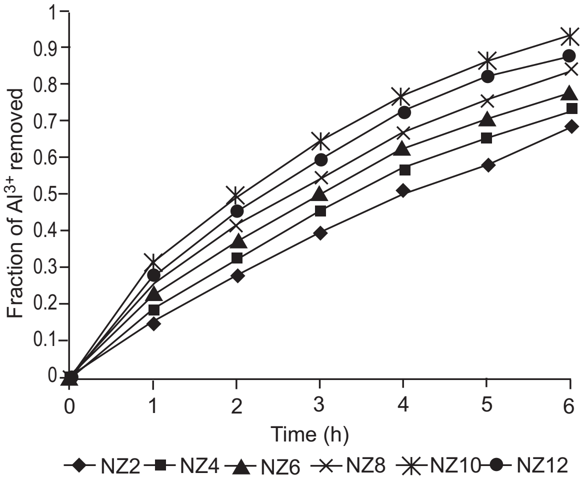

Fig. 3. Plot of fraction of Al^{3+} removed *vs* time for samples activated at different acid concentrations.

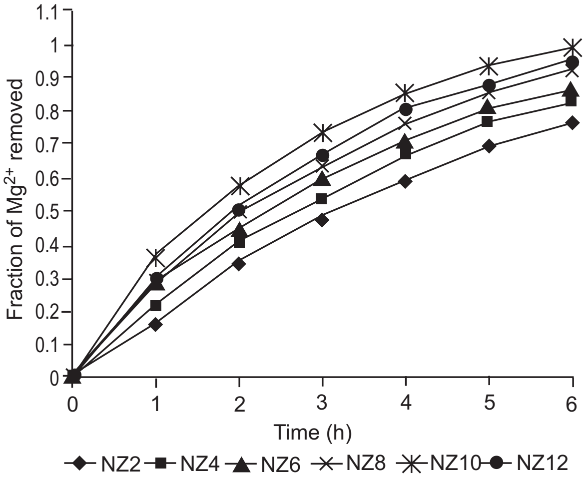

Fig. 5. Plot of fraction of Mg^{2+} removed *vs* time for samples activated at different acid concentrations.

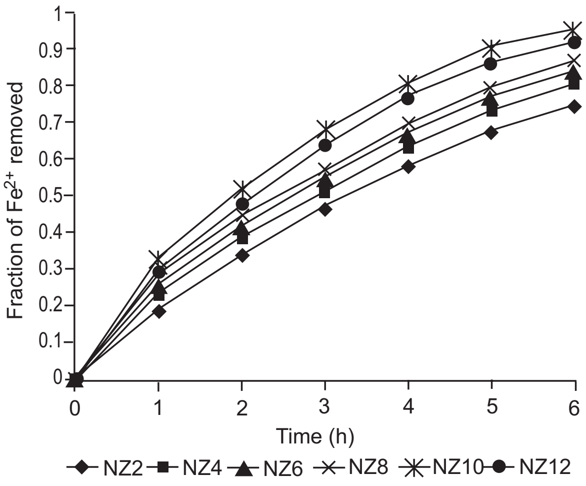

Fig. 4. Plot of fraction of Fe^{3+} removed *vs* time for samples activated at different acid concentrations.

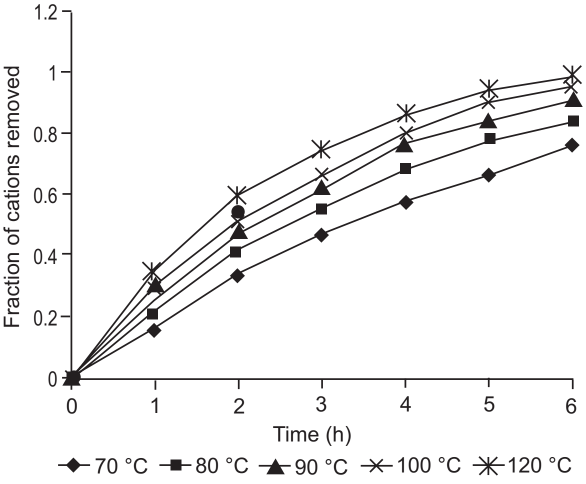

Fig. 6. Plot of fraction of cations removed after modification at different temperatures (using 10 mol/L HCl activated sample).

Fourier transforms infrared (FTIR) spectroscopy analysis. The FTIR spectra of the natural and hydrochloric acid-leached samples were carried out in the range from 400-4000 cm^{-1} to study the effect of acid-leaching on the clay mineral. The FTIR spectra of the raw and acid-leached samples are shown in Fig. 7-8, respectively. The changes in the functional groups provide the indication of the modifications that occurred during the activation process. During the acid-leaching of the clay samples the protons from the acid medium penetrate into the clay structures attacking the OH groups thereby causing the alteration in the adsorption bands attributed to the OH vibrations and octahedral cations. The intensities of the stretching bands observed at 3623, 3432, 1641, and 920 cm^{-1} (associated with O-H, along with Al-OH stretch) decreased after acid-activation. The increase in the severity of acid caused the disappearance of the stretching bands at 4660, 3694, 2376, and 998 cm^{-1} assigned to the H-O-H stretching. The peak assigned to Si-O-Si stretch at 788 and 1066 cm^{-1} remained after acid leaching, similar result was reported by others (Christidis *et al.*, 1997; Komadel *et al.*, 1990). The bands at 525, 690, and 998 cm^{-1} disappeared after the acid treatment of the clay sample. The transformation of the tetrahedral occurred at 788 cm^{-1} which was increased after the acid treatment.

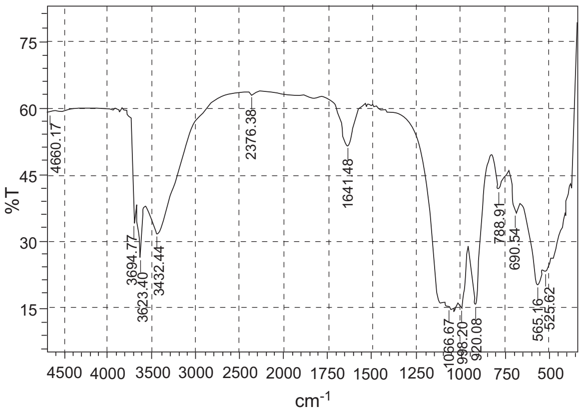

Fig. 7. FTIR spectra of natural Ntezi clay.

Activation kinetics studies. The kinetic studies showed that the acid modification reaction is controlled by the product layer diffusion and can be represented by

$$[1-(1-X)^{1/3}]^2 = k\,t \tag{1}$$

where:

X = fraction of the bentonite dissolved at time t. The activation energy was determined to be 24.98 kJ/mol.

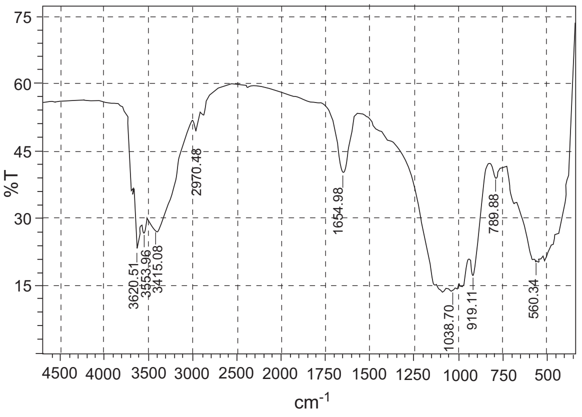

Fig. 8. FTIR spectra of 10 mol/L HCl acid-activated Ntezi clay.

The reaction between a solid and a fluid may be represented by

$$\text{A (fluid)} + \text{b B (solid)} \rightarrow \text{products} \tag{2}$$

The rate of reaction between a solid and a fluid can be expressed by heterogeneous and homogeneous reaction models. According to the shrinking-core model, the reaction is considered to take place at the outer surface of the unreacted particle. When no ash forms, the reacting particle shrinks during reaction and finally disappears. For a reaction of this kind, the following three steps are considered to occur in succession during reaction (Levenspiel, 1972).

1. Diffusion of fluid reactant through the fluid layer to the surface of the solid.
2. Reaction of the fluid reactant and solid on the surface of the solid.
3. Diffusion of the products through the film layer to the bulk fluid.

The slowest of these sequenced steps is the rate-determining step. If the reaction is controlled by film diffusion, it becomes

$$X = [3bk_cC_A / \tilde{n}_BR]\,t = k_f\,t \tag{3}$$

if it is controlled by chemical reaction, it becomes

$$1 - (1 - X)^{1/3} = [bk_sC_A / \tilde{n}_BR]\,t = k_r\,t \tag{4}$$

the product layer diffusion control is given by

$$1 + 2(1 - X) - 3(1 - X)^{2/3} = [2M_BDC_A/\tilde{n}_BbR^2]\,t = k_d\,t \tag{5}$$

where:

X = fraction of B dissolved in A, ñ$_B$ is the molar density of solid reactant (mol/m^3), R is the radius of a sphere (m), b is the stoichiometric coefficient of the solid, k_c, k_f, k_s, k_r, and k_d are rate constants, D is the effective diffusion coefficient (m^2/s), M_B is the molecular weight of B, and C_A is the concentration of A in the bulk solution (mol/m^3).

The experimental data of Figs. 3-5 were tested with the above kinetic models, but it was determined statistically that the dissolution reaction did not fit the models. The data were then analysed using the kinetic model as developed by Jander (1927) given by:

$$[1-(1-X)^{1/3}]^2 = k_q t \qquad (6)$$

Using this equation, the plot of $[1-(1-X)^{1/3}]^2$ *versus* time gave straight lines passing through the origin as shown in Figs. 9-11 for Al^{3+}, Fe^{3+} and Mg^{2+}, respectively. The coefficient of determination (R^2) values was used to determine the fitness of the data to the equation. As can be observed from the values of R^2, it is evident that the fitness is close to unity for all the data.

The experimental data of Fig. 6 was tested with the kinetic equation and straight lines passing through the origin were obtained as shown in Fig. 12. The apparent reaction rate constants calculated from the slopes of Fig. 12, were plotted against the reciprocal of the temperature according to the Arrhenius equation to determine the activation energy of the processes. The activation energy was determined to be 24.98 kJ/mol with a correlation coefficient of 0.963, which is in close agreement with the value calculated by Uzun and Gulfen (2007) of 21.42 kJ/mol for the dissolution of red mud in sulphuric acid solution.

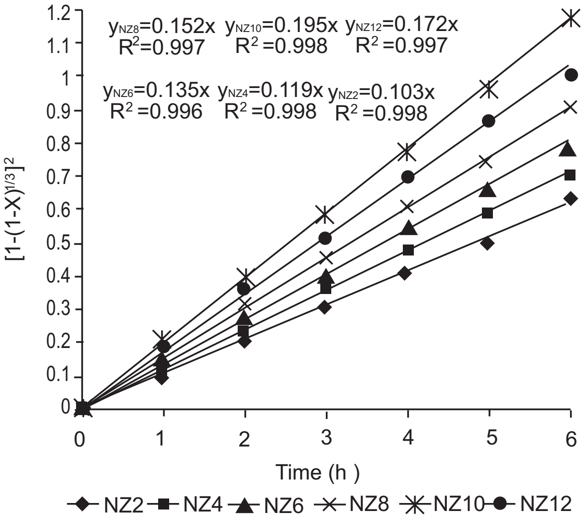

Fig. 9. Plot of $[1-(1-X)^{1/3}]^2$ *vs* time for Al^{3+} removal at different acid concentrations.

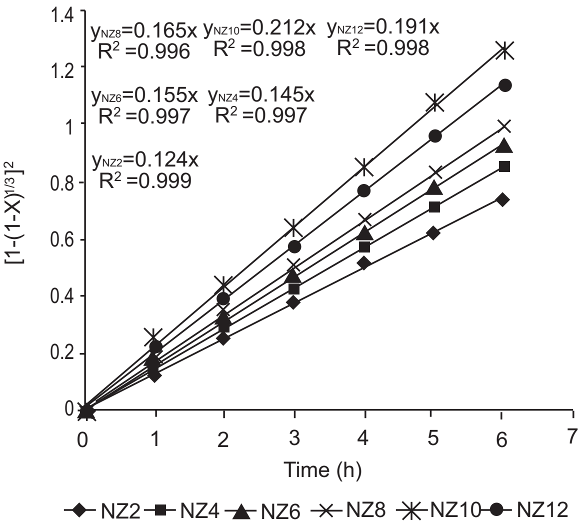

Fig. 10. Plot of $[1-(1-X)^{1/3}]^2$ *vs* time for Fe^{3+} removal at different acid concentrations.

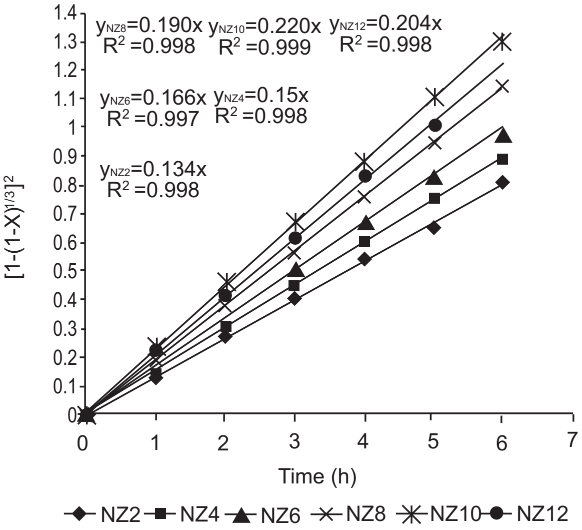

Fig. 11. Plot of $[1-(1-X)^{1/3}]^2$ *vs* time for Mg^{2+} removal at different acid concentrations.

Adsorption performance of the activated bentonite. Oils and fats are bleached in order to remove undesired colourants because these colourants can negatively affect the taste of the oil and in part because the colour

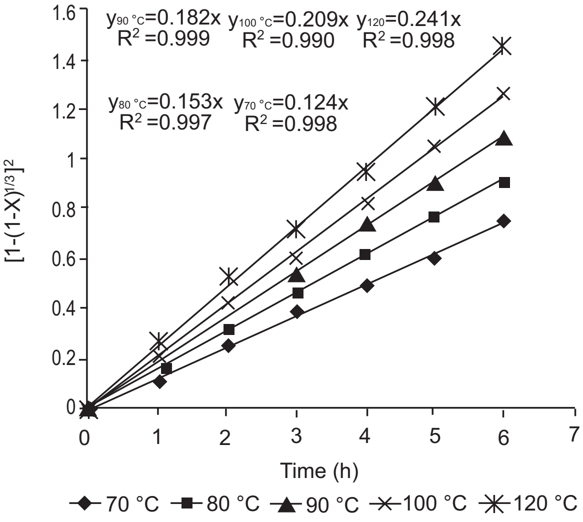

Fig. 12. Plot of $[1-(1-X)^{1/3}]^2$ *vs* time at different temperatures.

would disturb the consumers, therefore, on the whole, these colourants limit use and marketability. In addition to that, some particles or pigments that promote deterioration to oil quality is also being removed during bleaching process mainly due to their pro-oxidative properties that promotes oxidation. As a result, these undesirable pigments are removed using appropriate adsorbents, such as activated clays. To investigate the adsorptive performance of the acid treated samples, the samples were used to adsorb colour pigments from palm oil and the results are presented in Fig. 13. The figure shows that the adsorption power increased gradually as the intensity of the acid treatment increased and reached a maximum with 10 mol/L treated sample.

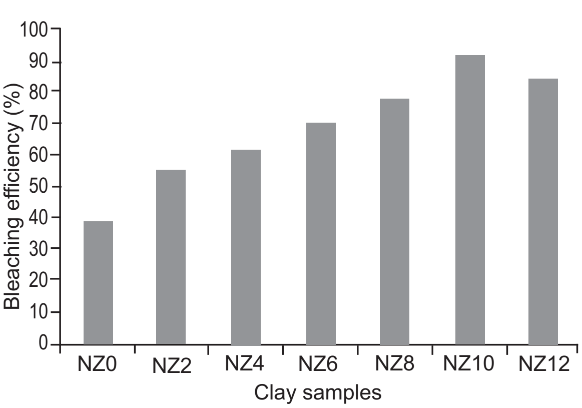

Fig. 13. Plot of the bleaching efficiency of the natural and acid activated Ntezi bentonite.

Further increase in the intensity of treatment caused a reduction in the adsorption capacity and this could be as a result of reduced surface area (Fig. 1) and Si/[Al + Fe + Mg] ratio (Table 1).

Conclusion

The structural modifications of Ntezi bentonite after hydrochloric acid activation and kinetics of the process have been investigated in this work. The acid activation caused reorganisation of the clay structures by the removal of the di- and trioctahedral cations and subsequent modifications of the tetrahedral arrangement. These resulted to samples with increased surface area, adsorption capacity, and reduced cation exchange capacity. The activation process could be described by the product layer diffusion kinetic model with activation energy of 24.98 kJ/mol. The results reveal that acid activation of bentonite with 10 mol/l HCl acid can be employed as an economical technique for modification of bentonite to enhance its surface properties and adsorption capacity.

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Analysis and Appraisal of Urban Road Traffic Noise of the City of Cuttack, India

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Abstract. The road traffic noise environment in the Cuttack city, commercial and judicial capital of the Indian state, Odisha, has been appraised in the present study. Noise pollution was analysed in 17 different squares (road sections) during four different specified times to assess the level of noise pollution of the city. Noise descriptors such as L_{10}, L_{50}, L_{90}, L_{eq}, TNI (traffic noise index), NPL (noise pollution level), NC (noise climate), Q (traffic volume) and P (truck-traffic mix ratio) were analysed to reveal the extent of noise pollution due to heavy traffic in this city. A systematic comparison between TNI and L_{eq} noise levels for all selected locations reveal that the TNI values are much more than respective L_{eq} levels. This simply demonstrates that although the noise levels during any period of the day are generally constant but the presence of single event noise is sufficient to affect the values of L_{10}, L_{50}, L_{90}, L_{eq} and consequently the TNI. Analysis of variance (F-test) is also computed for investigated squares to infer the level of significance. Even the minimum NPL and TNI values are more than 100 dB. Noise levels at all the road sections exceeded the standard ambient noise levels prescribed by WHO (70 dB).

Keywords: community response, Cuttack city, noise descriptors, traffic noise, traffic volume

Introduction

Major contribution to outdoor noise often comes from road transportation and is the main source of pollution. Noise survey in various cities throughout the world have revealed that traffic noise is typically the largest contributor to recorded sound levels and one of the most important sources of annoyance (WHO, 1999). With rapid urbanisation and the corresponding increase in the number of vehicles on roads, the noise pollution is increasing at an alarming rate in most of the important Indian cities. In India, some studies on the traffic noise monitoring have been carried out at different cities like Delhi (Prakash *et al.,* 2006, Nirjar *et al*., 2003; Singh and Jain, 1995; Kumar and Jain, 1994), Mumbai (Naik, 1998), Aurangabad (Bhosale *et al,*. 2010), Amravati (Patil *et al*., 2011), Dehradun (Ziaudin *et al.,* 2007), Lucknow (Kisku *et al*., 2006), Varanasi (Pathak *et al*., 2008, Tripathi *et al*., 2006), Jaipur (Agarwal and Swami, 2009a; 2009b; Agarwal *et al*., 2009; Choudhary *et al*., 2003), Kolkata (Chakraborty *et al.,* 2002), Asansol (Banerjee *et al.,* 2009; 2008; Banerjee and Chakraborty, 2006), Bolpur (Padhy and Padhi, 2008), Burdwan (Datta *et al*., 2006), Visakhapatnam (Rao and Rao, 1992), Chennai (Kalai Selvi and Ramachandraiah, 2009), Thiruvanatapuram, Kochi, Kozhikode (Sampath *et al*., 2004), Jharsuguda (Patel *et al*., 2006), Bhadrak (Goswami, 2011) and Balasore (Goswami, 2011; 2009) etc. The noise levels are showing an alarming rise and in fact, the levels exceed the prescribed levels in most of the areas. In the light of the rapid growth of vehicular population, there is a need to study noise pollution from the transportation point of view. In this study, an attempt has been made to study noise pollution due to vehicular traffic in this commercial city of Odisha state, India. As it is evident that primarily noise problem is the result of growing busy traffic, each year there is an increase in the number of vehicles in this city. This has led to overcrowded roads and pollution around this city. The road traffic noise levels at 17 different squares of this city have been assessed to predict the extent of vehicular noise pollution around the Cuttack, the business capital of Odisha. Total population of Cuttack is 2,618,708. Demographic characteristics of Cuttack (Table 1) explicitly demonstrate that the population is increasing at an alarming rate. An emerging IT hub, the boom in the metals and metal processing industries, around 3 universities, hundreds of colleges have made Cuttack as one of the fastest developing cities of India in recent years. The increase in number of industries, market complexes, institutions, urban highways constructed around residential and community areas of this city, growing population and consequently increase in number of vehicles have inevitably caused major noise pollution

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Table 1. Decadal population trend in the city of Cuttack, India

Year	Population	Male	Female	Population density
1961	3063072	1532583	1530489	278.94
1971	3827678	1927033	1900645	341.42
1981	4628800	2346690	2282110	799.56
1991	1122739	1027747	944992	528
2001	2341094	1207781	1133313	595
2011	2618708	1,339,153	1,279,555	666

Source = District Statistical Handbook, Odisha & Census of Odisha.

problems to city dwellers. Thus, noise level measurements were taken up with emphasis on traffic noise. The study also analysed variation of noise around the squares (road sections) and its relationship with traffic volume.

Materials and Methods

Acoustic study. The present study of noise monitoring was conducted with the help of sound level meter (Model LUTREN, SL-4010). This light weight instrument (wt = 460 g with batteries) is primarily designed for community noise survey. It is calibrated acoustically using an external reference source, which is placed over the microphone. Sound level meter works on the principle of evaluation of sound pressure on a linear or weighted scale. It normally indicates root mean square (rms) value of the sound.

Cuttack city is located at $20^0 05'$ north latitude and $85^0 38'$ east longitude and has an average elevation of 36 m. The city is basically situated at the apex of the Mahanadi delta. The geographical area of this city is 3932 sq. km. The noise levels were measured following standard procedure using calibrated sound level (dB) meter in between the month of May and June, 2011 at seventeen important and crowded squares (road sections) of Cuttack (Link road square, Buxi bazar square, College square, Naya bazar square, Chandini Chowk square, OMP square, Chandi mandir square, Sati chaura square, Dolamundai square, Ranihat square, Badambadi square, Mangalabag square, Choudhury bazar square, High court square, Balu bazar square) (Shelter square and Biju Pattanaik square) (Stephenson *et al*., 2011; Al-Ghonamy, 2010; Ghatass, 2009; Ozer *et al*., 2009; Szeremeta and Zannin, 2009; Zannin and Marcon, 2006; Piccolo *et al*., 2005; Yang and Kang, 2005; Yusoff and Ishak, 2005). Link road square and OMP square are located along the National Highway (Kolkata-Chennai: NH-5). All buses go to Bus stop (Badambadi) of the city of Cuttack through Link road square. Buxi bazar, Dolamundai, Ranihat, Mangalabag, Choudhury bazar squares are all commercial areas of the city and are located in the heart of the old Cuttack. College square is located near Ravenshaw university and Cuttack railway station. High court square is located near High court and office of the district administration. Famous temples of this city are located along the Chandini chowk, Chandi mandir, Dolamundai and Ranihat squares. The major residential colonies are located near Naya bazar, Sati chaura, Balubazar, Shelter and Biju Pattanaik squares. Irrespective of nature and composition of the above mentioned investigated squares, the noise source is predominantly attributed to road traffic noise.

Total 180 measurements were made within 3 h duration (i.e., at 1 min interval) during some specified times from 7-10 a.m., 11 a.m.-2 p.m., 3-6 p.m. and 7-10 p.m., in all 17 squares by holding sound level meter in hand at arm's length at the chest level in order to reduce errors due to reflection of sound from the body of investigator holding the instrument (Swain *et al.,* 2013; Goswami and Swain, 2012; Swain *et al*., 2012; 2011). The noise monitoring was done in a good climatic condition, where there was no sign for cloud. Also the monitoring was done in all working days excluding Sunday and local holidays in order to get good result.

***L_{eq}*.** L_{eq} represents the equivalent energy sound level of a steady state and invariable sound. It includes both intensity and length of all sounds occurring during a given period. The noise levels of different squares in different time intervals were predicted along with their equivalent noise levels (L_{eq}). The value of L_{eq} in dB (A) unit is calculated by using the formula of Robinson (1971) i.e.,

$$L_{eq} = L_{50} + (L_{10}\text{-}L_{90})^2 / 56$$

For the present study, different percentile noise levels used are:

L_{10} : the level that were exceeded during 10% of the measuring time in dB(A)
L_{50} : the level that were exceeded during 50% of the measuring time in dB(A)
L_{90} : the level that were exceeded during 90% of the measuring time in dB(A)

NPL. As L_{eq} is an insufficient descriptor of the annoyance caused by fluctuating noise (Robinson, 1971), noise pollution level (NPL) expressed in dB is calculated by using the following formula:

$$NPL = L_{eq} + a\,(L_{10}\text{-}L_{90})$$

where:

a = 1.0 (constant in the equation)

NPL takes into account the variations in the sound signal and hence serves as better indicator of the pollution in the environment for physiological and psychological disturbance of the human system.

TNI. Traffic noise index (TNI) is another parameter, which indicates the degree of variation in a traffic flow. This is also expressed in dB (A) and can be computed using the following relation (Robinson, 1971):

$$TNI = 4\,(L_{10}\text{-}L_{90}) + L_{90} - 30 \text{ dB (A)}$$

NC. Noise climate (NC) is the range over which the sound levels are fluctuating in an interval of time and is assessed using the following formula (Robinson, 1971):

$$NC = (L_{10}\text{-}L_{90})$$

where:

L_{90}, the level exceeded for 90 % of the time of record, is very near to the background noise level in the absence of any motor vehicle traffic.

Traffic volume (Q). The noise level near the highway depends on the number of vehicles. The noise level increases with an increase in traffic volume. Traffic volume is defined as the total number of vehicles flowing per hour (Robinson, 1971). The number of vehicles passing through a fixed point on the road was counted.

Truck-traffic mix ratio (P). Trucks and buses are contributing more noise to the environment, than compared to automobiles. It is evident that, besides the total noise level, the number of heavy vehicles will be an important parameter in the annoyance function. This is especially the case in the transition range between continuous noise and "just annoying noise events" (Gjestland, 1987). The ratio of heavy trucks and buses to total traffic is called truck-traffic mix ratio (Robinson, 1971). This was computed in terms of percentage. An increase in this ratio will increase the noise level.

Statistical analysis. The analysis of the measured noise levels generally depicts that there are existence of variations of noise with variables as the time of day, categories of zone specific sites, road way types, etc., (Goswami *et al*., 2011, Goswami and Swain, 2011). In order to determine the existence and statistical significance of these variations and trends, a cross classification analysis along with F-test were assessed on the data.

Survey of social attitudes. The questionnaire addressed the socioeconomic characteristics of the individual and individual attitudes towards traffic noise and their interference of noise with daily activities, such as sleeping, relaxation, speaking and studying etc. A sample of 315 general public (236 male and 79 female; including 60 students) was interviewed using the said questionnaire from May to June, 2011 to delineate the perception about the noise and its significance on health of community. The questionnaire consisted of general information about the purpose of the public health survey, i.e., collection of health-related data in order to improve health-care planning and prevention (Mohapatra *et al*., 2010), nowhere stating that traffic noise pollution specifically would be studied (Bodin *et al*., 2009). A random criterion was employed for the selection of the interviewed people. However, there was a substantial proportion of non-responders. To estimate annoyanace and sleep disturbances, questions with a scale of four were used: “yes, often”, “yes, sometimes”, “no, never” and “not relevant”. It is imperative to note that none of these questions involved the word ‘noise’ in order to avoid inducing responses about this issue. The word ‘noise’ (negative connotation) was replaced by “sound” (neutral connotation) (Szeremeta and Zannin, 2009). Depending on the exposure to environmental noise, two different groups i.e., exposed and nonexposed group were categorized. People of exposed group were those residing or having regular activity near the studied 17 squares, where sound pressure level exceeded 70 dB (A), while, nonexposed group was of those who lived or used to perform their activity away from noisy areas herein Cuttack, where sound pressure level did not exceed 55 dB (A). It is believed that in the present study, all the respondents belong to exposed group.

Results and Discussion

Noise pollution was assessed and analysed in seventeen different 17 traffic squares of the city (Table 2). The noise data collected from different monitoring sites displayed wide ranges of noise level varying in 4 different specified times namely; 7-10 a.m., 11 a.m.-2 p.m., 3-6 p.m. and 7-10 p.m. (Table 2). Central Pollution Control Board (CPCB), India has not mentioned prescribed basic noise levels on the roads and even there is no defined regulation for road traffic noise in ‘the Noise Pollution (regulation and control)

Table 2. Noise level (dB) variations at different squares of the city of Cuttack at different time intervals

Squares/ road sections	7 a.m. - 10 a.m.						11a.m. – 2 p.m.						3 p.m. – 6 p.m.						7 p.m.- 10 p.m.					
	Min	Max	L_{10}	L_{50}	L_{90}	L_{eq}	Min	Max	L_{10}	L_{50}	L_{90}	L_{eq}	Min	Max	L_{10}	L_{50}	L_{90}	L_{eq}	Min	Max	L_{10}	L_{50}	L_{90}	L_{eq}
Link road square	74.5	121.1	102.3	93.3	80.5	101.7	75.1	119.8	100.1	92.2	79.6	99.7	76.6	124.3	104.8	92.8	79.2	104.5	77.3	126.9	104.2	92.4	79.6	103.2
Buxi bazar square	72.1	125.7	97.4	85.2	75.9	93.4	72.9	120.5	98.6	81.7	75.6	91.1	73.5	124.8	98.2	86.4	76.7	94.6	76.7	123.3	99.6	87.7	80.6	94.1
College square	72.4	119.6	100.2	85.4	77.6	94.5	70.1	120.7	100.8	83.7	73.7	96.8	74.2	122.4	101.4	86.2	79.2	95.0	79.4	124.7	102.6	88.5	82.5	95.7
Naya bazar square	72.6	124.6	98.4	84.5	76.5	93.0	69.5	121	97.3	79.4	74.8	88.4	73.6	127.3	99.7	84.3	74.7	95.4	76.6	128.9	101.4	89.2	81.6	96.2
Chandini chowk square	74.6	119.6	98.4	85.2	77.8	92.7	70.6	123.4	96.6	81.4	75.1	89.6	76.5	120.4	101.3	89.5	81.8	96.2	78.3	131.8	104.6	90.4	86.2	96.4
OMP square	70.5	121.3	100.6	80.2	74.2	92.6	70.1	120.7	98.3	79.6	75.5	88.8	69.1	124.6	101.2	81.7	74.6	94.3	71.6	129.9	103.2	83.5	74.6	98.1
Chandi mandir square	68.4	120.6	101.4	82.5	72.7	97.2	71.6	120.4	100.6	80.2	74.7	92.1	68.2	121.4	102.3	83.5	73.6	98.2	70.3	125.6	104.5	86.1	72.6	104.2
Sati chaura square	74.2	120.3	100.1	88.5	80.6	95.2	72.6	121.7	99.4	86.1	76.7	95.3	75.3	119.9	99.7	90.1	79.8	97.1	80.3	121.8	102.3	90.3	83.2	96.8
Dolamundai square	70.5	126.3	100.7	85.1	74.8	97.0	69.7	124.7	98.7	80.4	73.6	91.6	71.8	128.9	102.3	87.4	75.7	100.0	71.1	126.8	104.5	86.5	76.6	100.4
Ranihat square	80.9	124.3	100.1	90.3	82.7	95.7	74.2	121.4	100.3	91.2	80.4	98.2	78.4	126.7	101.8	93.1	82.6	99.6	81.1	130.4	102.1	90.4	85.7	95.2
Badambadi square	72.6	123.7	100.6	90.3	79.2	98.4	71.1	121.6	100.6	89.2	77.4	98.8	79.5	125.8	101.1	92.1	85.7	96.3	82.3	129.6	102.3	93.2	88.7	96.5
Mangalabag square	70.8	120.3	102.3	91.5	76.6	103.2	74.1	121.3	100.2	89.1	77.6	98.2	72.7	120.4	102.3	90.1	78.6	100.1	71.6	126.9	102.6	91.4	79.5	100.9
Choudhury bazar square	71.1	121.1	100.6	89.4	75.8	100.3	70.8	127.3	102.1	84.5	76.6	96.1	72.3	122.6	100.2	89.1	78.6	97.4	73.8	128.6	103.1	92.2	79.6	102.0
High court square	70.5	123.7	101.1	87.5	76.2	98.5	70.4	124.1	101.1	87.2	73.9	100.4	71.1	125.6	102.2	89.4	75.5	102.1	72.2	129.7	102.3	89.5	78.6	99.5
Balubazar square	70.1	121.3	99.2	80.3	73.8	91.8	67.1	119.4	98.7	81.6	72.5	93.8	70.8	126.4	100.3	85.3	74.6	97.0	71.8	130.4	104.5	86.4	75.2	101.7
Shelter square	71.8	121.4	101.3	87.3	76.6	98.1	70.8	120.3	100.8	85.4	75.7	96.6	70.1	126.5	100.5	88.3	72.6	102.2	75.3	124.7	101.3	89.4	80.6	97.0
Biju pattanaik square	69.1	123	98.5	82.6	74.7	92.7	68.1	119.2	98.4	80.2	74.5	90.4	68.6	124.7	99.1	85.3	74.6	96.0	73.3	126.8	99.4	88.1	78.6	95.8

rules, 2000'. Thus, the detected noise levels of the study area in day time were compared with the prescribed basic noise level (tolerance limit) on roads (traffic noise) during day-time of United Kingdom i.e., 70 dB (A) (WHO, 1999) and of Nepal (Krishna Murthy *et al.*, 2007).

L_{10} values of all 17 monitored sites ranged from 97.4 to 102.3 dB; 96.6 to 102.1 dB; 98.2 to 104.8 dB and 99.4 to 104.6 dB during 7-10 a.m., 11 a.m.-2 p.m., 3-6 p.m. and 7-10 p.m., respectively (Table 2). Similarly, L_{50} and L_{90} values of all 17 monitored sites vary from 80.2 to 93.3 dB and 72.7 to 82.7 dB; 79.4 to 92.2 dB and 72.5 to 80.4 dB; 81.7 to 93.1 dB and 72.6 to 85.7 dB and 86.1 to 93.2 dB and 72.6 to 88.7 dB during 7-10 a.m., 11 a.m.-2 p.m., 3-6 p.m. and 7-10 p.m., respectively (Table 2). Accordingly, the calculated L_{eq} (equivalent noise levels) values ranged from 91.8 to 103.2 dB; 88.4 to 100.4 dB; 94.3 to 104.5 dB and 94.1 to 104.2 dB during 7-10 a.m., 11 a.m.-2 p.m., 3-6 p.m., and 7-10 p.m., respectively (Table 2). NPL values of all 17 monitored sites ranging from 100.1 to 128.9 dB; 110.9 to 127.6 dB; 111.7 to 130.1 dB and 110.1 to 136.1 dB during 7-10 a.m., 11 a.m.-2 p.m., 3-6 p.m., and 7-10 p.m., respectively (Table 3). TNI values ranged from 122.3 to 157.5 dB; 130 to 158.6 dB; 117.3 to 158.4 dB and 113.1 to 170.2 dB during 7-10 a.m., 11 a.m.-2 p.m., 3-6 p.m. and 7-10 p.m., respectively. Even the minimum NPL and TNI values are more than 100 dB. These high and distressing values of noise pollution level (NPL) and traffic noise index (TNI) clearly demonstrate that the extent of noise pollution in the studied crowded squares is alarming. It was also observed that at some locations the characteristics of noise caused by fast moving traffic, different from those caused by congested or slow moving traffic. Noise from congested traffic was found to contain occasional peaks and varied more in levels. A systematic comparison between TNI and L_{eq} noise levels for all selected locations revealed that the TNI values were much more than respective L_{eq} levels. This simply demonstrated that although the noise levels during any period of the day were generally constant but the presence of single – event noise was sufficient to affect the values of different noise percentile levels and consequently the TNI. This is due to overpopulated road ways with bad conditions, broken roads, minimal traffic management and hooting behaviour of drivers (Agarwal and Swami, 2009a). Similarly, NC values ranged from 17.4 to 28.7 dB; 19.9 to 27.2 dB; 15.4 to 28.7 dB and 13.6 to 31.9 dB during

Table 3. Noise descriptors (TNI, NPL, NC) variations observed at different squares of the city of Cuttack at different time intervals

Monitoring sites	7 a.m. - 10 a.m.			11a.m. – 2 p.m.			3 p.m. – 6 p.m.			7 p.m.- 10 p.m.		
	TNI	NPL	NC	TNI	NPL	NC	TNI	NPL	NC	TNI	NPL	NC
Link road square	137.7	123.5	21.8	131.6	120.2	20.5	151.6	130.1	25.6	148	127.8	24.6
Buxi bazar square	131.9	114.9	21.5	137.6	114.1	23	132.7	116.1	21.5	126.6	113.1	19
College square	138	117.1	22.6	152.1	123.9	27.1	138	117.2	22.2	132.9	115.8	20.1
Naya bazar square	134.1	114.5	21.9	134.8	110.9	22.5	144.7	120.4	25	130.8	116	19.8
Chandini chowk square	130.2	113.3	20.6	131.1	111.1	21.5	129.8	115.7	19.5	129.8	114.8	18.4
OMP square	149.8	119	26.4	136.7	111.6	22.8	151	120.9	26.6	159	126.7	28.6
Chandi mandir square	157.5	125.9	28.7	148.3	118	25.9	158.4	126.9	28.7	170.2	136.1	31.9
Sati chaura square	128.6	100.1	19.5	137.5	118	22.7	129.4	117	19.9	129.6	115.9	19.1
Dolamundai square	148.4	100.7	25.9	144	116.7	25.1	152.1	126.6	26.6	158.2	128.3	27.9
Ranihat square	122.3	113.1	17.4	130	118.1	19.9	129.4	118.8	19.2	121.3	111.6	16.4
Badambadi square	134.8	119.8	21.4	140.2	122	23.2	117.3	111.7	15.4	113.1	110.1	13.6
Mangalabag square	149.4	128.9	25.7	158.6	120.8	22.6	143.4	123.8	23.7	141.9	124	23.1
Choudhury bazar square	145	125.1	24.8	148.6	121.6	25.5	135	119	21.6	143.6	125.5	23.5
High court square	145.8	123.4	24.9	152.7	127.6	27.2	152.3	128.8	26.7	143.4	123.2	23.7
Balubazar square	145.4	117.2	25.4	147.3	120	26.2	147.4	122.7	25.7	162.4	131	29.3
Shelter square	154.4	122.8	24.7	146.1	121.7	25.1	154.2	130.1	27.9	133.4	117.7	20.7
Biju pattanaik square	139.9	116.5	23.8	140.1	114.3	23.9	142.6	120.5	24.5	131.8	116.6	20.8

7-10 a.m., 11 a.m.-2 p.m., 3-6 p.m. and 7-10 p.m., respectively (Table 3). All these values clearly show high noise levels in Cuttack city mostly throughout the day in general and during the evening (7 p.m. to 10 p.m.) in particular.

Analysis of variance is computed from all the seventeen investigated squares at their respective peak hours i.e., 7-10 p.m. (Table 4). The observed value of F (0.95) is less than the tabulated values and is not significant at both 5% and 1% levels of significance. Thus, it explicitly demonstrates that the noise levels of different squares do not differ significantly at their peak hours.

Every day, thousands of autorickshaws, two wheelers and cars, hundreds of cargo carrying trucks, dumpers and buses run along these roads. A comparative data on the number of different types of vehicles passes through the studied traffic squares in a day is presented in the Table 5. Maximum number of total vehicles passing in unit time was observed at Badambadi Square (14001) followed by Link road square (13963) and OMP square (13834), whereas, minimum number of total vehicles passing in unit time was observed at High court square (11689), Biju pattanaik square (11725) and College square (11744). The noise level increases with an increase in traffic volume. The numbers of vehicles passing through a fixed point on the studied road are counted to assess the traffic volume (Q) (Table 6). It was observed that noise levels are increasing with increased traffic volume. The percentage of heavy trucks and buses to total traffic is calculated to work out truck-traffic mix ratio (P) (Table 6). The data reveals that an increase in this ratio increases the noise level.

Moreover, individual contribution to environmental noise by the air horn of different motor vehicles has been assessed at and around Cuttack. A noise of short duration (typically less than one second), particularly of high intensity, such as that produced by an air horn by any vehicle, occurring at regular or irregular intervals is known as episodic and impulsive noise. The episodic and impulsive noise levels of different types of vehicles are presented in Fig. 1. Noise produced from cargo carrying truck, bus, bolero/trekker/travera, car,

Table 4. Analysis of variance for different traffic square locations

Peak hours	Sources of variation	Sum of squares (SS)	Degree of freedom (DF)	Mean squares	F-values	
					Observed	Tabulated
7 p.m.-10 p.m.	Between traffic squares	1599.4	16	99.9	0.95	$F_{0.5} = 1.57$
	Within traffic squares (error)	69145.1	662	104.4	–	$F_{0.5} = 1.88$
	Total	70744.5	678	–	–	–

Table 5. Total number of vehicles passing across different road squares in unit time and at different time-spels of a typical day

Monitoring sites	Number of vehicles that passed in a day												Total number of vehicles
	7 a.m. - 10 a.m.			11a.m. – 2 p.m.			3 p.m. – 6 p.m.			7 p.m.- 10 p.m.			
	2 & 3 W	LMV	HMV	2 & 3 W	LMV	HMV	2 & 3 W	LMV	HMV	2 & 3 W	LMV	HMV	
Link road square	2511	497	372	2404	645	313	2526	661	277	2743	628	386	13963
Buxi bazar square	2427	464	355	2164	529	286	2404	591	70	2557	585	68	12500
College square	2365	479	62	2321	426	53	2357	517	74	2483	523	84	11744
Naya bazar square	2543	637	89	2458	543	84	2511	564	69	2667	678	75	12918
Chandini chowk square	2437	582	102	2627	566	91	2489	528	83	2556	624	88	12773
OMP square	2562	615	278	2541	631	222	2401	651	285	2709	634	305	13834
Chandi mandir square	2473	611	96	2416	473	86	2481	555	86	2512	647	91	12527
Sati chaura square	2306	578	87	2469	461	75	2486	537	73	2445	624	86	12227
Dolamundai square	2381	524	63	2223	412	56	2474	486	66	2495	576	74	11830
Ranihat square	2527	457	71	2341	447	61	2426	534	81	2614	582	87	12228
Badambadi square	2568	604	286	2467	461	373	2612	663	281	2751	638	297	14001
Mangalabag square	2442	489	127	2511	592	86	2528	567	92	2564	506	95	12599
Choudhury bazar square	2416	476	93	2405	534	75	2435	547	76	2487	489	84	12117
High court square	2448	435	68	2351	418	59	2369	447	79	2411	513	91	11689
Balubazar square	2492	472	61	2362	434	62	2384	496	75	2451	584	82	11955
Shelter square	2436	423	70	2378	452	72	2394	501	66	2427	527	79	11825
Biju pattanaik square	2407	416	66	2366	445	68	2381	472	72	2446	509	77	11725

2 & 3 W = two and three wheelers; LMV = light motor vehicles; HMV = heavy motor vehicles.

Table 6. Q (traffic volume) and P (truck-traffic mix ratio) at different squares of the city of Cuttack at different time intervals

Monitoring sites	7 a.m. - 10 a.m.		11a.m. – 2 p.m.		3 p.m. – 6 p.m.		7 p.m.- 10 p.m.	
	Q	P (%)	Q	P (%)	Q	P (%)	Q	P (%)
Link road square	1127	11	1121	9.27	1155	7.96	1252	10.3
Buxi bazar square	1082	10.9	993	9.56	1022	2.34	1070	2.15
College square	969	2.16	933	1.92	983	2.54	1030	2.72
Naya bazar square	1089	2.75	1028	2.72	1048	2.19	1140	2.19
Chandini chowk square	1040	3.27	1095	2.74	1033	2.71	1089	2.66
OMP square	1152	8.07	1131	6.54	1112	8.54	1216	8.38
Chandi mandir square	1060	3.01	992	2.92	1041	2.78	1083	2.77
Sati chaura square	990	2.92	1002	2.49	1032	2.32	1052	2.75
Dolamundai square	989	2.12	897	2.12	1009	2.18	1048	2.38
Ranihat square	1018	2.35	950	2.1	1014	2.66	1094	2.65
Badambadi square	1153	8.24	1100	11.27	1185	7.93	1229	8.05
Mangalabag square	1019	4.12	1063	2.73	1062	2.91	1055	3.03
Choudhury bazar square	995	3.11	1005	2.48	1019	2.45	1020	2.74
High court square	984	2.33	943	2.12	965	2.69	1005	2.98
Balu bazar square	1008	1.98	953	2.2	985	2.54	1039	2.59
Shelter square	976	2.35	967	2.48	987	2.23	1011	2.57
Biju pattanaik square	963	2.28	960	2.39	975	2.46	1011	2.57

motorcycle, tractor, and tempo, ranges from 108.5 - 126.4 dB, 102.4-120.1dB, 94.8-118.3 dB, 94.0-115.5 dB, 91.5-114.2 dB, 107.3-119.4 dB and 96.7- 116.9 dB, respectively (Fig. 1). The findings of individual contribution of vehicle towards noise pollution are more than the traffic noise-limit i.e., 70 dB (A).

However, the peak traffic was observed during two specified times such as 7-10 a.m. and 7-10 p.m. at all

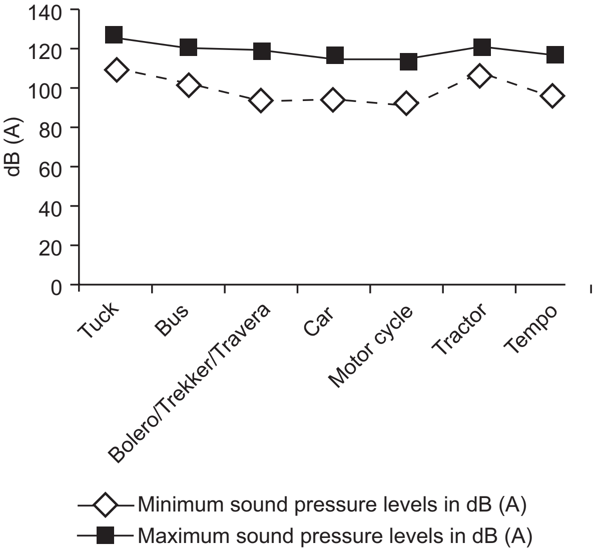

Fig. 1. Episodic and impulsive noise levels (40 observations) by the air horn of motor vehicles at Link road and OMP squares, Cuttack.

the monitoring squares of the city. Maximum numbers of peoples are traveling during the morning and evening time for office work and schools having similar working hours. High frequency sound emitted from electric horn and air horn of buses, trucks, cars, motorcycles, auto-rickshaws, engine of vehicles, crowding of general public create tremendous noise. The present study explicitly demonstrates that in most of the cases the average assessed noise levels are more than the permissible limit i.e., 70 dB for road traffic noise (Krishna Murthy *et al*., 2007; Kudesia and Tiwari, 2007; WHO, 1999) during day time.

Discussion on survey of social attitudes. A comprehensive questionnaire survey was undertaken, which sought information about traffic noise traits and its effects on exposed individuals. Noise (58%) and air (42%) pollution were recognised as the most important transport related urban problem. 62% of interviewed individuals opined that they personally affected by noise pollution more than any other pollution. 62% of interviewees stated that they are highly annoyed by the vehicular noise. The reasons for traffic noise pollution were evaluated as horn (61%) followed by traffic jam (30%), silencer (5%) and engine (4%). The distribution of annoyance due to vehicle categories are as 49% due to auto-rickshaws (tempos), followed by 21% due to bus and truck, 21% due to motorcycle and 9% due to four wheelers. 37% of the sample population reported frequent headaches as a result of being exposed to traffic noise. Nervousness was reported by 26% and 30% reported that traffic noise causes hearing damage. 31% respondents identified hypertension and loss of concentration as the main health effect of noise pollution. 12% interviewees were feeling mental stress and 11% were suffering from insomnia. 45% of students reported that their study was disrupted by frequent air horns of vehicles. 42% believed that traffic noise could cause loss of sleep. To estimate sleep disturbances questions with a scale of four were used: 11% opined “yes, often”; 23% respondents said “yes, sometimes”, 31% opined “no, never” and 35% said “not relevant”. It warrants a systematic survey of sleep quality, number of awakenings or number of changes in sleep state, changes in sleep pattern, sleep stages, subjective sleep quality to estimate the extent of sleep disturbance. The potential health impacts of traffic noise on individuals are also investigated. Excessive noise can lead to mental and physical health problems such as headache, bad temper, hearing problem, hearing impairment, loss of concentration, oral communication disturbances etc. (Lam *et al*., 2009; Kudesia and Tiwari, 2007). Non-auditory physical health effects in general and annoyance from noise exposure in particular include changes in blood pressure, heart rate, and levels of stress hormones, ischemic heart disease, biochemical effects, immune effects, birth weight and congenital effects (Bodin *et al.* 2009; Babisch, 2005). It has also effect on psychosocial well-being and performance.

Conclusion

It is inferred that the average assessed noise levels are often exceeding the permissible limit i.e., 70 dB for road traffic noise (WHO, 1999) during day time. The whole population of the Cuttack city including thousands of floating population coming to this commercial city for different purposes from nearby hundreds of small towns and villages are exposed to this urban noise levels of more than 70 dB (A). This is very high level, corresponding to the day time limit recommended by CPCB (2000) i.e., 55 dB for residential area and 65 dB for commercial area. Thus, it is concluded that noise level in and around Cuttack is high and much above the community annoyance limits recommended by WHO.

Recommendation

It is also worth noting that from the noise point of view, it is better to concentrate traffic along main roads then to distribute between parallel roads. Banning of hydraulic horns; improvement and streamlining of roads and parking system; controlling noise from heavy vehicle exhausts and engine brakes; design and fabrication of silencing devices and public awareness would also be helpful in reduction of the present noise level of the city. Vegetation buffer zones must be created in different parts of this city by massive plantation of trees with dense foliage (rich canopy), as they were found to be highly effective in absorbing the acoustic noise and act as very good screens in bringing down the noise levels. Effective road design, road use and development should be examined time to time.

Thus, Integrated Road Traffic Noise Strategy (IRTNS) must be developed at government level to minimise noise pollution at this commercial city of Odisha State. Central Pollution Control Board (CPCB), India should lay down legal standards for noise levels from roads and Ministry of Environment and Forest should launch programmes to reduce noise from the motor vehicle. Therefore, Cuttack Municipal Corporation, Commissioner of Police, Cuttack and State Pollution Control Board should take some imperative steps and regulatory measures to abate such noise pollution.

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Depositional Environments of the Bara Formation Sandstone From Lakhra Areas Sindh, Pakistan

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Abstract. Twenty four samples of the Bara formation from east and west sections of Lakhra areas have been investigated, to interpret the environments of deposition and to propose a suitable classification for the sandstones present in the studied sediments. Values of different statistical parameters of the studied sediments grain size data, for example mean, median; standard deviation, skewness, and kurtosis were determined for plotting the cumulative curves and histograms to analyse the data. Study of the shapes, roundness and the sphericity of the grains provided valuable information regarding the environment of deposition. The 92 percentage negative and 8 percentage positive values of skewness, respectively, indicated that the studied sediments are composed of coarse grained-fine grained sediments and deposited under the high-low energy conditions of fluviatile and beach environments. The presence of abundant amounts of Quartz and SiO_2 in the bulk-rock samples also suggested fluviatile/beach environments. The inclusive graphic standard deviation diagrams and the size distribution data also indicated that fine-medium grained sediments, were deposited in the study areas. Occurrence of three groups of sediments for example, sediments from lower lagoon; sediments from upper lagoon and river; and the sediments from the dead-end marsh channels from the deeper parts of the basin of deposition, have been recognized. The kurtosis values indicated that studied sediments are composed of Platykurtic, Leptokurtic and Mesokurtic groups of sediments. The sandstones, present in the Bara formation of the Lakhra west and the east areas, showed the textural maturity, therefore, have been classified as sub-mature, and sub-mature to mature sandstones, respectively.

Keywords: sedimentation, cumulative curves, skewness, kurtosis, fluviatile, spherity, textural maturity

Introduction

This study describes the results which helped in interpretation of the environment of deposition and proposing a suitable classification for sandstone of the Bara formation from the Lakhra east and west areas. The studied areas are located in the western side of Khanot railway station, district Jamshoro, Sindh, Pakistan. Lakhra coalfield covers an area of about 680 Sq Km; situated between (latitudes: 25° 30' to 25° 45' N, longitude: 68° 00' to 68° 15' E) Quadrants. Bara formation of Sindh province has been investigated, for its coal deposits, by many workers including Abbas and Atique (2005), Shah (2002; 1977) Khan (1998; 1994) and Shah (1988). These workers have contributed to the stratigraphy, coal resources and the paleontological record of the Bara formation. Prior to this study, none of the previous workers investigated the conditions of the depositional environments of these sediments. The present study is first of its kind in this direction. The grain size data of the studied sediments was obtained by the sieving method for plotting the cumulative curves and histograms. Different methods of statistical analysis including the plotting of grain size data as cumulative curves and histograms were applied for collecting information regarding the environments of the deposition. Sedimentologists have used the values of the diameters of sedimentary grains, nature of sorting, values of the median, mode, kurtosis, and skewness, for the interpretation of environments of deposition of sediments.

General geology and stratigraphy. The Bara formation is composed of sandstones, shale and minor amount of siltstone; it is the oldest formation and occurs in the core of the Lakhra anticline, whereas, the Laki formation is the youngest formation of this area and occurs on the flanks of the Lakhra anticline. Structurally, the Lakhra anticline is a part of long doubly plunging anticline, which runs north-south direction and starts from

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survey of Pakistan (SOP) toposheet nos. 40 C/1 to 40 C/4. The geological map of Lakhra area and the stratigraphic succession, respectively, are shown in Fig. 1 and Table 1. The exposed section of the Bara formation in Lakhra areas is 20 meter thick; it is located, near Lailian Nala, and is composed of sandstone, shale and minor siltstone. The sandstones are yellow, purple, white and red in colours, loose, friable, poorly sorted, unconsolidated-consolidated, and cross-bedded (Fatmi *et al.,* 1995). Shale is splintery, fissile and earthy in colour. Siltstone is interbedded with shale and sandstones. These sandstones are fine to medium and medium to coarse grained in texture, friable, fairly siliceous and ferruginous, poorly to moderately sorted and sub-rounded to sub-angular shapes of grains. Shale is brownish yellow in colour, loose, easily weathered and interbedded with sandstones.

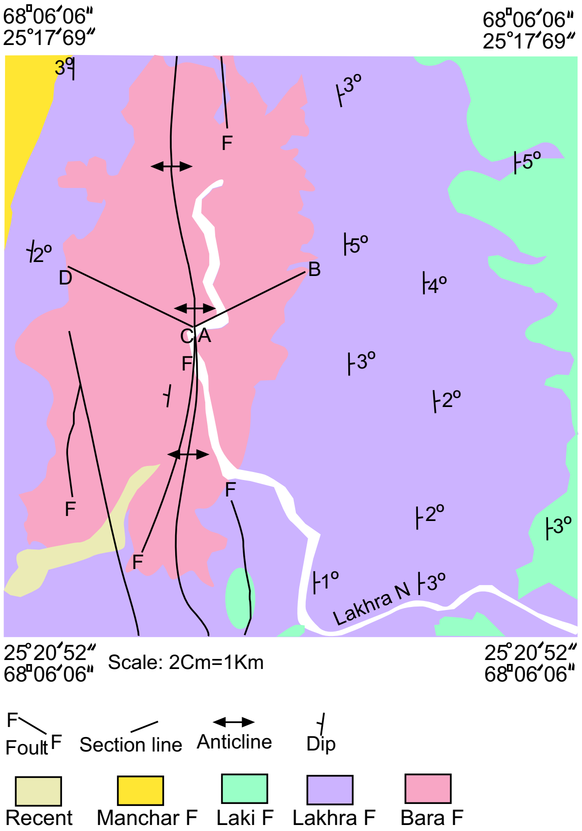

Fig. 1. Geological map of Lakhra area, Sindh.

Table 1. Stratigraphy of Lakhra area, Sindh province

Age	Formation	Lithology
Eocene	Laki formation (sonhari member and meting limestone)	limestone, sandstone, shale
Late Paleocene	Lakhra formation	limestone and shale
Middle Paleocene	bara formation	sandstone, siltstone, shale

Materials and Methods

Twenty four samples were collected from the outcrop of the Bara formation from the eastern and western flanks of Lakhra anticline. Two stratigraphic sections were measured from the eastern and western flanks of Lakhra anticline for recording the thickness of the Bara formation of Ranikot group; the section lines can be seen in Fig. 1. Both stratigraphic sections are illustrated in Fig 2 (a-b).The measurements of these sections were completed by the Jacob's staff method. The Quardinates of Lakhra east section is (latitude: 25° 38' 35"N, longitude: 68° 09' 09"E to latitude: 25° 41' 03"N, longitude: 68° 10' 46"E). The eastern section of the Bara formation started from axis of Lakhra anticline to the contact of Lakhra formation towards East along the Lailian Nala. The Quardinates of Lakhra west section is (latitude: 25° 38' 36"N, longitude: 68° 09' 08"E to Latitude: 25° 40' 21"N, Longitude: 68° 07' 02"E). The western section of the Bara formation started from the axis of Lakhra anticline to the contact of Lakhra formation towards West along the Lailian Agaro Nala. The lower contact of Bara formation is not exposed in Lakhra area, whereas its upper contact is conformable with the Lakhra formation.

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Statistical parameters. Statistical parameters of sedimentary grains e.g., mean, median, kurtosis,

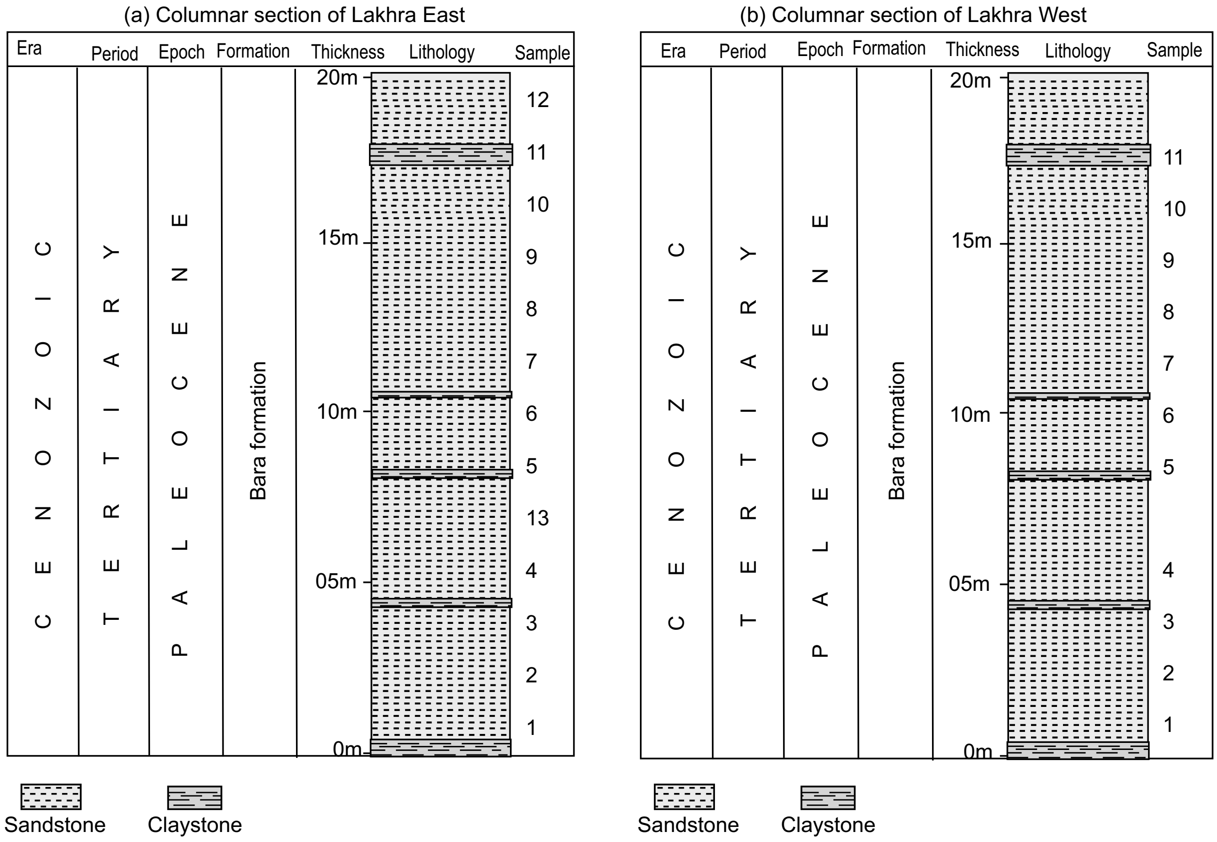

Fig. 2. Columnar sections of Bara formation from Lakhra-east (a) and Lakhra-west(b) areas.

skewness and the dimensions of grains of sediments, play important role in understanding the environments of deposition of sediments. The values of statistical parameters e.g., mean, median, kurtosis, skewness, inclusive graphic standard deviation and the inclusive graphical skewness of the grain size data of studied sediments were determined, for plotting the cumulative curves and histograms. Grain size data was also plotted for the interpretation of the environments of deposition according to the diagrams given by Passega (1964) and Stewart (1958). Details of various statistical and graphical presentation methods used in the present study for the analysis of grain size of data and interpretation of the environments of deposition are described below:

Interpretation of the environments of deposition. The results of the studied sediments provided evidences which helped in the interpretation of the environments of deposition and proposing a suitable classification for the sandstones, present in the investigated sediments. Selley (1985) used the grain size data of sediments for the interpretation of the environments of deposition. According to Selley (1970), sedimentary environment is a "part of the earth's surface which physically, chemically and biologically is distinct from the adjacent areas."

Grain size analysis by sieving method. The grain size data of sediments obtained by the sieve analysis method is commonly used for knowing the distribution of the grains of sands and other sediments. The grain size analysis of the studied sediments was done by following the procedure described by Folk (1968). Thirteen samples of the friable sandstone of the Bara formation were prepared for the sieve analysis. One hundred gram of each sample was taken for sieving analysis. Each sample was dumped on white paper sheet then disintegrated with the help of fingers slowly and carefully. Afterwards, the sample was mixed with hands by corners of paper so that all particles of unconsolidated sediments were mixed with each other.

The sieving analysis of the studied samples was done by the sieve shaker method. The standard sieves were used for sieving, and the sand samples were weighed in an electronic balance; thus the sand fractions of each sieve were obtained and transferred into a container.

Screens of all sieves were cleaned carefully, by turning the sieve face down and striking the table evenly with the rim. Screen was not touched by finger and finally it was wiped with a soft brush. A graph paper and a scientific calculator were also used. The sieve analysis was completed at the Sedimentology Lab of the Department of Geology, University of Karachi. One hundred gram (100 g) of each sample was used for the sieving analysis. The sieves used were of -2φ, -1φ (granules), 0 φ (very coarse sand), 1 φ (coarse sand), 2 φ (medium sand), 3 φ (fine sand), and 4 φ (very fine sand) for sieving the samples. The sieved data of friable sandstone of the Bara formation is demonstrated by the histogram and cumulative curves (Fig. 3-4).

Study of shapes, roundness and sphericity. The shapes, roundness, and sphericity of the grains of thirteen samples were observed, under a binocular microscope by using the charts given by Zingg (1935), and Wadell (1932). Shapes of the sedimentary grains were divided into four classes e.g., spherical (equant), oblate (disc or tabular), blade and roller (rod shape) or prolate as illustrated by Zingg (1935). According to Wadell (1932) the sphericity is the ratio of the surface area of a sphere of the same volume as the particle to the actual surface. The textural characters of the grains of studied sediments have provided important clues which helped in the interpretation of the environments of deposition.

Ten gram of unconsolidated samples was placed on a glass plate which was settled on the floor of the binocular microscope below the eyepieces, and thus each sample was analysed. Majority of grains of the friable sandstone samples of the Bara formation from Lakhra sections are of equant and oblate shapes, subangular, low sphericity and the subangular class of sphericity. The use of the Power's roundness images for sand grains were facilitated by a logarithmic (rho, *P*), scale in which the limits of the very angular class are taken as 0.01-1.0, angular (1.0-2.0), subangular (2.0-3.0), sub-round (2.0-4.0), round (4.0-5.0), and the very round (5.0-6.0) *P*, as mentioned by Folk (1974). Samples from Lakhra sections showed the variable roundness of grains from subangular and sub-rounded; subrounded – rounded; indicating the history of their transportation and deposition. The shapes of the samples of loosely friable sandstones were studied under binocular microscope at Department of Geology, University of Karachi, Pakistan. The grains of studied samples showed equant to equant/oblate shapes, and roundness of graind varied from subangular, to subrounded to rounded; the sphericity of grains was low, therefore, the grains fall in the class of subangular to subrounded.

Results and Discussion

The Bara formation of Lakhra anticline is composed of sandstone, shale and minor amount of siltstone; its physical characters including colours, shapes, roundness, sphericity of the grains of sandstones and shales have been described under the heading of materials. Section measurement data of the stratigraphic column of Lakhra area is shown in Fig. 2(a-b). Results of all investigated samples are shown in Table 2 and Fig. 1-7.

Graphical presentation of grain size data. The grain size data of the studied sediments was analysed by preparing histograms, plotting of cumulative curves, using the grain size data as the abscissa (X-axis) and the measure of percentage frequency as the ordinate (Y-axis). The values of the mean, median, standard deviation, skewness and the kurtosis were determined for using the methods of statistical analysis, to gain some insight regarding the environments of deposition. The histograms and the cumulative curves of the loose sediments of the Bara formation shown in Fig. 3-4 were prepared by the data of the statistical parameters shown in Table 2.

The graphical presentation of the grain size data has been considered as the most important and meaningful method, for understanding the environments of deposition of sediments (Folk,1968). Farshori (1967) used the values of skewness, kurtosis and the sphericity, for knowing the trends of the distribution of the grains, and the provenance of the sediments, of the Indus River. Duane (1964) highlighted the significance of skewness in the study of recent sediments, while, Folk and Ward (1957) described the importance of the grain size parameters in the investigation of sedimentation. Inman and Chamberlin (1955) studied the particle size distribution in near-shore sediments and according to Sahu (1964) the presence of coarse grains of clastic sediments reflect the fluidity (viscosity) factor of the depositing medium and the energy factor of the environments of the site of deposition. McCammon (1962) stated that when the values of more percentiles are read in cumulative curves, they confirm that the method is accurate. The percentile values of the loosely cemented sediments of the Bara formation from Lakhra sections were read from the cumulative curves. The values of the percentile read are 5% (-0.5 to 1.1 φ),

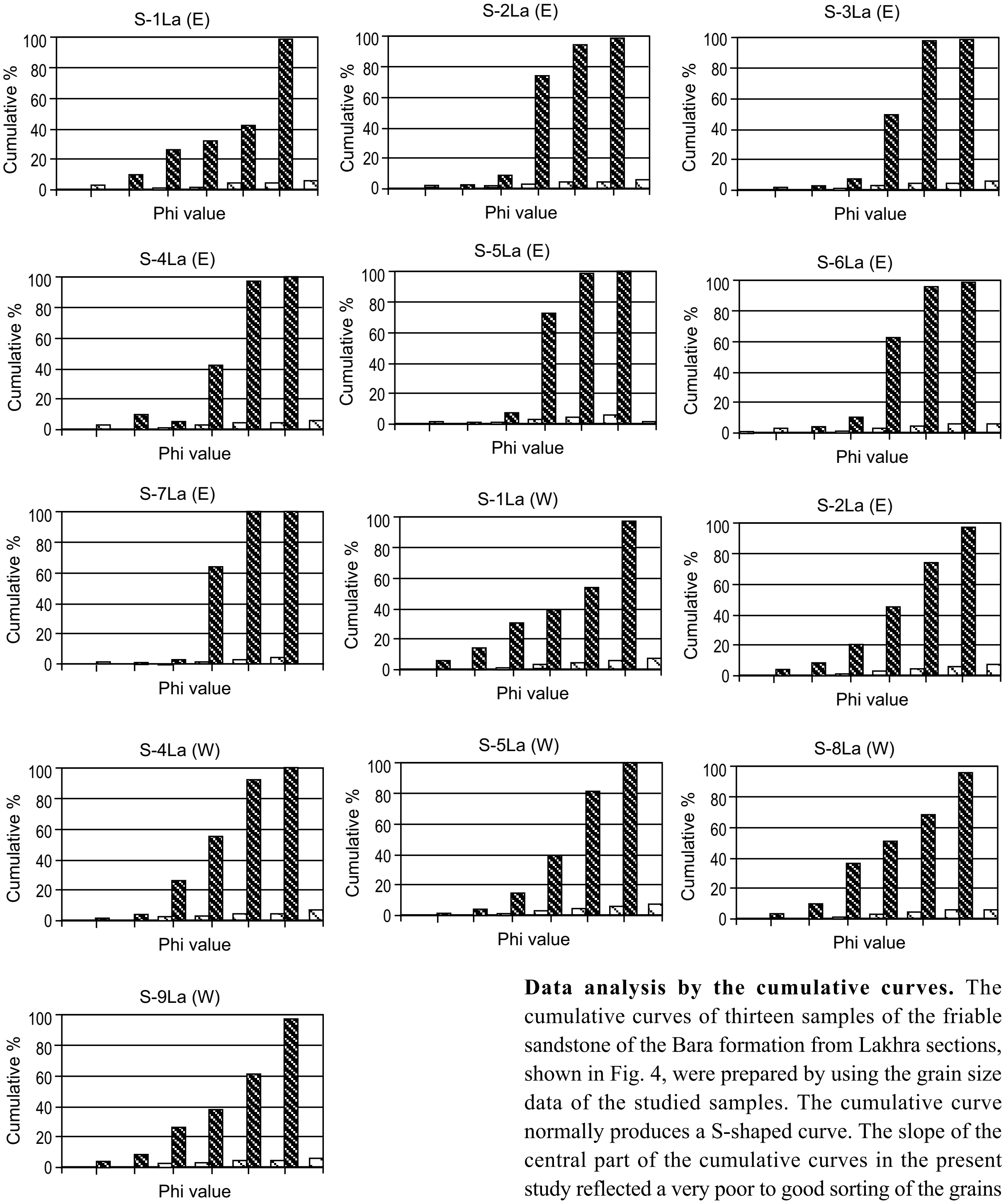

Fig. 3. Histogram of Bara formation from Lakhra sections.

16% (0.3 to 1.6 φ), 25% (0.7 to 1.8 φ), 50% (1.8 to 3.0 φ), 75 %(2.0 to 3.1 φ), 84% (2.2 to3.4 φ), and 95 % (2.5 to 4.2 φ). These values were plotted for the statistical analysis of the grain size data of loose sandstones of the Bara formation from the Lakhra section.

Data analysis by the cumulative curves. The cumulative curves of thirteen samples of the friable sandstone of the Bara formation from Lakhra sections, shown in Fig. 4, were prepared by using the grain size data of the studied samples. The cumulative curve normally produces a S-shaped curve. The slope of the central part of the cumulative curves in the present study reflected a very poor to good sorting of the grains by very gentle and very steep slopes, respectively. The central parts of the cumulative curves of four and nine samples, respectively, are steep and gentle. This observation indicated that the studied sediments were deposited under the river and beach environments, which were close to the river. The poor and good, both types of sorting exhibited by the grains further suggested that these sediments were deposited under the fluviatile

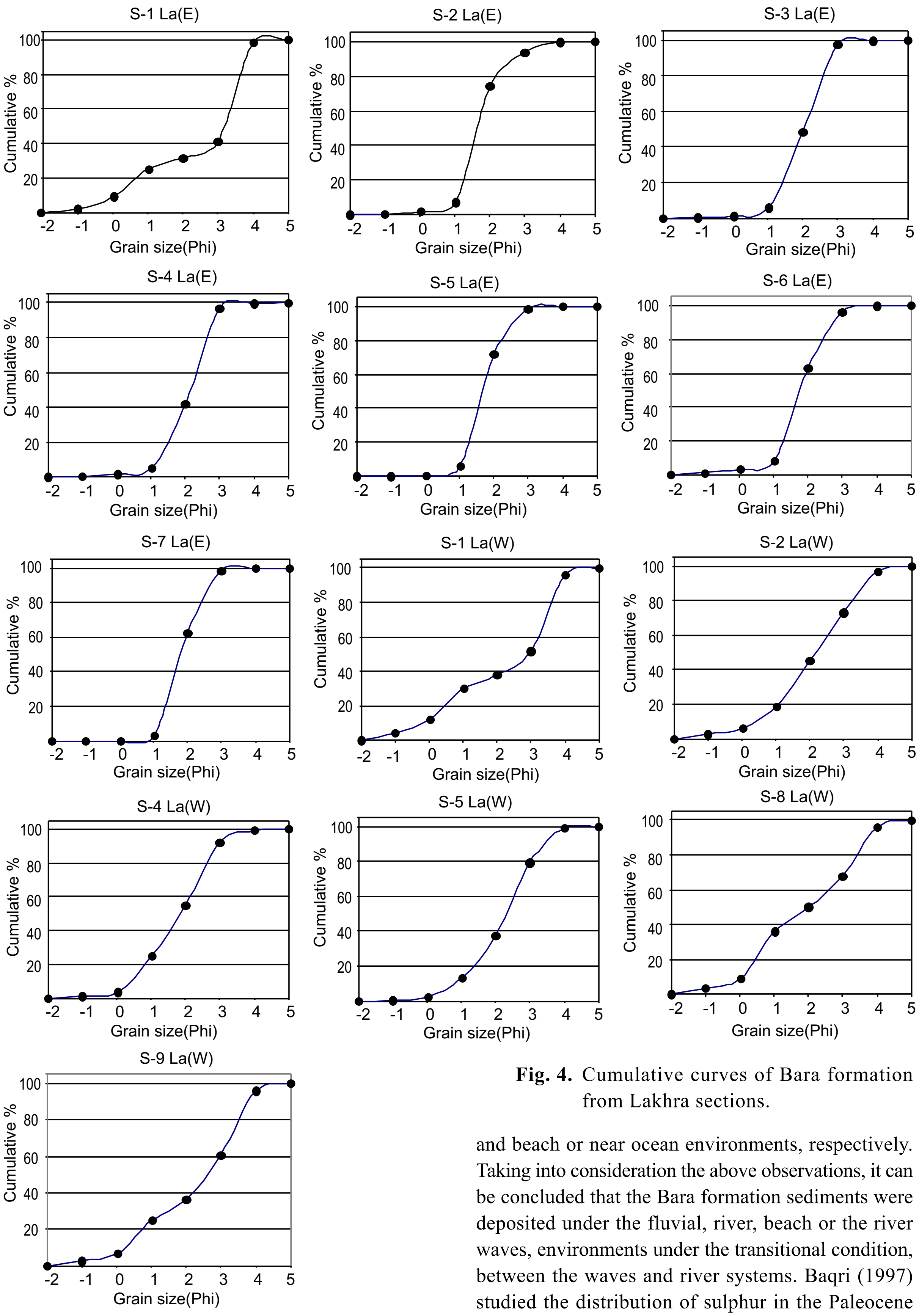

Fig. 4. Cumulative curves of Bara formation from Lakhra sections.

and beach or near ocean environments, respectively. Taking into consideration the above observations, it can be concluded that the Bara formation sediments were deposited under the fluvial, river, beach or the river waves, environments under the transitional condition, between the waves and river systems. Baqri (1997) studied the distribution of sulphur in the Paleocene coals of Sindh province and he reported a systematic variation and gradual increase of sulphur from east to west and concluded that Paleocene coal deposits of Sindh in the east areas were deposited under shallow continental lagoonal condition, whereas the deposition in the west area took place in deeper areas under brackish waters (deltas, estuarine) toward the Lakhra.

Analysis by graphic mean (MZ). Folk (1968) mentioned that the average graphic mean of the average size of sediments can be determined by the formula given below:

$MZ= (\varphi\ 16+ \varphi\ 50+ \varphi\ 84)/3$

The graphic mean values of the friable sandstones of the Bara formation from Lakhra areas were determined by using the above mentioned formula and the calculated values are presented in Table 2. The graphic mean values of the studied sediments, on comparison with the standard values reported by Folk (1968) clearly indicates that the dominant fraction of these sediments is composed of medium size sand particles, whereas the poorly sorted and fine grain sized sand is present in the sub-ordinate amount in the sediments of the Lakhra east area.

Analysis by median (MD). The median formula ($MD = \varphi\ 50$), given by Folk (1968) is commonly used for measurement in the study of sedimentology. It facilitates in the determination of the median grain size. The application of this formula in the present study indicated that particles of half of the samples by weight are coarser than the median, and the remaining half are finer. It is the diameter corresponding to the 50% mark on the cumulative curve and may be expressed either in φ (MD φ size). The median values of the studied sediments are tabulated in Table 2.

Analysis by inclusive graphic standard deviation or sorting. The inclusive graphic standard deviation or sorting formula, $\sigma I = (\varphi\ 84 - \varphi 16)/4 + (\varphi\ 95 - \varphi 5)/6.6$, formula given by Folk (1968) is one of the most useful methods to determine the nature of the sorting of sediments; its application provides information regarding the effectiveness of the depositional medium in separating the grains of different classes.

Table 2. Statistical parameters of Bara sandstones from Lakhra sections

Sample	Graphic mean	Graphic median	Sorting	Skewness	Kurtosis
1 La (E)	2.36	3	1.2	-1.6	1.34
2 La (E)	1.83	1.8	0.6	0.06	2.21
3 La (E)	1.93	2	0.5	-0.02	1.72
4 La (E)	1.98	2	0.4	-0.6	2.50
5 La (E)	1.9	1.9	0.4	-0.05	2.46
6 La (E)	1.9	1.9	0.5	-0.1	2.55
7 La (E)	1.9	1.9	0.3	-0.09	1.43
1 La (W)	2.16	3	1.6	-0.5	0.89
2 La (W)	2.13	2.3	1.4	-0.3	1.31
4 La (W)	1.7	1.9	0.8	-0.03	1.75
5 La (W)	2.26	2.6	0.9	-0.4	0.89
8 La (W)	1.9	2	1.5	-0.1	0.90
9 La (W)	2.26	2.	1.5	-0.4	1.11

The results of the inclusive graphic standard deviation of studied sediments (Table 2) shows that the values of sorting of loose cemented sandstone of the Bara formation from Lakhra sections, have showed a range from 0.3-1.2 φ indicating that these sediments are mixture of well sorted to moderately sorted to well sorted and poorly sorted grains, whereas, the samples from Lakhra west section shows a range from 0.8-1.6 φ indicating that these sediments are poorly to moderately sorted. These results supported a fluviatile system of deposition for the studied sediments. Nevertheless, the presence of well sorted sediments also supported the beach or near river type of environments of the deposition. River sand generally show poor sorting of grains than the beach sand, due to lower energy conditions, prevailing in rivers. The poor sorting of the grains of river sands due to the presence of fine grains are also distinguished by the positive skewness. A perfect discrimination between the beach and the river sands can be made by plotting the standard deviation (sorting) data against the skewness data. Dune sand, being finer than the coarser sand of beach, is also positively skewed. Friedman (1961) mentioned that due to the competence of the ocean waves, which are greater than that of the wind, the beach sand grains are coarser. The sorting of grains of the Bara formation sediments, from the Lakhra sections further indicated heterogeneity of the sediments and the depositional environments.

Analysis by inclusive graphic skewness (SKI). The skewness is the measure which depicts the uniformity of the distribution of sediments. The zero value of skewness is taken as a normal distribution of sediments which means that the cumulative curve is symmetrical and does not possess any tail. If the finer fraction is present in excess than the coarser fraction, in that case the value of the skewness is generally positive (Phi value) and in the reverse situation the skewness value is negative (Phi value +). In the present investigation the inclusive graphical skewness values were determined by Folk'sformula (1968) as given below:

$$SKI = \frac{\varphi84 + \varphi16 - 2\,(\varphi50)}{2\,(\varphi84 - \varphi16)} + \frac{\varphi95 + \varphi5 - 2\,(\varphi\,50)}{2(\varphi95 - \varphi5)}$$

The fluviatile environments of deposition of sediments are indicated by the sediments which are composed of large amount of clay and silt, commonly carried by rivers and showing the positive values of skewness. The skewness and the inclusive graphic skewness values of the loose cemented sandstone of the Bara formation from Lakhra east and west sections are ranging from -0.06 to -1.6 Phi. The 92% negative values of skewness indicated that coarse grained sediments were deposited under high energy depositional environments; only one sample showed 8% positive value of skewness which indicated deposition of fine grained sediments, under low energy condition. These observations indicated that the environments of deposition of the Bara formation were fluviatile. The beach sands according to Boggs (1987) tend to be negatively skewed because the fine sediments are winnowed out of beach sediment and are removed owing to bidirectional transport by the currents of unequal velocity than the ebb flow back down the beach, therefore, the fine particles may be removed by the return flow, leaving a negative skewed population of well sorted, coarser grains. The above discussion also supports that the environments of deposition of the studied sediments were more close to the beach and river depositional environments.

Analysis by graphic kurtosis (KG).

$KG = \varphi95 - \varphi5 / 2.44\,(\varphi75 - \varphi25)$

The values of graphic kurtosis of the loose cemented sandstone of the Bara formation from Lakhra sections as showed in Table 2, were determined by using the formula mentioned above (Folk, 1968). The kurtosis values showed a range from 0.89-2.55 indicating that these sediments are very platykurtic to mesokurtic to leptokurtic to very leptokurtic. The kurtosis data of the Bara formation sediments showed uniform distribution with negative excess, normal distribution and the positive excesses distribution, respectively. This data showed good agreement with the data given by Folk (1968).

Analysis by the Stewart diagram. Stewart (1958) plotted the values of median against the values of skewness and the standard deviation of the river sediments which were deposited under the wave dominant zones and the quiet water environments. He recognised three different types of sediments within the lagoon, sediments deposited by wave processes; rivers process, and the slow rate of deposition, from the quiet water. He also described the details of the relationship of the median against the Phi deviation and skewness and the Phi median diameter to the Phi deviation measure and the Phi skewness for his sediments.

The values of median, standard deviation and the graphic skewness of grain size data of loosely cemented friable sediments of the Bara formation from Lakhra sections of southern Sindh showed in Table 2, were plotted according to the diagram given by Stewart (1958). Fig. 5a-5b and 6a-6b, show the plots of the grain size data of the friable sandstone. Figure 5a, shows that the plotted samples were deposited under river and Fig. 5b, indicates that these samples were deposited between the boundary of rivers and waves, dominating in the wave's portion. The under discussion sediments according to this figure were deposited under the fluvial depositional environments near the sea. Fig. 6a, also shows that sediments were deposited under river between the boundary of river and waves condition.

Analysis by Passega (1964) diagram. The statistical parameters of the grain size data of the Bara formation sediments, varies from -2.0 to 0.3 (4000 to 832 microns) and the mounts of median varying from 1.9 to 3.0 (266.6 to 125 microns); were plotted according to the Passega (1964) diagram for getting more information regarding the environments of deposition. The values of one percentile and the median of the sediments of Lakhra sections (which are in phi scale), were converted into microns for using in the Passega diagram. Figure 7 shows the grain size data of loosely friable cemented sediments of Lakhra sections plotted according to Passega (1964) diagram. This plot has provided sedimentological evidences which supported the fluviatile environments of deposition. According to Passega (1964) the ratio of the one percentile (C) to the median diameter (M) could be used as an indicator of the dynamics of the depositional environments, the (CM) patterns on a logarithmic diagram are characteristic of the depositional agent.

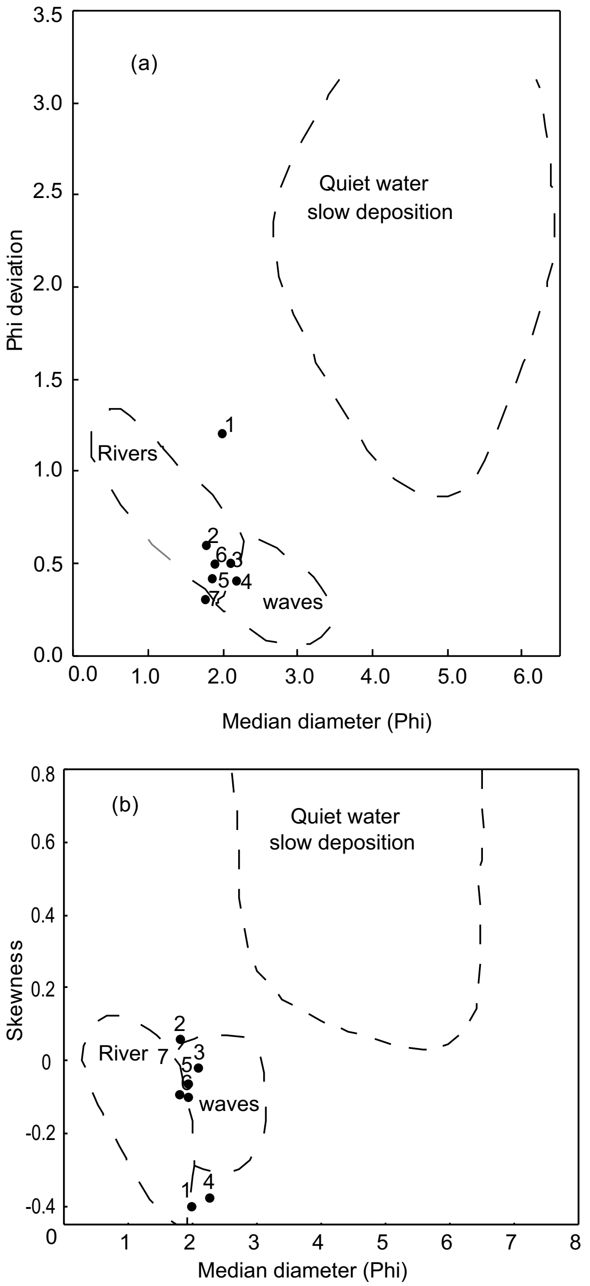

Fig. 5. Bivariate plots of loosely cemented sediments of Bara formation from Lakhra east section (after Stewart, 1958).

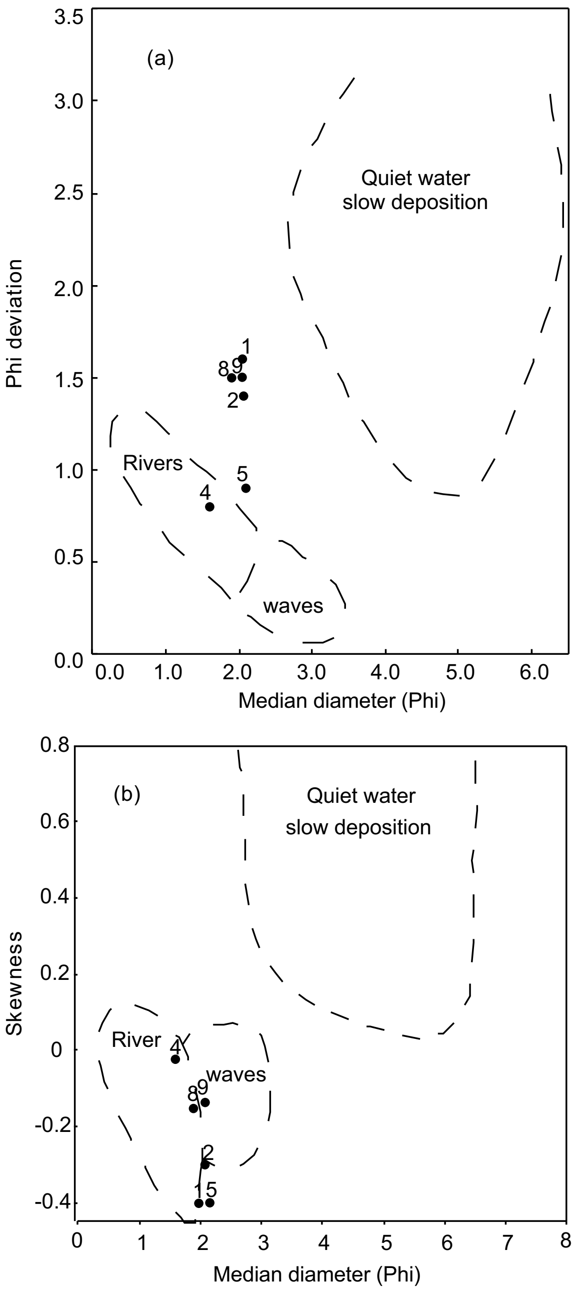

Fig. 6. Bivariate plots of loosely cemented sediments of Bara formation from Lakhra west section (after Stewart, 1958).

The data of the Bara formation plotted according to Passega (1964) diagram displayed that the studied sediments were deposited between the river and beach environment conditions.

Classification of Bara formation sandstone. In the present investigation, besides the interpretation of the depositional environments of studied sediments, an attempt has also been made to propose a suitable classification for the Bara formation sandstones. Different basis of the classifications of sandstone have been described by many sedimentologists including Pettijohn (1975); Friedman (1961); Dott (1964) and Dickinson (1985). Folk (1957) gave a classification of sandstone based on the textural maturity. According to him the textural maturities passes sequently through

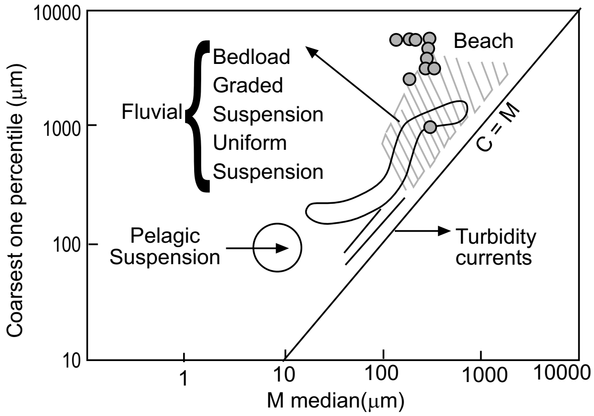

Fig. 7. Loosely cemented sediments of Bara formation of Lakhra section diagram after Passega (1964).

the following four stages:

(1) Immature stage: sediments in this stage contain over 5 percent terrigenous clay matrix, including sand grains which are usually poorly sorted and angular.

(2) Sub mature stage: sediments contain less than 5 percent clay, but sand grains are still poorly sorted (φ over 0.5φ) and are not well rounded.

(3) Mature stage: sediments contain little or no clay, and sand grains are well sorted (φ under 0.5φ), but still not rounded.

(4) Supermature stage: sediments do not contain clay, and the sand grains are well sorted and well rounded (Waddel roundness over 0.35; ρ over 3.0).

The classification of the loose cemented sandstones of Bara formation has been done on the values of the sorting stages displayed by the sand grains, which are ranging from 0.3 to 1.2φ and shown in Table 2. These values indicated that the studied sandstones are mixture of well sorted; moderately well sorted and poorly sorted grains which suggested that these sandstones belong to the sub mature to mature stages. The sub maturity and maturity of the studied sandstones also indicated that the energy of the medium of transportation was ranging between low to high. The sandstones of Lakhra west section, showed the range of sorting from 0.8-1.6, indicating that these are poorly to moderately sorted and are sub mature. Further, it also indicated that the sandstones were deposited under the low energy and fluvial condition of the deposition. The results of Lakhra east section indicated the sub- mature to mature stages of the sandstone which were deposited under the low high energy depositional environment.

Conclusion

Considering the above discussion, this study may be concluded as under:

The sediments of the Bara formation from the Lakhra east and west sections are composed of friable loose cemented sandstone and shales, displaying a variety of colours.

The grain sizes of the studied sediments ranges from coarse grained to medium grained and from medium grained to fine grained.

Plots of the cumulative curves of the studied samples indicated that during the deposition of studied sediments, the sorting of sedimentary grains was variable, and the sediments were deposited under the river/beach and fluvial environments.

The inclusive graphic standard deviation diagrams indicated that sediments were heterogeneous, composed of fine medium grains and were deposited under the high energy condition and fluviatile environments.

Studied sediments have been grouped into two groups; comprising the sediments from the upper lagoon and river; and the sediments from the dead end marsh channels from the upper parts.

The kurtosis values of the studied sediments indicated that these sediments are composed of Platykurtic, Mesokurtic and Leptokurtic groups of sediments.

Sandstones of Lakhra east section have been classified as mature to sub-mature on the basis of textural maturity, whereas the sandstones of Lakhra west section are classified as sub-mature sandstones.

The presence of abundant amounts of quartz and SiO_2, in the bul-rock samples also indicated that sediments were deposited under fluviatile (river/beach) environments.

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Surface Properties of Water Soluble Surfactants, Starch and their Complexes by Various Methods

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Abstract. Surface, interfacial tensions and reduced viscosities were measured for water soluble surfactant and starch solutions in order to determine their potential as stabilisers, emulsifiers or cleansers. The surface tension and reduced viscosity for an acid hydrolysed starch (potato) initially were declined with concentration and then reached an equilibrium value of 56 mN/m and 3.1dm^3/mol, at 20-40 wt.%. Surface, interfacial tensions and reduced viscosity of starch with surfactant mixture using the ratio 40/60 decreased more rapidly with concentration reaching values of 41-44 mN/m, and 2.5dm^3/mol, respectively, at 40 wt.%. There was little dependence of surface or interfacial tensions on degree of substitution between 0.3-0.8 and amylose content of starch . Surface and interfacial tensions for starch /surfactants mixtures were lower than those for only starch, particularly at lower concentrations. Emulsions of soybean oil/water mixtures were successfully stabilised for >1 day by potato starch acetate/octenylsuccinate and acetate/ dodecenylsuccinate but not by starch and surfactants. Therefore, these starches may represent biodegradable, economically alternatives to some emulsifiers, soap or detergents filler with effective cleansing activity and coating polymers currently in use.

Keywords: starch, surfactant, surface tension, viscosity, emulsifier, cleansing

Introduction

The cleansing activity of soap detergent is one of the most important phenomena in daily life for the modern society. Thus the improvement activity of soap detergent is obviously required for better quality and performance. Green biodegradable polymers derived from natural resources are potentially very interesting substitutes for non biodegradable petroleum based polymers. An attractive field of application for these polymers is the use of packaging materials. For the current petrochemical based products recycling is often neither practical nor economically feasible (Thiebaud *et al.,* 1997). Natural polymers such as starch, cellulose or proteins are potentially very interesting starting materials for biodegradable packaging materials. In particular, starch is attractive as it is relatively cheap and abundantly available. However, the use of native starch for packaging materials is limited due to its low moisture resistance, poor processibility (high viscosity), high brittleness and incompatibility with hydrophobic polymers. Further modification of starch is therefore, required to introduce hydrophobicity and to improve mechanical and moisture barrier properties. Thus, the interactions may be intra or intermolecular. Hydrophobically modified water soluble polymers are useful in a number of areas, such as thickeners, coatings, emulsion stabilisers and detergents (Holmberg *et al.,*2002; Piirma,1992; Shalaby *et al.,*1991; Glass, 1989). The surface properties of these polymers are important to their function of intermolecular adhesion, spreading on surfaces and dispersing oils and other hydrophobic compounds. Presently research is focussed in replacing non degradable, petroleum based materials currently used with bio-based materials derived from renewable feed stocks (Swift, 2002). In particular, native and chemically modified starches have been prepared and studied for uses in these areas (Dokic-Baucal *et al.,* 2004; Tesch *et al.,* 2002; Srokova *et al.,* 2001; Ebringerova *et al.,* 2000; Viswanathan, 1999).

Surprisingly, there is relatively little published informa-tion on the surface and interfacial tensions of native and modified starches and existing data is conflicting or incomplete. Ray *et al.* (1958) and Scholz *et al.* (1958) determined critical surface tensions for wetting of 35-39 N/m for starch, amylose and amylopectin films, 40 N/m for amylose triacetate and approximately 32 N/m for starch tributyrate.

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Lawton (1995) reported contact angle data for various liquids on cast and extruded starch films and calculated surface energy values of 35-42 N/m using the harmonic mean method of Wu (1982); Wu and Brzozowski (1971). Using the same data and the van Oss/Chaudhury/Good (VCG) method, Biresaw and Carriere (2001) calculated a value of 43 N/m. Surface energies of 47-56 N/m were reported by Odidi *et al.* (1991) for discs made from compressed starch powder although surface roughness would be expected to influence the results. Krycer *et al.* (1983) measured a surface tension of 59 N/m for a 4% solution of corn starch in water. Rudolph and Glowaky (1978) found surface tensions of 36-60 N/m for dilute (1%) aqueous solutions of mixed (acetate/phthalate, propionate/phthalate, butyrate/phthalate) esters of hydrolysed starches of degree of substitution (DS) 1.56-2.3 (Rudolph and Glowaky, 1978). Interfacial tensions of 12-21 N/m were reported recently by Tesch *et al.* (2002) for 1-5% solutions of octenyl-succinate (USA) starch and vegetable oil but no information on the DS, molecular weight or preparation method for the USA starch was given. There have been no published reports on the surface properties of starch-surfactants of DS < 3 or mixed SDS/CTAB emulsifiers of starch.

The surface energy of starch is uncertain and there is little data or understanding of the effects of DS and concentration on the surface properties of starch derivatives. Part of the reason for this may be that most commercially available derivatives are low DS (<0.05) granular starches which tend to have poor solubility in water or other solvents. Recently, Shogren and Biswas (2006) reported a simple method for preparation of highly water soluble starch acetates and mixed esters using microwave heating under non aqueous, homogeneous conditions.

Though many researchers have paid their attention in this field but chemical reactions, bond formation on starch surfactants interaction are still open for discussion. The purpose of the present investigation was to explore the effect of starch interaction with various surfactants. Therefore, this study was taken to characterise the effects of SDS, Tween-20, NaOct and CTAB on the surface and interfacial tensions and reduced viscosities of aqueous starch solutions and to get better understanding of structure/property relations and help to determine feasibility of certain applications i.e., by the ternary phase diagram, interfacial surface tension and viscosity measurement.

Materials and Methods

Starch was synthesised by UNI-CHEM, chemical reagents made by China. The degree of substitution (DS) was 0.80. The starch was dissolved by heating the starch/water mixture in autoclave for 30 min at 120 °C. All solutions were prepared at least 24 h before measurements were performed.

Preparation of starch and mixtures. The basic procedure has been described previously (Swift, 2002). Typically, 70 g dry starch, 70 g CTAB, 7-35 g SDS, 0-7 g USA starch or 0-8.8 g Tween-20 were added to a 270 mL Teflon vessel. A magnetic stir bar was added and the mixture was stirred for 5 min. The vessel was then sealed, the thermocouple inserted and the vessel was heated in a ADVANTEC FC-610 forced convection oven (Milestone Inc., Shelton, Japan) from 25 to 150 °C over 3.5 min, then 150-160 °C over 1.5-2.5 min. After opening the reactor, the contents were placed in a Waring blender with 400 mL ethanol (99.5%) and blended until the precipitate was broken into fine particles. The ethanol supernatant was poured off and four additional ethanol extractions were performed. Excess ethanol was removed by filtration on a Buchner funnel and the starch surfactants mixture were dried in a forced air oven overnight at 50 °C and then in a vacuum oven overnight at 80 °C.

Surfactants. The surfactants used were commercial grade sodium dodecyl sulphate (SDS) and *n*-cetyl-*n*,*n*, *n*-trimethyl ammonium bromide (CTAB) were analytical grade made from LOBA Chemical Pvt., Ltd., India.

Other chemicals. The water was ion exchanged and distilled .Its conductivity, reduced viscosity was 2.0 µs, 4.0 dm^3/mol and its surface tension was 71.5±0.5 N/m at 30 °C. All other chemicals were analytical grade and were used without further purification.

Surface and interfacial tension measurement. Surface tension was measured with a drop weight method (Stalagmometer instruments). In the calculation of surface tension, the correction factors of (Huh and Mason, 1975) were used. The temperature was 25 °C or 30 °C, depending on the Krafft point of the surfactants used. The reproducibility between measurements on the same sample was ± 0.5 N/m This was probably due to the very low concentrations of starch (0.01 wt.%). The results of the surface tension measurement were presented as (g) values calculated from

$$\gamma = \frac{mg}{2\,\pi rf}$$

where:

$f = \frac{1}{v^3}$; v = volume of the drop; r = radius; m = the weight of falling drop; g = surface tension.

A drop of the weight (m) given by the above equation has been designated by Harkins and Brown (1919) as the ideal drop. Repeated measurements were conducted on each sample from which equilibrium surface or interfacial tension values were obtained by averaging the values at very long periods, where the surface and interfacial tension values showed little or no change with time. Prior to running tests with the starch solutions, the instrument was calibrated with water and then checked by measuring the interfacial tension between water and pure starch.

Viscosity. Ostwald viscometer of British Standard Institution with thermostat (the Fisher Scientific TM 200) with fluctuation of ± 0.1 °C was used to determine viscosities. The flow of time was recorded by a timer accurate up to ± 0.01 second. At certain surfactant/starch ratios the aggregates formed were very mobile flocks, which tended to form in the samples. This could be partly avoided by draining the capillary fully between measurements. The results of the viscosity values were calculated from

$$\eta_{red} = \frac{\frac{(t-t_o)}{t_o}}{c}$$

where:

t = the measured efflux time of solutions; t_o = the efflux time of the pure solvent (water) and c = the weight concentration of the surfactant, starch and surfactants mixed polymer (starch).

Results and Discussion

The surface tension value of starch, surfactant and their mixtures are given in Table 1-3. Figures 1 and 2 show that starch molecule have many hydroxyl groups and hydrogen atoms which bind with surfactant molecule through H-atom called H-bond formation. So bond breakdown of hydrophilic and hydrophobic part of surfactant molecules finally increases cleansing activity. Although starches are surface inactive but due to H-bonding with ionic surfactants, it became more surface active which has proved the lowering value of surface tension and reduced viscosity at CMC point (Figs. 3-6). Tables. 1-3 also prove the gradual decreased condition of the value of surface tension but at CMC point the leveling value stops. Not only these, but CMC (critical micelle concentrations) have also been changed by the variation of mole fraction (Table 4).

From comparison studies at fixed starch concentration (0.01 to 0.1% w/v) and variable surfactants concentration (0.05, 0.15 & 0.45% w/v), it has been found that at certain concentration of surfactant surface tension, value is minimum which indicates maximum cleansing activity appearing in the mentioned points. It also shows from Figs. 5-6 log conc., *versus* surface tension plot at a fixed concentration (CMC) the value of surface tension is minimum but after increasing

Table 1. The value of surface tension (N/m) of all types of surfactants(0.05%) with added starch (0.01-0.1%) solution

% Log conc., of surfactant solution	% conc., of surfactant solution × 10^{-2}	Surface tension of SDS mixed starch sol^n. (N/m)	Surface tension of CTAB mixed starch sol^n. (N/m)	Surface tension of Tween-20 mixed starch sol^n. (N/m)	Surface tension of NaOct mixed starch sol^n. (N/m)
-2.00	0.01	50.61	50.44	50.36	50.13
-1.69	0.02	49.52	48.40	48.44	48.33
-1.52	0.03	46.85	46.92	47.00	46.59
-1.39	0.04	45.81	46.13	45.86	44.63
-1.30	0.05	44.63	45.40	44.87	44.15
-1.22	0.06	44.45	44.62	44.09	43.49
-1.15	0.07	44.23	43.94	43.70	43.23
-1.09	0.08	43.85	43.71	43.30	43.13
-1.04	0.09	43.82	43.70	43.75	43.11
-1.00	0.10	43.81	43.66	43.72	43.11

Table 2. The value of surface tension (N/m) of all types of surfactants(0.15%) with added starch (0.01-0.1%) solution

% Log conc., of surfactant solution	% conc., of surfactant solution × 10^{-2}	Surface tension of SDS mixed starch sol^n. (N/m)	Surface tension of CTAB mixed starch sol^n. (N/m)	Surface tension of Tween-20 mixed starch sol^n. (N/m)	Surface tension of NaOct mixed starch sol^n. (N/m)
-2.00	0.01	49.86	49.94	49.86	49.63
-1.69	0.02	48.77	47.90	47.94	47.83
-1.52	0.03	46.10	46.42	46.50	46.09
-1.39	0.04	45.06	45.63	45.36	44.13
-1.30	0.05	43.88	44.90	44.37	43.55
-1.22	0.06	43.70	44.12	43.59	42.99
-1.15	0.07	43.48	43.44	43.20	42.73
-1.09	0.08	43.10	43.22	42.80	42.63
-1.04	0.09	43.08	43.20	42.76	42.61
-1.00	0.10	43.08	43.20	42.76	42.61

Table 3. The value of surface tension (N/m) of all types of surfactants(0.45%) with added starch (0.01-0.1%) solution

% Log conc., of surfactant solution	% conc., of surfactant solution × 10^{-2}	Surface tension of SDS mixed starch sol^n. (N/m)	Surface tension of CTAB mixed starch sol^n. (N/m)	Surface tension of Tween-20 mixed starch sol^n. (N/m)	Surface tension of NaOct mixed starch sol^n. (N/m)
-2.00	0.01	49.11	49.19	49.11	48.88
-1.69	0.02	48.02	47.15	47.19	47.08
-1.52	0.03	45.35	45.67	45.75	45.34
-1.39	0.04	44.31	44.89	44.61	43.38
-1.30	0.05	43.13	44.15	43.63	42.80
-1.22	0.06	42.95	43.37	42.84	42.24
-1.15	0.07	42.73	42.69	42.45	41.98
-1.09	0.08	42.55	42.46	42.05	41.88
-1.04	0.09	42.52	42.45	42.05	41.86
-1.00	0.10	41.51	42.41	42.07	41.86

Table. 4. Critical micelle concentrations of binary surfactant mixtures (CTAB = cetyl sodium dodecyl sulphate and trimethylammonium bromide, NaOct = sodium octanoyate SDS

Mole fraction	SDS/ CTAB	SDS/ Tween-20	CTAB/ Tween-20	NaOct/ CTAB	NaOct/ Tween-20	SDS/ NaOCt
0	0.98	0.071	0.071	25.0	23.0	8.32
0.17	1.10	0.074	0.081	28.2	27.9	9.75
0.25	1.26	0.090	0.092	30.1	28.6	10.5
0.50	1.60	0.128	0.122	39.6	37.2	15.0
0.75	2.32	0.212	0.236	52.7	56.3	24.4
0.83	3.03	0.296	0.406	62.3	72.3	32.2
0.91	3.67	0.403	-	73.2	76.5	-
1	95.5	0.993	96.7	95.5	97.5	95.5

log conc., the results show that surface tension curve is level off. Present investigation is based on the critical micelle concentration (CMC) point and either any type of surfactants only or mixtures with starches, same results are found due to saturation and maximum interaction occurred in this points. Although, starch itself is surface inactive, however, when it has been added with surfactant as a soap or detergent filler, it

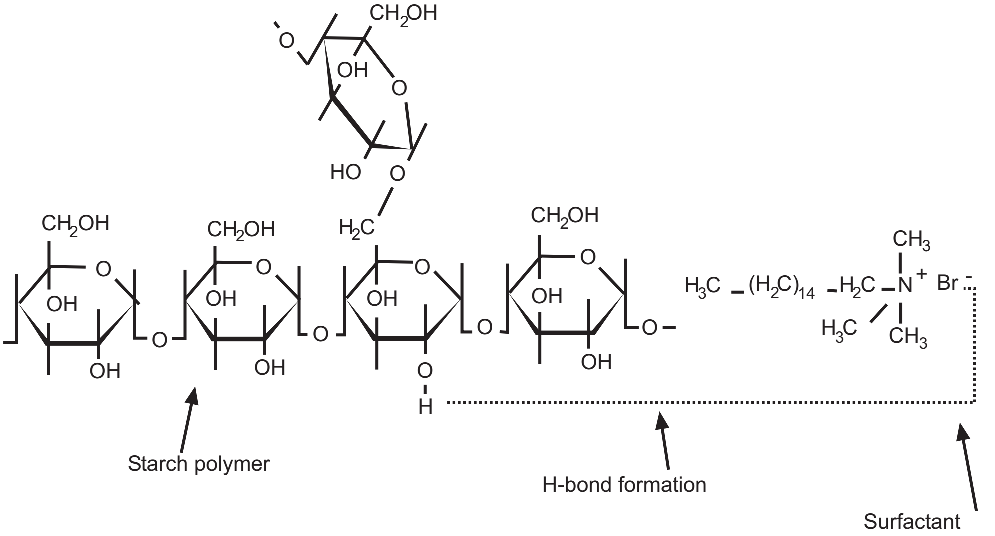

Fig. 1. H - Bond formation starch with cationic anionic surfactants.

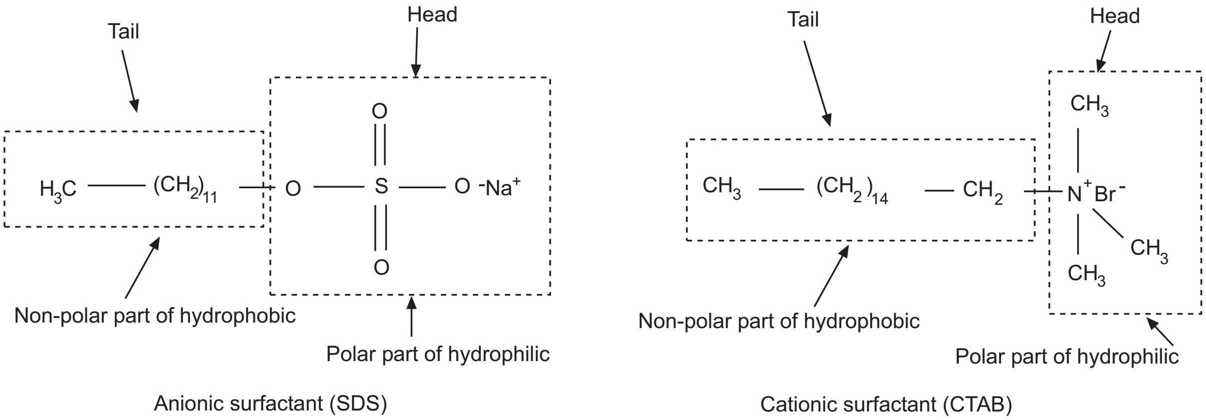

Fig. 2. Structure of both cationic and anionic surfactants having polar and non polar group.

reduces the surface tension value which means it reacts and makes bond formation like H-bond processes, where, both cationic and anionic of non polar part induced to break down the bond hence, it goes to dirty particle quickly which ensure prompt cleansing activity of starch mixed surfactant solution.

Figure 5 shows the surface tension of solutions of NaOct and NaOct/CTAB mixtures in 0.01 w/v starch solutions as a function of the surfactant concentration. Critical micele concentrations (CMC) are indicated by sudden changes in the slopes of the curves. When part of the NaOct is replaced by CTAB, the CMC increases with increasing mole fraction of the short-chain surfactant. At concentrations considerably above those corresponding to charge equivalence between the amounts of surfactant and starch, a complex phase containing high concentrations of surfactants and polymer is formed. The phase separation can be observed visually as a clouding of the sample. The two phase area is represented by a dashed line in Fig. 5 and 6. Phase separation takes place at higher surfactant concentrations when the fraction of NaOct increases (Fig. 6). Increasing the mole fraction of NaOct above 0.83 does not significantly affect the CMC, but the two-phase area extends to higher concentrations. Fig. 5 shows the surface tension when a mixture of NaOct and shorter-chain surfactant is added (1:1mole ratio) at constant starch concentration. Although the effect is not very marked, the CMC is always higher than for pure NaOct. The shift decreases when the chain length of the second surfactant increases. The concentration at which the gel phase separates increases in the order NaOct<CTAB<SDS<Tween-20. Redissolution,

which is not complete with this highly charged starch (DS=0.80), also takes place at a slightly higher concentration in the shorter of the chain length of the second surfactant.

Figure 3 shows the reduced viscosity of starch solutions containing different surfactant mixtures. The viscosity drop occurs at lower concentrations as the hydrocarbon chain length of the second surfactant increases. Thus, the interaction depends markedly on the surface activities of the surfactants. The viscosity increase when excess surfactant begins to dissolve. At the same time, the added excess surfactant begins to form free micelles. This results in an increased viscosity. The surfactant concentration at which the sudden viscosity reduction occurs increases when the NaOct/CTAB molar ratio decreases. The minimum of viscosity due to charge neutralization also occurs at a higher surfactant concentration than with pure NaOct. The chemical

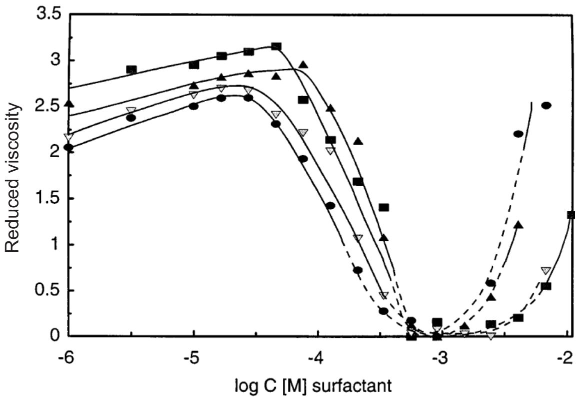

Fig. 3. Reduced viscosities of solutions of potato starch (0.01 wt.%, DS = 0.80) and Na Oct/ second surfactant mixtures. The surfactants were NaOct1 (⬬), NaOct/CTAB (▼), NaOct/SDS (▬), and NaOct/Tween-20) (▲). The molar ratio of the surfactants in the surfactants mixtures was 1:1. The two phase domain is indicated by the dotted line.

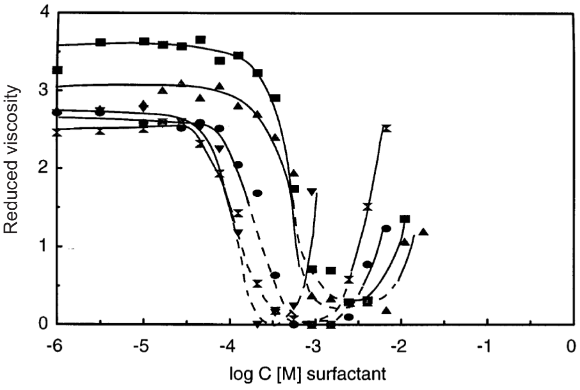

Fig. 4. Reduced viscosities of solutions of starch (0.01 wt.%, DS = 0.80) and SDS/CTAB mixtures. The molar ratio of the surfactants were 1:0. (▼), 3:1 (⧗), 1:1 (⬬), 1:3 (▲) and 1:5 (▬). The two phase domain is indicated by the dotted line.

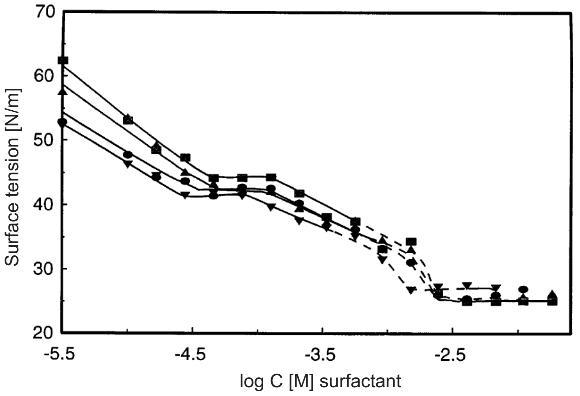

Fig. 5. Surface tension of solutions of potato starch (0.01 wt.%, DS = 0.80) and NaOct/second surfactant mixtures. The surfactants were NaOct (⬬), NaOct/CTAB (▼), NaOct/ SDS (▬) and NaOct/Tween-20 (▲). The molar ratio of the surfactants in the surfactant mixture was 1:1. The two phase domain is indicated by the dotted line.

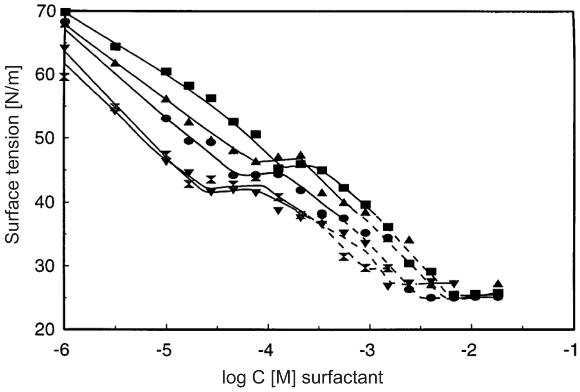

Fig. 6. Surface tension of solutions of potato starch (0.01 wt.%, DS = 0.80) and SDS/CTAB mixture. The molar ratio of the surfactants were 1:1 (⬬) 3:1 (⧗), 1:0 (▼), 1:3 (▲) and 1:5 (▬). The two-phase domain is indicated by the dotted line.

structures of the starch surfactants (SDS,CTAB) by the H-bonding process in Fig. 1-2. The efficiencies were high, typically 100% or higher, as reported previously (Shogren and Biswas, 2006). Values over 100% reflect direct esterification with acetic acid in addition to reaction with acetic anhydride. Reaction efficiencies of SDS (55%) and CATB (29%) were lower, reflecting the slower rates of reaction of starch with surfactants. Water solubility of the samples were >95% (w/w) except for high amylose starch which was 70%. For comparison, the water solubility of potato starch of degree of substitution was 0.03 prepared by the aqueous suspension method (Jeon *et al.,* 1999) was only 25%, even with prior heating and stirring an aqueous solution to 140 °C in a sealed reactivial. Reduced viscosities were low for potato starch and increased with amylose content as noted previously (Shogren and Biswas, 2006).

In models of mixed micellisation (Holland and Rubingh, 1992), the Gibbs energy of mixed micelle formation is discussed in terms of several contributions as follows:

(1) Contact energy of the surfactant. When the hydrophobic moiety of the surfactant is transferred from an aqueous environment into the liquid hydrocarbon like interior core of the micelle, there is a favourable change in the contact energy depending on the hydrocarbon chain length but is mainly due to the creation of water/water contacts.

(2) Conformational entropy. The transfer of the hydrophobic moiety of the surfactant into the micelles also implies an energetically favourable change in their conformational energy.

(3) Aggregate core-water interfacial Gibbs energy. If the hydrophilic moiety is not very bulky, the formation of a micelle generates an interface between the hydrophobic core region and the surrounding aqueous solution.

(4) Head group steric interactions: In the formation of micelles, the polar head groups of the surfactant molecules crowd into the aggregate surface. This generates steric repulsions between the head groups.

(5) Head group. Ionic and dipole interactions for ionic surfactants, repulsing electrostatic interactions arise at the micellar surface for zwitter ionic surfactants. One has to consider the interactions between the permanent dipoles of the polar groups.

Conclusion

The investigations presented in this paper show that strong ionic interaction between cationic and anionic surfactants (CTAB, SDS, Na Oct) except non ionic surfactant (Tween-20) and starch polymer, leads to phase separation and precipitation of the formed amorphous complexes. Complex formation on starch depends on the chain length difference and is exactly in the same way as for free mixed micelles .The separated complex phase is a hydrophobic which is highly viscous and gel like containing 40 to 60% water. The high and low water content of the complex phase indicates that the interactions between the starch and ionic surfactants are very strong. The ionic surfactants (CTAB, SDS, NaOct) at concentrations above its CMC reduces the inter- polymer association through micelles formation around hydrophobic (alkyl group) groups. The presence of a miscible starch molecule also reduces inter-polymer association by preferential solvation of the hydrophobic groups.

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Seasonal Variations in Dissolved Heavy Metals in Pompom River, Itakpe, Nigeria

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Abstract. Seasonal variations in dissolved heavy metals cadmium (Cd), copper (Cu), nickle (Ni), lead (Pb), and zinc (Zn) in Pompom river, flowing across Itakpe iron mine, Nigeria, was studied using flame atomic absorption spectroscopy (FAAS). Precision for the determination of heavy metals in water ranged 3-16 % and recovery studies gave 79-104 %. The average concentrations in the dry and rainy seasons for heavy metals in Pompom river were 0.03±0.003, 0.05±0.002, 0.01±0.002, 0.01 ±0.001 and 0.04±0.002 mg/L for Cd, Cu, Ni, Pb and Zn, respectively. Seasonal variation showed metallic levels in water to be higher during the rainy season than dry season. Cu, Ni, Pb and Zn metallic levels of the studied metals were within the values of Federal Environmental Protection Agency (FEPA) of Nigeria and WHO permissible guidelines for drinking water.

Keywords: mining, seasonal variations, heavy metals, river, monitoring

Introduction

The existence of metals in aquatic environments has led to contamination of natural waters due to their hazardous effects. Sources of metals in waters can be natural or anthropogenic. Natural sources are weathering effects on rocks and minerals, while anthropogenic sources are associated with mining, agricultural applications, untreated industrial wastes, atmospheric sources etc., (Abolude *et al.,* 2009; Papafilippaki *et al.,* 2008; Marcovecchio *et al.,* 2007; Laws, 2000). Worldwide industrial discharge is reported to be responsible for dumping 300-400 million tonnes of heavy metals and other wastes into water annually (Palaniappan *et al.,* 2010). Such discharges have resulted into toxic substances released into the environment contributing to a variety of toxic effects on living aquatic organisms in food chain and degradation of water quality. Traichaiyaporn and Chitmanat (2008) reported that due to metal pollution in the upper Ping river, Thailand, death of fish and migration of some aquatic organisms occurred. Health effects in humans such as kidney dysfunction, cancer and sometimes death have been reported due to water pollution (Lawson, 2011).

Many developing regions of the world are facing unmonitored mining activities which have resulted in metal polluting the water ecosystems. Selenga river Basin in Mongolia mine vicinity for example, is reported to contribute 1 % and 3 % of the world flux of dissolved Fe and Pb, respectively (Thorslund *et al.,* 2012). Heavy metals are of particular interest considering their toxicity at low concentrations, synergistic effects, average long life, persistence, ability to bioaccumulate and potential adverse health effects to humans, animals, plants and ecosystems in general (Traichaiyaporn and Chitmanat, 2008; Marcovecchio *et al.,* 2007). In mining sites the potential to pollute the environment is enhanced by the high content of metals in mineral ore, and their proximity to streams. Acid mine drainage is reported to be responsible for the degradation of more than 12,000 km of streams in the Appalachaian region of the northeastern, USA (DeNicola and Stapleton, 2002). Heavy metal concentration in wells located near mining sites has been reported to contain levels that exceed drinking water criteria. Surface waters in the vicinity of abandoned mine sites also require monitoring. Studies of spoil heaps which polluted water flows in an abandoned mercury mine site in Asturias, in Spain reported acidic conditions and high As contents (Loredo *et al.,* 2005).

Agricultural activities also release metals into water bodies which significantly affect the quality of water. The concentration of metals dissolved in water may give a misleading picture of the degree of contamination and hence under estimation of the total metal concentration in the water body (Palaniappan *et al.,* 2010; Abolude *et al.,* 2009; Laws, 2000). Thus heavy metal concentrations and flow data require strict

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monitoring to determine concentrations below health-risk based guideline values.

The accurate determinations of heavy metals in aquatic environment are of ultimate importance for controlling their pollution. Numerous studies abound on the concentration levels of heavy metals in aquatic environments globally but a few has been carried out in water ecosystems of Nigeria. This work is an exploratory approach for baseline data for water quality through the determination of concentration of heavy metals in Pompom river flowing across Itakpe iron mine, Nigeria. The studies aims to determine the seasonal variation of Cd, Cu, Mg, Ni, Pb and Zn in the Pompom river and providing data on water quality assessment.

Materials and Methods

The study area is the Itakpe mining environment located in Okehi local government of Kogi State, Nigeria. The mine deposit is located within longitude 6° 16′E and latitude 7° 36′N. The climate of the area is characterised by 6 months (May to October) of rainy season (RS) and 6 months (November to April) of dry season (DS). Agricultural practice in this area is at subsistence level with cultivation of food crops. River Pompom flows across the mining site. This river serves for irrigation, fishing, drinking, domestic and grazing purposes.

All the water samples were collected from the river Pompom between January, 2010 and December, 2010. A total of 150 water samples (25 samples per sampling location and 75 samples per season) were collected each in 4 litters plastic container and properly closed during each season from river Pompom at L4 (up stream), L3 (point of entry of industrial effluents) and L2 (downstream). The dry season (DS) samples were collected in January 2010, while the rainy season (RS) samples were collected in July 2010. Figure 1 shows map of Itakpe mining environment with the sampling points, while, Table 1 shows sample descriptions and locations.

Water samples were collected by immersion of the container below water level. The containers were completely filled with water and the water samples were not filtered prior to analysis. 1% HNO_3 solution was added to acidify the sample to a pH of < 2 as preservative. The same treatment was given to the blank samples.

USEPA (2008) method was used to digest the water samples. 100 mL sample volume was transferred into a beaker and 6 mL of conc. HNO_3 was added. The beaker was placed on a hot plate and the sample was evaporated to near dryness, making certain the sample did not boil. The beaker was cooled and another 6 mL of conc. HNO_3 was added. The beaker was covered with a watch glass and returned to the hot plate. The temperature of the hot plate was increased for a gentle reflux. The sample was evaporated to near dryness and the beaker cooled, 5 mL of 1:1 HCl was added. The beaker was warmed and the sample pH adjusted to pH 4 with 5 M NaOH solution. The sample was then transferred to a volumetric flask and the volume diluted to 25 mL with deionised water. The extract was analysed using AAS. The same procedure was carried out for blank and spiked samples.

Atomic absorption spectrophotometer (AAS) model 210VGP, Buck Scientific Incorporated USA was used for the determination of heavy metals. The wave lengths used for measurements were 326.1 for Cd, 324.7 for Cu, 285.2 for Mg, 341.5 for Ni, 283.3 for Pb and 213.9 nm, for Zn with detection limits of 0.01, 0.005, 0.005, 0.1, 0.08, 0.005 mg/L.

Quality control was implemented through the use of precision analysis using 10 replicate samples, spiking was done using standards of concentration of each studied metal and reagent blank. Precision studies for the determination of heavy metals in water ranged 3-16% and recovery studies gave 79-104%. Data provided were average of three replicate samples. The values of these parameters were compared to FEPA and WHO permissible guidelines for drinking water.

Results and Discussion

The summary of the concentration of metals in the water sample for the rainy and dry seasons and their mean are listed in Table 2. Generally, the metal levels were low and there were no significant differences in metallic levels in the samples collected upstream and downstream of the river. Cd concentration in the three locations ranged from <0.01-0.06, Cu ranged <0.01-0.10, Ni ranged <0.01-0.01, Pb ranged <0.01-0.01 and Zn ranged 0.02- 0.04 mg/L. Cd concentration was lowest in L4 and the same in L2 and L3. Cu concentration was highest in L4 and the same in L2 and L3. Zn concentration in L2 and L4 were the same and higher than L3. The concentrations of the heavy metals were higher during the RS than the DS. The lowest metal concentration levels were observed during the DS for Cu, Cd, Ni and Pb (<0.01 mg/L). Significant seasonal variations were observed between DS and RS in the

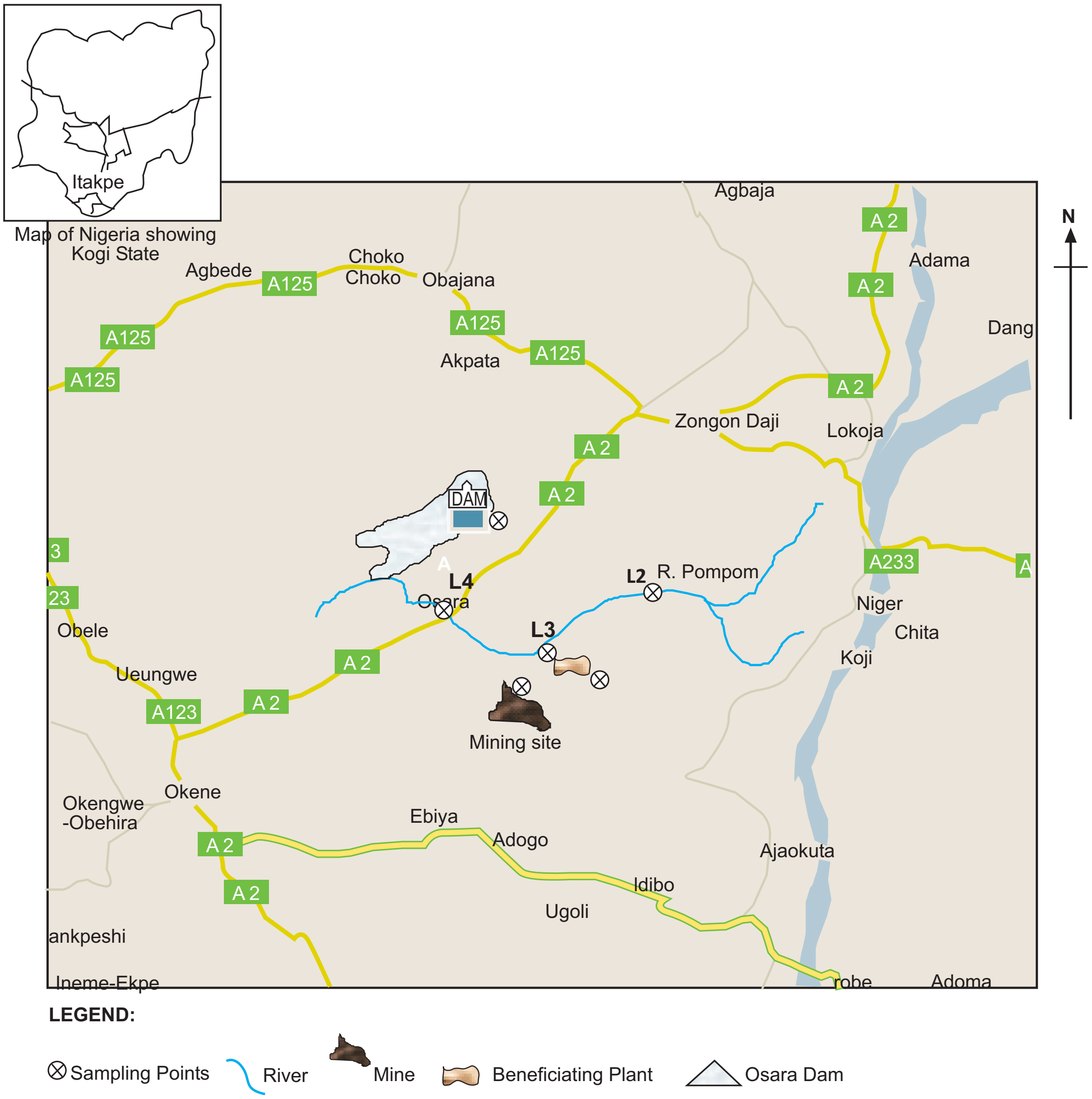

Fig. 1 Map of Itakpe mining environment showing sampling area.

Table 1. Sample descriptions and locations

Sample	Sample description	Source	Bearing
L2	Water	Beneficiating Plant area	7° 37.187′N 6° 19.673′E
L3	Water	Beneficiating Plant area	7° 37.052′N 6° 19.173′E
L4	Water	Mining site area	7° 36.929′N 6° 18.626′E

concentrations of Cd, Cu, Ni and Pb, whereas, in case of Zn the seasonal change was not significant. Cu level was highest during the RS followed by Cd. Ni and Pb were the same concentration in all the locations during the RS.

Heavy metals in natural water are present in colloidal, particulate and dissolved forms with the proportion of these forms varying with metals and for different water bodies. Rivers are pathway for metal transport with dispersion patterns dependent on the solubility, mobility and species of each metal. According to Papafilippaki

Table 2. Concentration (µg/L) of metals in the water samples in dry and rainy season

Metal	Location	Dry season (DS)	Rainy season (RS)	Mean (RS&DS)
Cd	L2	<0.01	0.06±0.004	
	L3	<0.01	0.06±0.004	
	L4	<0.01	0.04±0.001	
Mean		<0.01	0.05±0.003	0.03±0.003
Range		-	0.047-0.053	0.027-0.033
Cu	L2	<0.01	0.08±0.005	
	L3	<0.01	0.08±0.005	
	L4	<0.01	0.10±0.003	
Mean		<0.01	0.09±0.004	0.05±0.002
Range		-	0.086-0.094	0.048-0.052
Ni	L2	<0.01	0.01±0.001	
	L3	<0.01	0.01±0.001	
	L4	<0.01	0.01±0.004	
Mean		<0.01	0.01±0.002	0.01±0.002
Range		-	0.008-0.012	0.008-0.012
Pb	L2	<0.01	0.01±0.001	
	L3	<0.01	0.01±0.001	
	L4	<0.01	0.01±0.001	
Mean		<0.01	0.01±0.001	0.01±0.001
Range		-	0.009-0.011	0.009-0.011
Zn	L2	0.03 ±0.001	0.04± 0.001	
	L3	0.02±0.002	0.03 ±0.002	
	L4	0.03± 0.001	0.04± 0.003	
Mean		0.03± 0.001	0.04± 0.002	0.04±0.002
Range		0.029-0.031	0.038-0.042	0.038-0.042

et al. (2008) metals undergo numerous changes in their speciation during transportation due to dissolution, precipitation, sorption and complexation phenomena which affect their behaviour and bioavailability. Their behaviour depends on the sediment, suspended particulate matter and water composition, while the pH, redox, temperature and river flow control their solubility and speciation (Thorslund *et al.,* 2012; Papafilippaki *et al.,* 2008; Marcovecchio *et al.,* 2007). Natural mass flow of heavy metals in dissolved form was reported by Thorslund *et al.* (2012) to increase by an order of magnitude due to mining. Gold mining at the Zaamar mine in Mongolia is reported to increase the total riverine mass flows of Al, As, Cu, Fe, Mn, Pb and Zn by 44.300, 30.1, 65.7, 47.800, 1.480, 76.0 and 65.0 tonnes/yr, respectively (Thorslund *et al.,* 2012).

All the metals studied were present in the water sample. There was no specific distribution pattern with metallic concentration levels in the locations. This is due to the varieties of sources and the several factors which determine the release of these metals into the river. These sources may be attributed to industrial waste, weathering of rocks and minerals, soil leaching and the geochemical characteristics and mineralisation of the tailings. Non-point sources such as agricultural activity and atmospheric sources also introduce heavy metals into the river Pompom. Climate change could impact on the sources of these metallic pollutants. Other possible sources of heavy metals into the Pompom river could be due to the discharge of industrial effluents as a result of leakages from waste pipes and reagents added during mineral processing. Hg and CN have been reported to be part of the components of reagent used in mineral processing (Ato *et al.,* 2010; Cordos *et al.,* 2003). Inorganic Hg could be methylated in the water environment and lead to levels in fish and other high-level predators which pose a human health risk (Loredo *et al.,* 2000). CN affects all components of the aquatic ecosystem: change in water quality, decrease in a number of fish species and some of the microalgae and mollusks species have been reported to disappear (Cordos *et al.,* 2003).

The generally low metallic levels observed in the studied metals could be due to the distance of the mine from the river and the low level of contaminants entering the river Pompom as a result of the stoppage of mining. Sedimentation process could take place leading to the less soluble metal forms accumulating in suspended or sediment phase. Laws (2003) reported the transport of Cd downstream in suspended form, while Panutrakul *et al.* (2003) findings reported more than 70% of all the studied metals to be present in particulate form with Fe more than 95%. Low concentration levels of some metals could be due to the speciation of metals which makes them readily absorbed by marine plants and organic matter resulting in their consequent settlement to the bottom of the river.

The higher metallic levels during the RS could be due to the introduction of lots of detritus and pollutants through erosion. Acid mine drainage (AMD) occurs as a result of the exposure of sulphide minerals present in heaps of tailings in the vicinity of the mines to water and oxygen. Series of chemical reaction results in water discharges high in acidity and concentration of metals. Furthermore, ferric ions produced by the oxidation of the pyrite minerals are capable of dissolving other heavy metal minerals (Makhoukh, 2011; Cordos *et al.,* 2003;

DeNicola and Stapleton, 2002). High acidity, increased concentration of heavy metals and precipitate of metals caused by AMD runoff into rivers results in reduction of benthic macroinvertebrate abundance and diversity (DeNicola and Stapleton, 2002). The high level of Cd and Cu during the RS could be due to impute from agrochemicals which results in the introduction of heavy metals into soil which is leached into the river. Cd and Cu have been reported to be components of fertilisers and pesticides (Traichaiyaporn and Chitmanat, 2008). Cu is a trace element essential to life, but, at high concentrations it can be toxic to humans (Nirel and Pasquini, 2010). Cadmium is very soluble in water and is one of the most toxic elements. At high concentrations Cd can lead to chronic kidney dysfunction, carcinogenic effects in humans, induction of cell injury and death by interfering with Ca regulation in biological systems in human. Studies by Traichaiyaporn and Chitmanat (2008) reports combustion of fossil fuels used in mining activities as leaking heavy metals such as Pb into the atmosphere. Exposure to Pb in drinking water above the permissible level can result in delays in physical and mental development, along with deficits in attention span and learning abilities in babies and children (Lawson, 2011).

Rainfall causes dissolution of gases such as carbon dioxide, oxygen, sulphur dioxide and nitrogen present in air through windblown dust, deforestation forest fires and volcanic particles. This results in toxic run off dissolving and picking up other substances causing an increase in metallic levels in the river during the RS (Lawson, 2011). Findings by other researchers have reported low metallic levels during the RS to be due to excessive rains which cause dilution in soil solution and results in the reduction of metal concentrations flowing into water bodies (Sankar *et al.,* 2010; Palaniappan *et al.,* 2010; Papafilippaki *et al.,* 2008; Ezeronye and Ubalua, 2005).

The low metallic levels observed during the DS could be as a result of low flow of contaminants due to reduction in the volume of water. According to Makhoukh *et al.* (2011) during the DS due to low hydrodynamics particles are settled and heavy metals are trapped in sediments and organic matter. Some researchers have reported low levels during DS to be due to high temperatures in the water and alkalinity of water which leads to increase in concentration of sulphides due to their precipitation (metals are reported to precipitate along with the sulphides) (Papafilippaki *et al.,* 2008; Salem *et al.,* 2000). Papafilippaki *et al.* (2008) and Cordos *et al.* (2003) reported high temperature during DS and its impact on the rates of metabolism, resulting in death of aquatic organisms with the release of metals. This is also reported that high levels during the DS could be due to sulphide oxidising bacterial activity increasing with temperature and concentrating the dissolved pollutants due to water evaporation (Papafilippaki *et al.,* 2008).

Some other researchers have found no variation in metal levels during rainy and dry seasons (Dan'azumi and Bichi, 2010; Obasohan *et al* 2006; Ezeronye and Ubalua, 2005; Salem *et al.,* 2000). According to Salem *et al.* (2000) this could be as a result of the influence of the nature of contaminants discharged into the river.

The distribution pattern of heavy metal in the Pompom river may have been affected by environmental conditions such as the release of heavy metals into surface waters from sediments, natural rocks and soils in the mining area. Deposition of large quantities of tailings into rivers results in alteration of instream substrata (Besser *et al.,* 2007). A decreased redox potential in the river when there is deficiency of oxygen, changes composition of metal complexes releasing metal ions (Lawson, 2011). In soils containing high amounts of soluble substances, such as limestone the runoff will have high concentrations of calcium carbonate (Lawson, 2011). The presence of carbonate formations results in alkaline conditions which favours adsorption and complexation of metals, most of which become insoluble and precipitate causing restrictions in the transport of heavy metals (Kumanova *et al.,* 2012; Thorslund *et al.,* 2012; Makhoukh *et al.,* 2011; DeNicola and Stapleton, 2002). Findings by DeNicola and Stapleton (2002) report the precipitation of dissolved metals such as Al, Zn, Cu, and Pb when AMD runs into alkaline condition in streams. The physical layout and topography of the land can have an increased effect on the weathering and erosion rates of surrounding environment (Cordos *et al.,* 2003). Mine tailings scoured by precipitation could converge into rivers with the topography as factor controlling the water flow paths. Thorslund *et al.* (2012) reported mining and ore excavation as causing acidification and heavy metal transport in the downstream water system.

There were no big differences in metallic concentration for samples collected upstream and downstream of the river. Water could become more polluted as it flows downstream due to increased imputes. However, there could be variations in metallic levels upstream and downstream due to several reasons such as the continuous, multiple, varying adsorption/desorption mechanisms depending on the transportation processes of suspended solids and dynamically changing discharges entering into the river. Heavy metals found in the suspended and colloidal phases could sediment at the upstream resulting in decrease in their bioavailability downstream. Physical and chemical conditions in the sediment and hydrology could affect the transport of metals from upstream mining areas resulting in high concentrations of dissolved heavy metals in downstream parts of the river (Thorslund *et al.,* 2012; DeNicola and Stapleton, 2002). There could be distribution of heavy metals to tributaries as the river flows. According to Cordos *et al.* (2003) the physical and chemical characteristics of tributaries that flow into the river downstream may aid chemical reactions that increase or decrease the concentrations levels of heavy metals. Increase in atmospheric deposition could take place as the river flows down stream. The presence of a dam could cause secondary sources of pollution increasing the metallic concentration level downstream (Cordos *et al.,* 2003).

Cu, Ni, Pb and Zn metallic levels of the studied metals were within values of FEPA and WHO permissible guidelines for drinking water.

Conclusion

Significant difference ($P<0.05$) were found between rainy and dry season in some of the studied metals (Cd, Pb, Cu and Ni). The seasonal variations may be due to anthropogenic causes such as mining, agricultural practices, geochemical structure and industrial waste. Cd, Pb, Cu and Ni metallic levels of the studied metals were within levels of Federal Environmental Protection Agency (FEPA) of Nigeria and WHO permissible guidelines for drinking water. The accurate determinations of heavy metals in aquatic environment are of ultimate importance for controlling their pollution. There will be need to have a regular check of level of heavy metals in the water, sediments and soil samples in the Itakpe mining environment to assess environmental impact to avoid pollutants eventually becoming potential health risk to residents in the vicinity of the mining area.

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Effect of Repeated Laundering on Durability and Bactericidal Activity of Some Antibacterial Finishes

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Abstract. This paper investigates imparting antibacterial properties to a woven and a knitted cotton fabric using polyhexamethylene-biguanide hydrochloride (PHMB), silver salt and 5 chloro-2-(2,4-dichlorophenoxy) phenol based commercially available finishes. The antibacterial functions of the treated fabric samples are determined by the nature of the bacteria as well as number of repeated washing cycles. This research shows that these finishes are more effective against species of perspiration bacteria than *Escherichia coli.* A higher concentration of finishes is required to improve their effectiveness against *E. coli* and their durability to repeated laundering. The effect of antibacterial finishes on the tensile strength and burst strength of woven and knitted fabrics has also been investigated, respectively. The antibacterial finishes have no drastic effect on tensile strength and burst strength of the fabrics.

Keywords: antibacterial finish, *E. coli*, cotton, polyhexamethylene-biguanide hydrochloride, chlorinated phenoxy compound, silver salt

Introduction

Cotton textiles are excellent substrate for microbial growth (Gao and Cranston, 2008) and their growth causes a range of undesirable effects on textile articles such as bacterial and fungal originated odours, stains, discolouration, reduction in the fabric strength and skin irritation. The environmental concern to the public is the likelihood of cross-transmission of diseases in hospitals and partially or completely unhealthy indoor air quality in working areas is caused by the contaminated textiles (Chen-Yu *et al*., 2007; McQueen *et al*., 2007; Flindt, 2006; Purwar and Joshi, 2004; Payne and Kudner, 1996). Antimicrobial processed fabrics are expected to be able to completely eliminate these concerns (Gouda *et al*., 2008; Gouda and Ibrahim, 2008). Biocidal agents kill bacteria however, they act on slow-release mechanism and are anticipated to be durable to washing if sufficient agents are incorporated into the fabric material (Gao and Cranston, 2008; Purwar and Joshi, 2004). Hospitals spend a great deal of funds on sterilisation of reusable textile items. Sterilised items still have risk of contamination due to process ineffectiveness as well as recontamination after sterilisation. In an effort to assure that no contamination is present, fabrics with biocidal properties offer an attractive alternative for this problem.

To date considerable work has been done on biocides for medical textiles and agents which will inactivate microorganisms. However, very less information is available for the use of biocidal agents for textile fabrics. The product designing of textile fabrics involve optimisation of treatment which should improve antibacterial characteristics parallel to performance properties of fabrics or it should not have any adverse effects on performance properties. In this study the most common antibacterial agents like polyhexamethylene-biguanide hydrochloride (PHMB), silver salt and 5 chloro-2-(2,4-dichloro phenoxy) phenol are imparted to cotton fabrics to observe (a) the antibacterial activity of finishes against *Escherichia coli* and bacteria isolated from sweated cloths using agar plate test (Standard Method AATCC 147, (b) the impact of treatments on tensile and burst strength of cotton fabrics using Standard Methods ASTM D 5035-06 and ASTM D3786-01, respectively, (c) the durability of antibacterial treatment to laundering using Standard Method BS EN ISO 15487: 2001.

Materials and Methods

Materials. A 100% woven fabric of 1/1 plain weave, 64x60/25x24 quality, 111 g/m weight and a 100% knitted fabric of 3 wales/inch, 37 course/inch, 20.3 count and 150 g/m weight, obtained from Yarn Market Faisalabad, were used throughout this study. The fabric

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*Author for correspondence; E-mail: i_tayyab@hotmail.com samples were treated with three different chemical classes of antimicrobial compounds through conventional pad-dry-cure procedure. Reputex 20; a polyhexamethylene biguanide hydrochloride (PHMB) compound, was obtained from BASF. Silpure FBR-5; silver salt based compound was obtained from CIBA. Ultrafresh NM-V2; 5 chloro-2-(2,4-dichlorophenoxy) phenol compound was obtained from Thomson Research Associates Ltd. Acetic acid and sodium hydroxide of local grade were used to maintain the required pH of padding bath.

Fabric treatments. Reputex 20 was applied at 1, 1.5 and 2% chemical, Silpure FBR-5 was applied at 1, 1.25 and 1.5% chemical, and Ultrafresh NM-V2 was applied at 2, 3 and 5% chemical on the dry weight of the fabric to ensure good antibacterial properties as recommended by the suppliers. The bath pH levels for chemicals Reputex 20, Silpure FBR-5 and Ultrafresh NM-V2 were 4, 6 and 4, respectively.

The fabric samples (30 x 42 cm^2) were impregnated in the pad bath containing antibacterial compound for 5 min. The samples were padded through the squeeze rollers of TSUJII padding mangle to obtain 80% pick-up, then dried in TSUJII stenter for 1 min at 110 °C, and finally cured for 45 sec at 150 °C.

Fabric evaluation. The qualitative method, agar plate test (AATCC 147) was used to test the antimicrobial activity of the untreated fabrics and all treated fabrics against *E. coli* and perspiration bacteria. The perspiration bacteria were isolated from the sweated cloths in four replicates. 500 mL nutrient agar medium was prepared and sterilised by autoclaving for 20 min at 15 psi and 121 °C. Petri plates were autoclaved and dried in hot air oven. 20 mL of nutrient agar was poured into each of the plates and allowed to solidify. The culture was then transferred to the agar surface of the plate in five parallel streaks to test *E. coli*, and a bacterial lawn was used to test perspiration bacteria. A 100 µL of perspiration bacteria was poured onto the agar surface and spread by using sterilised spreader. Circular cut fabric pieces were placed in the center of the plates. The sample plates were then incubated at 37 °C for 24-48 h. A clear area of interrupted growth underneath and along the sides of the test fabric indicated the antibacterial activity. In qualitative testing, the zone of inhibition was calculated for different fabrics.

Prior to testing all fabric samples were conditioned at 65 % RH and 20 °C. The tensile strength of unwashed, 5 and 25 times washed woven fabric samples were evaluated using standard procedure ASTM D 5035-06. The burst strength of unwashed, 5 and 15 times washed knitted fabric samples were evaluated using standard procedure ASTM D3786-01. The treated samples were washed according to standard procedure BS EN ISO 15487: 2001 at 40 °C for 100 min with an additional load of 1 kg (polyester fabric) then air dried.

Results and Discussion

Figures 1-3 represents the bactericidal activity of cotton woven fabrics finished with Reputex 20, Silpure FBR-5 and Ultrafresh NM-V2 applied against *E. coli* and perspiration bacteria, respectively. It was observed that the increased concentrations of finishes appeared to increase their antibacterial effect against *E. coli* and perspiration bacteria. Knitted fabrics showed better zone of inhibition values than woven fabrics due to better penetration of finishes in its open structure. Knitted fabrics showed steady decrease in zone of inhibition as laundering cycles were increased to 5 and then to 15.

In case of woven fabrics, regardless of their chemical nature, the bactericidal response of fabric samples finishes with lower concentrations appeared to diminish after five laundering cycles. Fabric samples finishes with higher concentrations showed steady decrease in zone of inhibition as laundering cycles were increased to 25. The existence of finishes on the fabrics and the ability of fabrics to combat bacteria after 25 washes indicated that a relatively higher concentration is required to improve the durability of finishes on woven fabric.

Among all the finishes fabrics treated with Reputex 20 showed better antibactericidal activity against perspiration bacteria. Reputex 20, chemically PHMB is a polymeric polycationic amine that binds to cellulose *via* an acid base interaction. The electrostatic interaction dominates at lower concentrations, however, at higher concentrations, the hydrogen bonding results in multilayer adsorption of PHMB (Simoncic and Tomsic, 2010; Abo-Shosha *et al*., 2008; Abo-Shosha *et al*., 2007; Moore and Gray, 2007; Blackburn *et al*., 2006), hence, improved the laundering durability of treated fabrics. Ultrafresh NM-V2 and Silpure FBR-5 do not establish any interaction with cellulose. Ultrafresh NM-V2 chemically 5 chloro-2-(2, 4-dicholoro phenoxy) phenol diffuses into the fibres and inhibit the growth of microorganisms by blocking the synthesis of lipids (Yazdankhah *et al*., 2006; Purwar and Joshi, 2004).

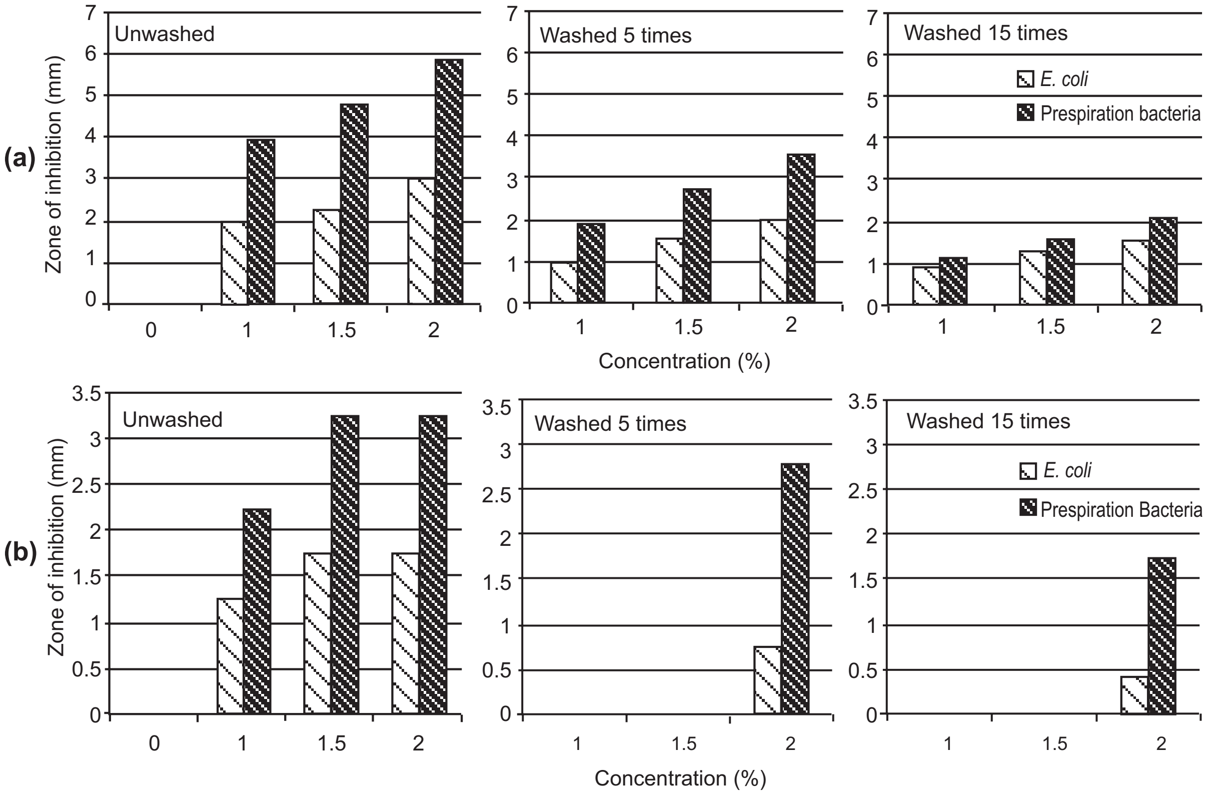

Fig. 1. Antibacterial activity of unwashed and washed Reputex 20 treated (a) knitted fabrics and (b) woven against *E. coli* and perspiration bacteria; zone of inhibition (mm) *vs* concentration (%).

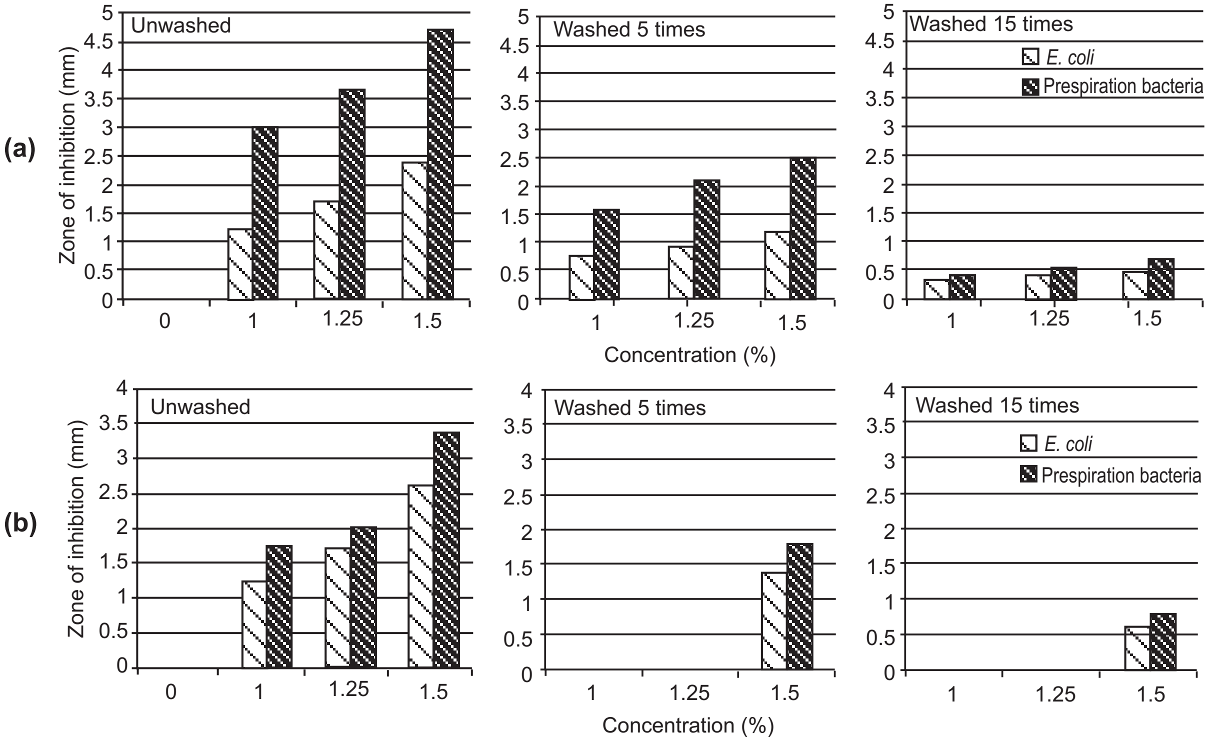

Fig. 2. Antimicrobial activity of unwashed and washed Silpure FBR-5 treated (a) knitted fabrics and (b) woven against *E. coli* and perspiration bacteria; zone of inhibition (mm) *vs* concentration (%).

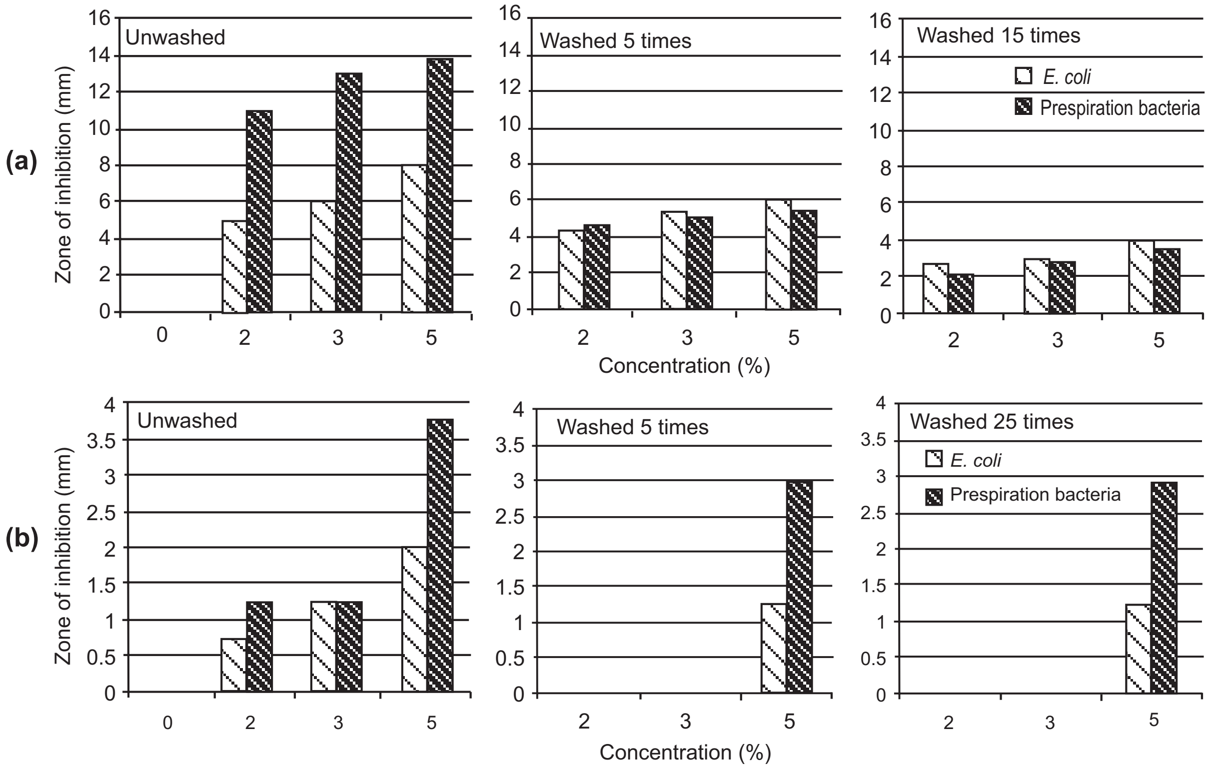

Fig. 3. Antimicrobial activity of unwashed and washed Ultrafresh NM-V2 treated (a) knitted and (b) woven fabrics against *E. coli* and perspiration bacteria; zone of inhibition (mm) *vs* concentration (%).

During use of fabric, it migrates to the surface of treated textiles at a slow sustained rate to provide excellent antimicrobial efficacy (Chen-Yu *et al*., 2007; Purwar and Joshi, 2004) and laundering durability as can be seen from the results. There is slight reduction in bactericidal activity of treated fabrics after 5, 15 (in case of knitted fabrics) and 25 (in case of woven fabrics) laundering cycles. Furthermore, Ultrafresh NM-V2 treated fabrics also showed better bactericidal activity against *E. coli* compared with the fabrics treated with Reputex 20 and Silpure FBR-5. *E. coli*; gram-negative bacteria have an additional layer of outer membrane. This extra cell wall gives cell protection and makes these bacteria more persistent in survival and more difficult to be inhibited than gram-positive bacteria (Chen-Yu *et al*., 2007). Silpure FBR-5; silver metal salt exerts a detrimental effect upon bacteria (Thomas *et al*., 2010; Williams *et al*., 2005; Lansdown, 2002; Nakashima *et al*., 2001), however, it require a cross-linking agent to establish its structure on the fibre surface and to control the release of metal ions which consequently prolong the release time and improves wash durability and resistance (Simoncic and Tomsic, 2010; Purwar and Joshi, 2004). In this study Silpure FBR-5 was applied to woven as well as knitted fabrics without cross-linking agent and its absence had caused drastic reduction in bactericidal activity in laundered fabrics.

Application of antibacterial finishes, regardless of their chemical nature, caused slight reduction in the tensile strength of treated fabrics as compared with the tensile strength of original fabric. Repeated laundering caused further reduction in tensile strength values as shown in Fig. 4. The reduction in tensile strength of treated fabrics after 5 and 25 repeated laundering cycles is not due to change in morphological behaviour of fabrics as these finishes are not chemically attached to the fabric but infact is due to the mechanical action of washing drum. The ability of fabric to move freely is very low due to high loading and small diameter of drum. Swelling of the fibres reduces slippage and cause damage to fibres which consequently reduced the tensile strength of woven fabrics. The open structure of knitted fabrics allowed fibre slippage and consequently caused less damage to fibres. There is no considerable reduction in

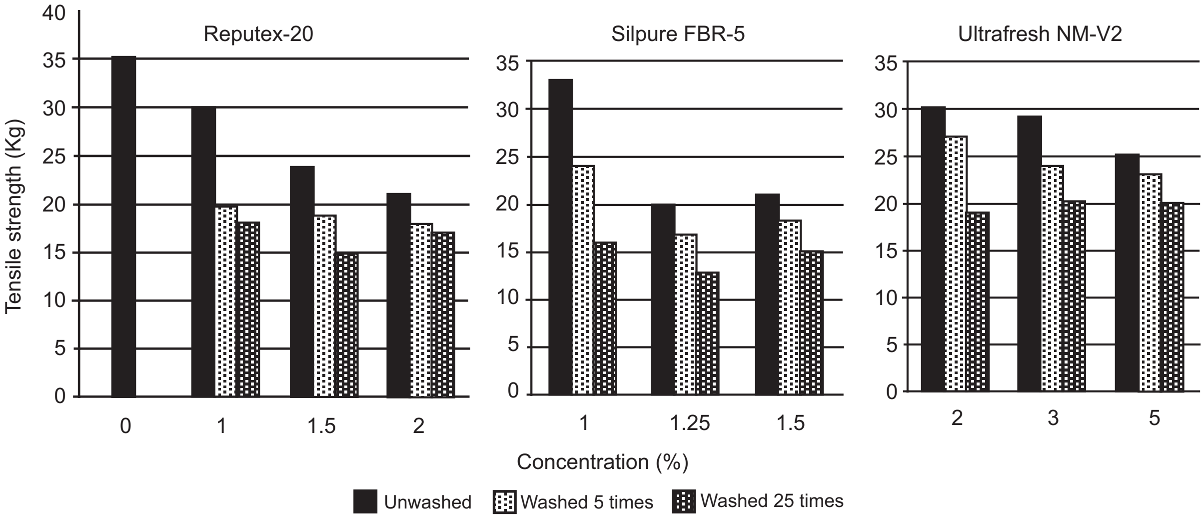

Fig. 4. Tensile strength (kg) of antibacterial finishes woven fabrics *vs* concentration (%) of finishes.

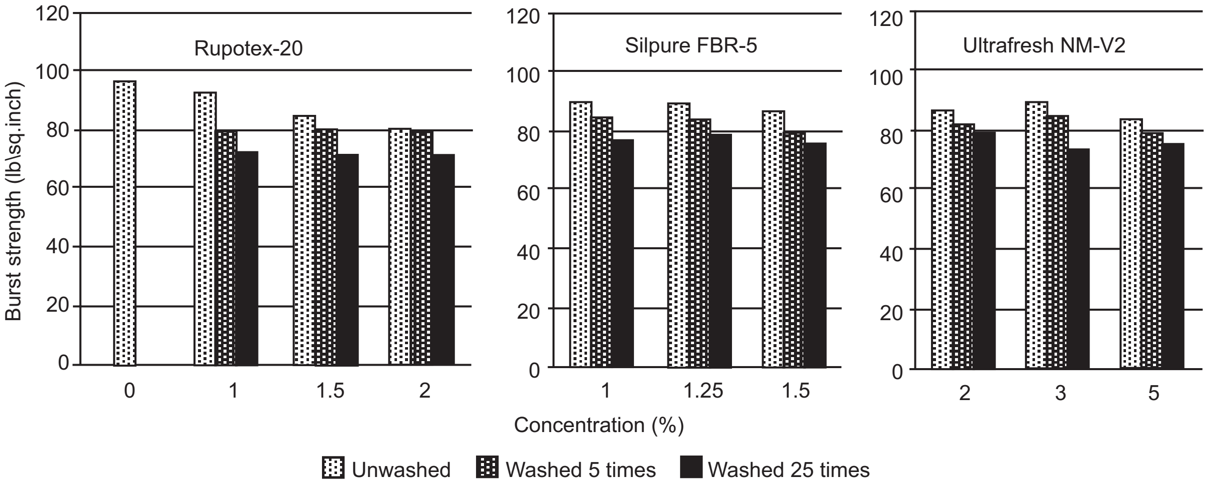

Fig. 5. Burst strength (lb/sq inch) of antibacterial finishes knitted fabrics *vs* concentration (%) of finishes.

burst strength of treated fabrics as compared with the burst strength of original fabric and then subsequent 15 laundering cycles caused slight reduction in burst strength of treated fabrics as shown in Fig. 5. This also indicates that antibacterial finishes has no drastic effect on burst strength of fabrics.

Conclusion

Three commercially available bound finishes Reputex 20, Silpure FBR-5 and Ultrafresh NM-V2 were applied to woven and knitted cotton fabrics. The loose structure of knitted fabric allowed better penetration of finishes into the fibre structure which consequently showed (a) better zone of inhibition against species of perspiration bacteria and *E. coli*, (b) better durability to repeated laundering. All three finishes are more effective against species of perspiration bacteria than *E. coli*, however, the bactericidal activity of Silpure FBR-5 finished fabrics is lower than Ultrafresh NM-V2 and Reputex 20. The finishes have no considerable effect on tensile and burst strength of woven and knitted fabrics, respectively. The durability of the finishes to repeated laundering showed that bactericidal activity against bacteria decreased as number of laundering cycles increased. The results conclude that the effectiveness of an antimicrobial finish depends upon the concentration of the finish and the effectiveness of interaction developed between the finish and the fibre.

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Investigation of Soil Fertility at a Remote Site in Karachi, Pakistan

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Abstract. This study reveals chemical and physical properties of soils collected from a remote site at Karachi, Pakistan. Altogether 23 parameters were determined. Out of 12 soil samples 11 were categorised as sand or sandy loams, pH varied between 7.35-8.49, density ranged between 1.61-2.39 gm/cm^3, the conductivity of 1:2 water extracts varied up to a great extent i.e., between 0.437-16.47 mS/m^3. Sodium (Na) contents were higher in ammonium acetate extract when compared with 1:2 water extract. The bicarbonate (HCO_3) contents were ranged between 0.17-1.73 ppm. The organic matter contents were low (0.81-2.21%); these soils were also deficient in their macronutrient contents. Specifically, the ranges of nitrogen (N), phosphorous (P), potassium (K), calcium (Ca), magnesium (Mg) and sulphur (S) were 0.04-1.16%, 0.25-15.99 ppm, 4.40-135.89 ppm, 0.001-0.199%, 0.001-0.019% and 0.01-0.143%, respectively. Heavy metals were determined in diethylene-triamine-pentaacetic acid (DTPA) extracts and the levels of iron (Fe), copper (Cu), manganese (Mn), and zinc (Zn) in these samples were 1.86-32.80 ppm, 1.68-7.69 ppm, 16.51-75.28 and 0.25-20.75 ppm, respectively. Toxic heavy metals, lead (Pb) and nickel (Ni) contents were also estimated and their concentration was found low ranging between 0.91-5.63 ppm and 0.32-1.26 ppm, respectively.

Keywords: macronutrients, micronutrients, organic matter, soil fertility, soil texture, toxic metals

Introduction

Soil is the natural medium for the growth of plants. It provides support to the plants and also supplies essential nutrients and water. Soil is composed of four major components, the mineral matter is the most abundant component which comprises almost 45% volume of soil, organic matter occupies almost 5% volume, while, the remaining 50% of total pore space of the soil is occupied by water and air in a 1:1 ratio (Gupta, 2004). The mineral matter consists of stones, gravels, silt and clays and it also defines the structure of the soil. The organic matter of soil comprises of plant, animal and microbial residues, it gives colour to the soil, helps water retention, cementing action, buffering action, mineralisation and also affects the persistence and biodegradability of other organic compounds such as pesticides; hence, soil organic matter modifies and controls their rate of application (Schnitzer and Khan, 1978). The soil air has a relatively high concentration of carbon dioxide (0.25-3%) as compared to carbon dioxide levels in atmospheric air (0.03%), whereas, the oxygen levels are generally lower (<20%), however, the levels of nitrogen are almost the same (79.2%), in soil air as compared to atmospheric air (Tan, 2011).

The capacity of soil to provide essential nutrients for plant growth is called its fertility, which is necessary for productive soil, however, a fertile soil may not be a productive because there are other parameters which affect soil productivity. Essential elements for plant growth and completion of life cycle are classified into basic macro- and micronutrients. For example, carbon, hydrogen, and oxygen constitute 96% of total dry plant matter and are the basic nutrient required for plant development. In addition, these elements are abundantly present in the atmosphere and therefore, do not need to be physically applied to soils for plant development.

Macronutrients which are required in large quantity for plant growth include nitrogen (N), phosphorous (P), potassium (K), calcium (Ca), magnesium (Mg) and sulphur (S), in which N, P and K are major or primary nutrients, whereas, Ca, Mg and S are secondary nutrients. Primary nutrients are often deficient in soils and hence, applied as fertilisers. Micronutrients are essential for optimum plant growth in minute quantities, however, their excess concentrations may lead to harmful effects to the plant. Important micronutrients include iron (Fe), zinc (Zn), copper (Cu), manganese (Mn), boron (B), molybdenum (Mo) and chloride (Cl).

There are several factors that influence the release and availability of nutrients. These factors include soil pH, temperature, moisture, aeration, application of fertilisers such as manure and microorganism activity

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(Comerford, 2005). As nutrients are absorbed by the plant, nutrient concentrations become depleted in the soil layers near plant roots and are replenished by the mobility of nutrients through the soil medium. Most nutrients are present in soil in three forms: (1) unavailable nutrients that cannot be absorbed directly by the plant which need to be fixed into intermediate nutrients by microorganisms, (2) intermediate nutrients that act as long-term reservoirs that are in equilibrium with unavailable nutrients and (3) labile nutrients that are loosely held by the soil and readily available to soil solutions in the form of available nutrients. Equilibrium can be established between the intermediate and the labile nutrients over a short period of time. Deficiencies of nutrients can lead to the reduction of plant size, discolouration of leaves, slow growth, weak stalk, shrivelled fruits and seeds and the wilting of leaves among other negative consequences (Gerloff, 1987).

The reduction of soil productivity is referred to as soil degradation. There are many problems associated with soil degradation such as soil erosion, loss of fertility, salinity, alkalinity, acidity and water logging. Flooding and droughts can also contribute toward soil degradation. Soil testing practices are quite important for proper characterisation of soil and its fertility. The site of the study located at a remote site in Karachi, Pakistan was once known for its beautiful gardens, but during past 10 years the quality of this soil has been degraded up to a great extent. Apparently salinity and water logging are the main causes for this degradation, therefore, this detailed study was planned to determine the level of degradation and determination of its fertility. The results of the study would help the reclamation of the site and make it fertile once again.

Materials and Methods

Reagents and equipments. All chemicals used for the experiments were of AR grade, double distilled water was used for the preparation of reagents and samples. The equipments used during the course of this study were, Hitachi Z 5000 atomic absorption spectrophotometer equipped with Zeeman background correction, Jenway PFP 7 flame photometer, Jenway ion meter and Thermo Nicol UV-vis spectrophotometer. All equipments were used as per manufacturers' instructions and recommendations.

Methodology. Standard methods for the testing of soil were used to estimate various physical and chemical parameters. pH, conductivity, Na, K, HCO_3^-, S and Cl^- were determined in 1:2 soil water extract. Na content was also determined in ammonium acetate extract. HCO_3^- were estimated with HCl titration, Na and K were estimated on flame photometer. Ca and Mg were determined with ethylene-diaminetetraacetic acid (EDTA) complexometric titration, while, Cl^- was estimated by argentometric titration. S was estimated gravimetrically as $BaSO_4$. Soil texture was determined using hygrometer. Bulk and particle density was determined through pycnometer. Total organic carbon and organic matter were determined by Walky and Black rapid titration method, P was estimated spectrophotometrically using Murphy Riley solution, while, N contents were determined by Kjeldhal distillation method. Trace metals (Fe, Cu, Pb, Mn, Ni, and Zn) were estimated in diethylenetriaminepentaacetic acid (DTPA) extract on atomic absorption spectrophotometer (Gupta, 2004).

Site of the study. This study was conducted at PCSIR Laboratories Complex Karachi, Pakistan and its suburbs, which is located at a remote area of Karachi (24° 57' 45'' N, 67° 7' 30'' E). The area of the study is around 2 km^2. More than 60% of the area is lying vacant with wild vegetation. A residential colony, the Laboratory and PSTC Training Center are included in the study area. There are two fields in the vicinity which are utilised for field experiments on different crops like sunflower, corn, sugarcane etc., and some ornamental plants like roses, tube roses etc. There are 5 gardens at different locations and a graveyard is also included in the campus. The vacant land is acquired by wild shrubs which grow quickly.

Sample collection. The samples were collected from 12 different locations to cover almost all the campus area using standard protocol for the soil sampling. To estimate the soil quality at vegetation and non vegetation sites, the samples were selected, where there was some vegetation like gardens, fields etc., and in order to compare their quality some barren soils were also selected. Locations **1**, **2**, **6**, **7**, **11** were barren or covered with wild vegetation, whereas, location **3**, **4**, **5**, **8**, **12** were gardens and location **9** and **10** were the fields utilised for experimental crops. These locations are given in Fig. 1. The surface litter was scraped away then the soil surface was ploughed up to a depth of about 12 cm from 5 different spots at the location, and individual samples were then mixed together to make a composite sample. The representative sample was obtained by further quartering of composite sample to obtain approximately 500 g of soil (Iqbal *et al.*, 2001).

Fig. 1. Sample locations.

Results and Discussion

Physical testing of soil. The physical parameters i.e., soil texture, pH, density, conductivity and total dissolved soolids (TDS) are described in Table 1. Most of the samples collected from the study area lie in the category of sand or sandy loams (Table 1). Sandy soils can lose plant nutrients and water rapidly and hence affect soil fertility. Such soils are not considered perfect medium for the cultivation of crop plants (Oades and Waters, 1991).

The pH of the collected samples was slightly alkaline ranging from 7.35-8.49 which may be due to the low rainfall in the area. The rainwater contains dissolved carbon dioxide in the form of carbonic acids which leach away the basic cations like calcium, magnesium, potassium and sodium and replace it with H^+. The nutrient uptake of alkaline soils is also lower as compared to the acidic soils, however, this problem could be rectified by adding water soluble chelates onto the soil.

The soil density ranged between 1.590-2.395 g/cm^3, which is typical for normal soils (Tanji, 1990). The conductivity of 1:2 soil water extract varied in a significant range with the lowest value at the sampling point **1** (0.437 mS/m^3) and as high as 16.47 mS/m^3 at sampling point **10**. Conductivity plays an important role in soil fertility. Low conductivity (i.e., <0.8 mS/m^3) impose no deleterious effects on the crop, however, when conductivity is less than 0.2 mS/m^3, the soil is deficient in N and K, while, a range of conductivity between 0.8-1.6 mS/m^3 is critical for salt sensitive crops. A range of conductivity between 1.6-2.5 mS/m^3 may be critical even for salt tolerant crops, while, conductivity exceeding 2.5 mS/m^3 would be injurious for most crops (Wolf, 1999). Our study result showed that **8** sampling locations out of **12** are not suitable for cultivation and it seemed the reason behind low yield during field experiments on different crops like sunflower, sugarcane and high maintenance cost of the gardens.

Chemical composition of the soil. Sodium contents were determined both in 1:2 water extract and ammonium acetate extract and are given in Table 2. The contents were high in ammonium acetate extract as compared to the water extract. The concentration of Na in 1:2 water extract was very strongly correlated with the Cl

Table 1. Physical testing of studied soils

Sample	Soil texture				pH	Bulk density	Conductivity	TDS
	Sand %	Clay %	Silt %	Texture	(1:2 water extract)	(g/cm^3)	(mS/cm)	(ppm)
1	88.70	6.78	4.52	Sand	7.35	1.915	12.74	7640
2	63.84	11.30	24.86	Sandy loam	7.42	1.959	7.3	4760
3	79.66	2.26	18.08	Sand	7.60	2.395	2.39	1440
4	68.36	11.30	20.34	Sandy loam	8.09	1.827	2.70	1620
5	57.06	20.34	22.6	Sandy loam	7.87	1.701	1.523	910
6	70.62	9.04	20.34	Sand	7.88	1.733	2.75	1650
7	77.40	6.78	15.82	Sand	7.58	1.719	1.861	1120
8	63.84	11.3	24.86	Sandy loam	7.52	1.590	5.59	2760
9	72.88	11.3	15.82	Sandy loam	7.63	1.613	8.89	5330
10	61.58	13.56	24.86	Sandy loam	7.92	1.757	16.47	9880
11	54.80	40.68	4.52	Clay loam	8.25	2.059	4.46	2670
12	63.84	11.30	24.86	Sandy loam	8.49	1.759	0.437	260

concentration; (R^2=0.697, P>0.001), Cl^- contents were varied between 0.01-0.66%. The soil samples can be characterised as highly saline. The HCO_3^- contents were low, varying within the range between 0.23-1.73 ppm.

Table 2. Major cations and anions in studied soils

Sample	1:2 Water extract			Sodium (%)
	Sodium (%)	Bicarbonate (ppm)	Chloride (%)	in ammonium acetate extract
1	0.12	0.50	0.53	0.14
2	0.04	0.43	0.32	0.12
3	0.03	0.67	0.06	0.04
4	0.06	0.23	0.06	0.08
5	0.02	1.23	0.04	0.04
6	0.06	0.50	0.08	0.14
7	0.01	0.63	0.05	0.06
8	0.06	0.28	0.35	0.07
9	0.15	0.26	0.34	0.21
10	0.33	0.17	0.66	0.41
11	0.06	0.85	0.14	0.09
12	0.004	1.73	0.01	0.01

Organic matter. Organic matter in the soil consists of plants, animal and microbial residues at various stages of decay. It mainly contains 5% of total nitrogen, therefore, it serves as the resource for nitrogen (Beare *et al*., 1994). The organic matter (OM) decomposes to release the nutrient. The collected samples of soil contain 0.81-2.21% organic matter, while the total organic carbon (TOC) ranged from 0.60 to 1.27%. When organic matter content is correlated with the soil texture, it can be inferred that the organic matter contents are comparatively higher with increasing clay content of the soil (Greenland, 1965). The results of organic matter concentration are given Table 3.

Table 3. Organic matter and organic carbon in studied soils

Sample	Organic matter (OM, %)	Total organic carbon (TOC, %)
1	1.20	0.69
2	1.08	0.81
3	0.81	0.46
4	1.04	0.60
5	1.43	0.82
6	1.13	0.65
7	1.34	0.77
8	2.21	1.27
9	1.31	0.75
10	1.72	0.99
11	1.22	0.70
12	1.47	0.84

Macronutrients. During the course of this study, macronutrients (N, P, K, Ca, Mg, and S) were also estimated (Table 4). It has been observed that soil is deficient of primary and secondary macronutrients. The N contents of the collected samples for this study ranged between 0.05-1.16%, this indicates that the studied soil is nitrogen deficient. According to the literature N-deficiency produces small plants with light green or light yellow leaves, the chlorosis produces at the leaf tip and then the leaf either dries or drops down (Stevenson and Cole, 1999). In the present study, P concentration of soil varied between 0.25-15.99, while, K content between 4.40-135.89 ppm in 1:2 water extract. These ranges lie below the normal range for sandy soils (Gupta, 2004). Due to the deficiency of P there is limited root development which results in delayed maturity and hence affects fruit development. Similarly K deficient plants have also restricted growth and discolouration of leaves (Egilla *et al*., 2001; Stevenson and Cole, 1999).

Secondary macronutrients such as Ca (0.005-0.199 %), Mg (0.001-0.019%) and S (0.01-0.143) were found in low concentration when compared with the normal range of these macronutrients in sandy soils (Troeh and Thompsom, 2005). Ca and S deficiency in the soils affects the root growth, whereas, Ca if not supplied to the plant in sufficient quantity, would result in late emergence of fruits. The Mg and S deficiency affects the colour of the leaves (Marschner *et al*., 1996).

Heavy metals. Heavy metals can be characterised as micronutrients which are essential for optimum growth of plants and toxic substances which affect the crop quality. Certain micronutrients if present in high concentration may also act as toxic substances. United States Environmental Protection Agency (USEPA) has set limits for residential and industrial soil for inorganic pollutants. The concentration limitations for Pb, Cu, Ni and Mn concentration in soil are 400, 3100, 1600 and 1800 mg/kg, respectively, (USEPA, 1996). There is no limit for concentration of Fe and Zinc.

Fe, Cu, Mn and Zn are characterised as micronutrients. The levels of these metals in DTPA extracts in collected soil samples were 1.86-32.8 ppm for Fe, 1.68-7.69 ppm for Cu, 16.51-75.3 ppm for Mn, and 0.25-20.75 ppm for Zn. The results given in Table 5 indicate that all the micronutrients are present in sufficient quantity (Yu and Rengel, 1999). Toxic heavy metals like Pb and Ni were also estimated in these samples and results are also given in Table 5. Pb is supposed to be a considerably

Table 4. Macronutrients at studied soils

Sample	N (%)	P (ppm)	K (ppm)	Ca (%)	Mg (%)	S (%)
1	0.094	7.66	24.88	0.199	0.010	0.07
2	0.30	0.25	17.22	0.081	0.014	0.013
3	0.46	6.19	135.89	0.01	0.003	0.01
4	0.72	15.99	89.53	0.007	0.004	0.02
5	0.05	2.04	18.49	0.02	0.002	0.023
6	0.04	4.05	17.31	0.005	0.008	0.023
7	0.33	1.82	4.40	0.013	0.005	0.007
8	0.25	7.99	102.67	0.045	0.003	0.02
9	BDL*	2.03	24.76	0.051	0.011	0.023
10	0.64	10.80	78.73	0.109	0.019	0.143
11	0.48	2.06	68.73	0.003	0.003	0.023
12	1.16	12.77	58.80	0.001	0.001	BDL*

*BDL=below detection limit (for nitrogen 0.02 %, for sulphur is 0.005%).

Table 5. Heavy metals in studied soils

Sample	Micronutrients				Toxic metals	
	Fe (ppm)	Cu (ppm)	Mn (ppm)	Zn (ppm)	Pb (ppm)	Ni (ppm)
1	1.86	2.34	28.97	2.8	3.22	0.46
2	2.56	2.23	16.51	0.25	0.91	0.35
3	5.90	7.69	27.74	1.78	1.39	0.32
4	5.98	5.02	34.86	3.78	2.03	0.52
5	11.18	3.49	62.13	1.38	1.95	0.83
6	15.27	2.26	55.54	0.44	2.46	0.73
7	19.88	3.87	75.28	2.01	3.13	0.86
8	32.80	6.07	29.64	20.75	5.63	1.26
9	4.49	1.68	30.83	0.64	0.92	0.48
10	7.74	3.11	43.88	1.99	2.85	0.52
11	7.68	1.87	44.19	0.31	1.22	0.53
12	7.36	1.87	64.44	0.33	1.91	0.72

important toxic heavy metal however, Pb content was not very high in the soil samples and it ranged between 0.91-5.63 ppm, whereas, Ni contents also varied between 0.32-1.26 ppm. The highest metallic content was observed at PSTC site and the field around it, which may be due to the metals molding and smelting which takes place in these areas. The Ni and Pb contents in this area are comparable with an effluent irrigated soil from Korangi Industrial Area Karachi, Pakistan, where authors determined almost same range and average of these two metals in the soils (Haq, 2003).

Conclusion

The area under investigation has serious problems of soil degradation. The soil fertility parameters determined in this study are comparable with recently published data by Kabir *et al.* (2010). Their findings from another sandy loam textured soil from Karachi are showing that those soils are much better for cultivation as compared to the study area. Their investigated soils were low in TDS, Na and Cl contents, whereas they also have much improved macro and micronutrient contents (Kabir *et al.*, 2010). Present investigation reveals that the soil has apparently lost its productivity. The major problem of the soil is its salinity and high sodium content and the soil can be characterised as sodic soil as the Na content in ammonium acetate extract is more than 15% of total extractable cations. The Na content in ammonium acetate extract varies between 0.01-0.41%, while, in water extract it ranges between 0.004-0.33% which is very high and hence these soils can be characterised as saline sodic soils. The reclamation of the saline sodic soils cannot be achieved easily and quickly by simple leaching the excess salt with water and properly draining it out. These soils must be treated with a soil conditioner. The most commonly used soil conditioner for alkaline soils is gypsum. Sulphur replaces most of the Na ions with Ca. The deficiency of micro- and macronutrients may be overcome with the application of suitable fertiliser, which is leachable into the water system.

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