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Full Length Research Paper

Determination of levels of fluoride and trace metal ions in drinking waters and remedial measures to purify water

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Fluoride is recognized to be most effective caries-preventive agent. The main source of fluoride for people is generally food and drinking water. For this reason, fluoride and other metal ion concentrations in the drinking water samples were estimated. For the determination of fluoride, Na, Li and K an ion – meter and flame photometer were used. While the concentrations of other metal ions (Mn, Cd, Co, Ni, Pb, Fe, Zn and Cu) were estimated by flame atomic absorption spectrophotometer. Statistical parameters and multiple correlations between paired water samples were also calculated. For the purification of water, adsorption technique was adopted using Al_2O_3 and Al_2O_3 -Pb $_{0.1,}$ Al_2O_3 – Pb $_{0.01}$ doping systems. Adsorption isotherm equations were also applied to calculate the values of respective constants. Thermodynamic parameters (ΔG^o, ΔH^o and ΔS^o) were also calculated. According to the results obtained, the metal ion concentration in the drinking waters in the studied area are within the safe drinking water regulation limits and also the fluoride level is lower then the permissible limit for flouride.

Key words: Water samples, statistical analysis, purification of water samples, adsorption, Na metal, alumina, doping system.

INTRODUCTION

Water covers about 73% of the earth's surface. It is the major constituent of the lithosphere and atmosphere and it is an essential requirement of all living organisms. The largest water requirement is for municipal use but standard of purity required for this purpose is one of the prime factors in deciding the growth of towns and cities as well as industries (WHO, 1984).

Water contains many minerals especially magnesium bicarbonate and calcium sulphate. The minerals' level in drinking water could be responsible for kidney stones and similar mineral accretions in the human body. Trace metal analyses have gradually increased due to the fact that function of these elements in various areas such as biological systems, environment and geochemistry are now well understood. They play a major role in health; minute portion of them can significantly affect our health. Since some fluoride (fluorine) compounds in the earth upper crust are fairly soluble in water, fluoride exists in both surface and ground waters. The fluoride concentrations in ground water are within wide limits from 1 to 25 mg or more per liter (Tokalioglu et al., 2002). The main source of the fluoride in waters is CaF_2, which can be soluble up to 16 mg per liter at 18^{o}C and is found in the composition of volcanic rocks. Minerals such as fluorapatite CaF_2. $3Ca_3$ $(PO_4)_2$, fluorspar (CaF_2), cryolite $3NaF.AlF_3$ and mica also contain fluoride (Mizuike, 1983).

Fluoride is also added to some consumer products, such as toothpaste, toothpowder, mouth wash and vitamin supplements. Approximately 90% of the fluoride in the body is contained in the bones and tooth. Fluoride increases the resistivity of tooth enamel against acids which cause the initiation of tooth decay. It reduces tooth decay about 40-50%. When the fluoride concentration in drinking water is greater than 2 mg L^{-1}, it may cause fluorosis (Minczewski et al., 1982).

In the present study the levels of fluoride and the metal ions in the drinking water samples collected from five different zones of Karachi were estimated. The sources of water supply for inhabitants of Karachi are mainly from

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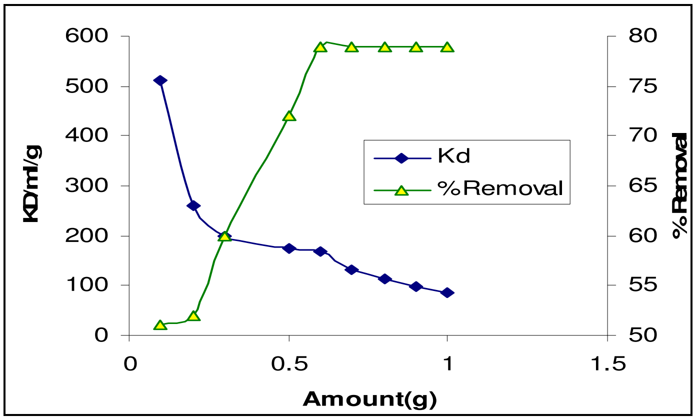

Figure 1. Influence of amount of alumina on the adsorption of Na (Na solution concentration = 500.0 mg/L).

Indus and Hub River in addition to limited supply of water from wells by the local municipal authorities. The Indus river pass through a crossection of rocks which range in composition from ultra basic and rocks of igneous origin, the metaphoric rocks of nearly all grades having varied chemical composition with respect to metallic and non metallic elements and the sedimentary rocks of varying chemical composition (Tokahoglu, 1997). The industrial wastes of different cities on either sites of the river Indus or its tributaries are among the major sources of contribution to the water thus the water in use is expected to be a potential source for the pollution exposed towards the inhabitants of Karachi (Elci, (1993). Adsorption technique was adopted for the purification of water using Al_2O_3 and Al_2O_3 -Pb $_{0.1,}$ Al_2O_3 – Pb $_{0.01}$ doping systems.

EXPERIMENTAL

Sample collection and preparation

To assess the concentration of trace metals, drinking water samples were collected from five zones of Karachi. Water samples were filter and stabilize at pH 2 with 5% nitric acid prior to direct aspiration for the trace metal analysis.

Deionized distilled water and calibration standards

The all-glass distilled water was passes through a mixed bed of cation and anion exchange resins to prepare deionize water, which is use in the present work either for dilution purposes or standard preparation. The purity of this water was found to be equivalent to STM type II reagent water of specification D 1193 (Ahmad et al., 1994).

For each trace metal, aqueous standard solutions was prepare by dissolving an accurately weigh amount of the relevant salt in deionize water to yield a metal ion concentration of 1000 or 500 mg L^{-1}. Appropriate aliquots were taken from these standards for subsequent dilutions. Each time, fresh standards were prepared and they were calibrated against previous standards in order to check any probable difference in the finished concentration. In order to quantify the results, standard calibration method was use in conjunction with the standard addition method, as indicated above (Ahmad et al., 1994).

Sample analysis

Water sample was analyze for the measurements of total metal concentrations of F, Na, Li, K on ion selective meter, flame photometer, while Mn, Cd, Co, Ni, Pb, Fe, Zn and Cu were measured by atomic absorption spectrophotometer. Triplicate subsamples were run to ascertain the precision of data.

Preparation of metal doped alumina samples

The alumina samples were prepared in the present study by incipient wetness technique (Saleem and Afzal, 2003). The impregnation of activated Al_2O_3 was carried out with nitrates of Ni, Cu, Zn and Pb. For these preparation, a predetermined amount of metal nitrates having concentration 0.01 M was magnetically stirred in 100 ml of distilled water with 10 g of activated Al_2O_3. The slurry formed was stirred at room temperature with a magnetic stirrer for one and half hour. After that the metal doped samples was placed in descicator for cooling. The metal impregnated with Al_2O_3 samples were designated as: Mx-Al_2O_3. While M stands for Pb and x represents the number of moles of metal ions per 100 g of Al_2O_3.

Purifaction of water

The removal of Na metal using Al_2O_3, and Al_2O_3 - Pb $_{0.1}$ and Al_2O_3 – Pb $_{0.01}$ doping systems from W50 water sample were carried out by adsorption technique. The adsorption measurements were carried out by batch technique at temperatures 303 -318 K taking W50 water sample of varying concentrations. Initial pH was adjusted using buffer solution of known pH and known amount of Al_2O_3, and Al_2O_3 -Pb $_{0.1}$ and Al_2O_3 – $Pb_{0.01}$ doping systems were added and placed in electric shaker for the desired time period. After required time, the filtrate was obtained and % absorbance of a portion of filtrate was determined by using flame photometer. The % absorbance of Na before and after adsorption on the surface of adsorbent gives this quantity of dye separated from aqueous solution. During the process of adsorption, a shorter or longer period equilibrium was established between molecules in the bulk and adsorbed phases. It is dynamic equilibrium because the number of molecules leaving the surface per unit time is equal to the number of newly adsorbed molecules; the total number of molecules in the adsorbed state remains constant.

Effect of amount of adsorbent

In order to find out optimum amount of adsorbent at which maximum adsorption takes place 50 ml of 500 mg/L stock solution of NaCl of pH 7 was added in each columns packed with different quantity of adsorbents e.g. 0.1, 0.2, 0.3, 0.4, 0.5, …1.00 g. The solution of NaCl was allowed to stand for 70 min. The results are shown in Figure 1 and Table 4.

Effect of stay time

For the determination of effect of stay time on adsorption, 0.5 g of adsorbent was packed in each column and 50 ml of 500 mg/L NaCl solution having pH 7.0 were added in each column for different intervals of time. When the solution of NaCl comes in contact with heterogenous surface of adsorbent, as usual unsaturated part of the solution strikes the surface of the adsorbent for adsorption. It was observed that the adsorption increases with increase in time to

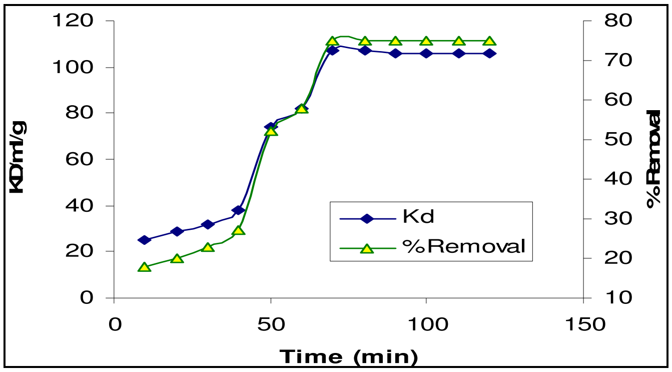

Figure 2. Influence of time on the adsorption of Na using activated charcoal (Na solution concentration = 500.0 mg/L).

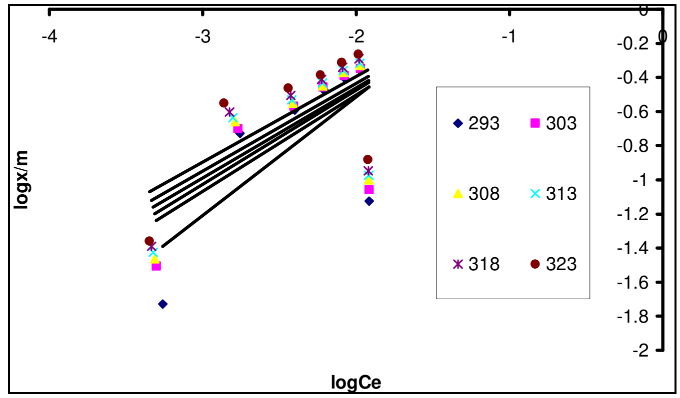

Figure 3. Freundlich plots for the removal of Na metal from water sample W50 using Al_2O_3 adsorbent at different temperatures.

70 min and reaches its maximum value thereby attaining a constant value when adsorption equilibrium is reached. At 70 min about 75% adsorption was observed. The results are shown in Table 5 and Figure 2.

Effect of temperature

For the determination of effect of temperature on the adsorption of Na under optimize adsorption conditions, the adsorption process was allowed to proceed at 293 - 323 K temperatures at an increase of 10 K ± 0.2°C.

RESULTS AND DISCUSSION

The levels of selected trace metals in water samples are presented in Table 1. The data in these figures afford a comparison of trace metal contents. Concentrations of F, Na, Li, K, Mn, Cd, Co, Ni, Pb, Fe, Zn and Cu were investigation. The present study revealed that in water samples maximum concentration of K and Na (630.0 and 2274 $mg.L^{-1}$ respectively) were found in sample W50. While in other samples, level of Na was also higher than maximum permissible limit. The reported data indicated that higher concentration of Na metal is in agreement with the work of other authors (Saleem and Afzal, 2003; ASTM, 2002). Table 2 summarizes the relevant statistical parameters for various metals in water samples in terms of average concentration values (X), standard deviation (±SD), median and mode values. Table 3 incorporates the correlation matrix for paired variables. The water vs. water system showed strong positive correlations between Cu-K and Cu-Zn with corresponding r values of 0.934 and 0.981, respectively.

The removal of Na metal from W50 water sample having concentration 2274 $mg.L^{-1}$ was carried out by adsorption technique at temperatures 293 through 323 K.

The dependence of Na adsorption on the amount of Al_2O_3, and Al_2O_3 – $Pb_{0.1}$ and Al_2O_3 – $Pb_{0.01}$ doping systems was investigated keeping the concentration of Na and shaking time fixed at 50.00 mg/L and 60 min, respectively, while the amount of Al_2O_3 was varied from 0.10 to 1.000 g. The results presented in Table 4 indicate that the values of distribution coefficient (K_D) and percentage adsorption increases with increasing amount of Al_2O_3 and attain maximum value at 0.500 g and then remains constant with further increase in the amount of Al_2O_3. This may be due to decrease in the effective surface area resulting in the conglomeration of the exchanger particles especially at its higher amounts. Therefore for all further studies, optimum amount of Al_2O_3 was used.

Another parameter which affects the extent of adsorption is the stay time. The influence of stay time has been studied by varying the time 10 to 120 min and 0.500 g of adsorbent as shown in Table 5 (Yalçin and Sevýnç, 2001; Choi and Moreau, 1993).

The data were fitted to Freundlich, Dubinin-Raduaskevich, (D-R) and Langmuir adsorption isotherms. These results were subjected to Freundlich isotherms.

$$X/m = KCe^{1/n} \qquad (1)$$

K and 1/n are empirical constants. The values of K and n were computed from slope and intercept of the Freundlich plots are tabulated in Table 6 and Figure 3. The values of n relate to the nature and strength of adsorptive forces involved. The higher fractional values of n signify the strong adsorption forces operating on the Al_2O_3, and Al_2O_3 – $Pb_{0.1}$ and Al_2O_3 – $Pb_{0.01}$ doping systems. However the higher values of K further confirmed the higher affinity of Na adsorption.

As an alternative to Freundlich isotherm, the data were fitted to Dubinin -Raduskevich (D-R) equation (Tahir et al., 1998)] in the linearized form as follows:

$$\ln X/m = \ln Xm - K'\varepsilon^2 \qquad (2)$$

$$\text{Where } \varepsilon = RT \ln(1+1/Ce) \qquad (3)$$

Values of Xm and K' were calculated from the intercept and slope and the values of mean free energy of sorption

Table 1. Concentration (mg/l) of selected metals and non metals from water samples collected from various area of Karachi

Water code	F	K	Na	Mn	Li	Cd	Co	Ni	Pb	Fe	Zn	Cu
W1	1.230	11.00	51.00	0.800	0.300	0.100	0.400	2.610	0.030	1.980	0.100	0.010
W2	0.600	12.00	61.00	0.330	0.400	0.100	0.300	2.660	0.030	1.970	0.100	0.010
W3	0.350	12.00	55.00	0.800	0.400	B.D.L	0.500	2.780	0.010	1.980	B.D.L	0.020
W4	0.350	11.00	58.00	0.500	0.400	B.D.L	0.500	2.610	0.030	1.980	B.D.L	0.020
W5	1.000	13.00	75.00	0.500	0.400	0.100	0.300	2.600	0.020	1.960	0.020	0.020
W6	0.520	12.00	70.00	0.630	0.300	B.D.L	0.400	2.630	0.030	1.970	0.030	0.030
W7	0.790	14.00	60.00	0.360	0.400	B.D.L	0.300	2.610	0.020	1.960	0.040	0.030
W8	0.410	12.00	62.00	0.500	0.400	B.D.L	0.300	2.600	0.030	1.970	0.010	0.010
W9	1.730	46.00	65.00	1.900	1.400	0.100	0.30	2.630	0.030	1.970	0.050	0.020
W10	0.580	14.00	59.00	0.550	0.300	B.D.L	0.30	2.610	0.010	1.970	0.010	0.020
W11	0.766	12.00	63.00	0.360	0.300	0.100	0.500	2.620	0.050	1.970	0.020	0.020
W12	1.260	9.000	63.00	0.330	0.400	0.100	0.400	2.630	0.040	1.960	0.010	0.010
W13	2.160	9.000	58.00	0.500	0.400	0.100	0.200	2.630	0.060	1.960	0.030	B.D.L
W14	1.250	10.00	67.00	1.200	0.600	B.D.L	0.400	2.620	0.010	1.980	0.040	B.D.L
W15	0.266	14.00	25.00	0.500	0.700	0.100	0.209	2.620	0.010	1.970	0.040	B.D.L
W16	0.286	10.00	65.00	0.600	0.400	0.100	0.200	2.620	0.050	1.960	0.040	B.D.L
W17	0.710	14.00	65.00	0.860	0.400	B.D.L	0.200	2.640	0.060	1.960	0.050	B.D.L
W18	0.950	9.000	68.00	0.500	0.400	B.D.L	0.300	2.630	0.070	1.950	0.010	0.020
W19	1.110	9.000	52.00	0.460	0.400	B.D.L	0.200	2.620	0.080	1.950	0.010	0.010
W20	1.180	13.00	550.0	0.700	0.400	0.100	0.200	2.620	0.030	1.970	0.020	0.010
W21	0.860	15.00	63.00	6.300	0.400	0.100	0.200	2.670	0.050	1.960	0.020	0.010
W22	1.170	13.00	63.00	1.060	0.400	0.100	B.D.L	2.620	0.010	1.960	0.010	0.010
W23	0.870	12.00	67.00	1.200	0.200	0.100	0.200	2.660	0.060	1.960	0.040	0.010
W24	1.290	312.0	69.00	0.350	0.200	B.D.L	0.200	2.240	0.070	1.950	B.D.L	0.010
W25	1.240	23.00	59.00	1.200	0.500	0.100	0.100	2.230	0.070	1.970	B.D.L	B.D.L
W26	1.830	23.00	47.00	1.500	0.500	B.D.L	0.200	2.370	0.080	1.980	0.030	B.D.L
W27	0.776	15.00	59.00	1.530	0.300	0.10	0.200	2.290	0.080	1.970	0.020	B.D.L
W28	0.890	11.00	64.00	0.300	0.400	B.D.L	0.200	2.290	0.050	1.950	0.060	B.D.L
W29	0.150	13.00	700.0	0.500	0.400	0.10	0.400	2.310	0.050	1.960	0.060	B.D.L
W30	0.580	9.000	56.00	0.860	0.900	0.10	0.100	2.280	0.060	1.960	0.070	B.D.L
W31	0.700	14.00	63.00	0.500	0.200	B.D.L	0.10	2.260	0.070	1.960	0.060	B.D.L
W32	0.470	13.00	63.00	0.500	0.500	B.D.L	B.D.L	2.210	0.030	1.970	0.030	B.D.L
W33	2.140	14.00	69.00	0.466	0.400	0.100	0.200	2.290	0.010	1.950	0.010	0.010
W34	0.596	14.00	80.00	0.66	0.400	0.100	0.400	2.290	0.020	1.960	0.010	0.010
W35	0.480	14.00	90.00	0.33	0.600	0.100	0.300	2.280	0.010	1.970	0.030	0.010
W36	0.760	12.00	66.00	0.550	0.300	B.D.L	0.100	2.250	0.010	1.970	0.030	0.010
W37	2.200	13.00	72.00	0.4330	0.300	B.D.L	0.300	2.300	0.010	1.960	0.030	0.010
W38	0.820	11.00	63.00	0.430	0.400	0.100	0.400	2.310	0.020	1.960	0.030	0.010
W39	0.150	13.00	58.00	0.500	0.500	0.100	0.300	2.320	0.030	1.960	0.010	0.010
W40	0.200	13.00	56.00	0.560	0.400	0.100	0.100	2.650	0.150	1.950	0.020	0.020
W41	B.D.L	13.00	62.00	0.450	0.200	0.100	0.100	2.310	0.090	2.600	0.010	0.020
W42	0.256	18.00	62.00	1.125	0.300	B.D.L	0.100	2.650	0.100	1.970	0.020	0.020
W43	0.025	16.00	55.00	0.160	0.500	0.100	0.200	2.640	0.090	1.970	0.020	0.030
W44	0.09	9.000	140.0	1.600	0.400	B.D.L	0.300	2.300	0.020	2.01	0.010	0.020
W45	0.106	10.00	55.00	0.600	0.400	0.100	0.100	2.320	B.D.L	1.970	0.020	0.020
W46	0.456	620.0	140.0	0.866	7.700	0.200	0.400	2.320	0.230	2.070	1.200	1.200
W47	0.150	630.0	63.00	1.360	8.200	0.200	0.100	2.310	0.260	2.420	1.400	1.300
W48	0.035	15.00	67.00	0.660	0.500	0.100	0.100	2.310	0.150	1.960	0.010	0.100
W49	B.D.L	13.00	69.00	0.460	0.400	0.100	0.300	2.290	0.040	1.970	0.030	0.010
W50	0.460	110.0	2274	0.860	7.700	0.200	0.200	2.650	0.230	1.970	0.030	B.D.L
W51	0.773	11.00	1725	1.300	8.200	0.200	0.400	2.640	0.260	1.960	0.030	B.D.L

Table 1. Contd**.**

W52	B.D.L	4.000	64.00	0.700	0.500	0.100	0.100	2.320	0.150	1.980	0.030	0.020
W53	0.010	14.00	69.00	0.800	0.400	0.100	0.200	2.310	0.020	1.980	B.D.L	0.020
W54	0.270	24.00	200.0	0.800	1.800	0.100	0.200	2.290	0.010	1.960	0.100	0.020
W55	0.216	14.00	63.00	0.600	0.600	0.100	0.300	2.300	0.020	1.960	B.D.L	0.02
W56	B.D.L	24.00	66.00	0.260	0.700	0.100	B.D.L	2.310	0.010	1.980	0.100	0.010
W57	0.140	13.00	60.00	0.930	0.500	0.100	B.D.L	2.300	0.020	1.980	B.D.L	0.010
W58	0.110	14.00	63.00	0.260	0.400	B.D.L	0.400	2.320	0.020	1.980	0.100	0.010
W59	0.090	14.00	70.00	0.030	0.300	0.100	0.200	2.210	0.010	1.970	0.100	0.010
W60	0.596	13.00	200.0	0.600	0.400	0.100	0.100	2.320	0.010	1.960	0.100	B.D.L
W61	0.410	14.00	72.00	0.430	0.300	B.D.L	0.100	2.310	0.010	1.970	0.100	B.D.L
W62	0.643	31.00	64.00	0.200	0.200	B.D.L	0.100	2.340	0.110	1.970	0.100	B.D.L
W63	0.356	25.00	63.00	0.430	0.400	B.D.L	0.300	2.340	0.020	1.950	0.100	B.D.L
W64	0.406	15.00	65.00	0.630	0.500	0.100	0.400	2.510	0.010	1.980	0.100	B.D.L
W65	0.573	13.00	200.0	0.620	0.800	0.100	0.300	2.520	0.100	1.970	0.100	0.010
W66	0.466	15.00	300.0	0.530	0.400	B.D.L	0.200	2.12.0	0.020	1.970	0.100	0.020
W67	0.310	12.00	60.00	0.860	0.400	B.D.L	0.200	2.140	0.020	1.970	0.100	0.010
W68	0.320	13.00	60.00	1.500	0.200	0.100	BDL	2.130	0.020	1.970	0.100	0.020
W69	0.446	16.00	200.0	0.463	0.300	0.100	BDL	2.150	0.020	1.970	0.100	0.010

Table 2. Statistical parameters of selected metals and non metal from water samples (n = 69) collected from various area of Karachi.

Metals	Range	Average	±SD	Median	Mode
F	0.00 to 2.2	0.628	0.535	0.48	0.020
K	4 to 630	37.62	109.0	13.00	13.00
Na	47 to 2274	160.1	345.8	64.00	63.00
Mn	0.03 to 6.3	0.763	0.774	0.560	0.500
Li	0.2 to 8.2	0.882	1.783	0.400	0.400
Cd	0 to 0.2	0.069	0.057	0.100	0.100
Co	0 to 0.5	0.230	0.133	0.200	0.200
Ni	2.12 to 2.78	2.430	0.181	2.320	2.310
Pb	0 to 0.26	0.053	0.059	0.030	0.010
Fe	1.95 to 2.6	1.984	0.094	1.970	1.970
Zn	0 to 1.4	0.078	0.216	0.030	0.100
Cu	0 to 1.3	0.047	0.209	0.010	0.010

(E_a) was calculated from D-R parameter K (Figures 4, 5 and Table 7). The values of E_a are calculated by using following equation:

$$E_a = (-2K)^{-1/2} \quad (4)$$

The values of E_a increases with the rise in temperatures, showing increase in adsorption with temperature.

The adsorption of Na on Al_2O_3, and Al_2O_3 – $Pb_{0.1}$ and Al_2O_3 – $Pb_{0.01}$ doping systems at various temperatures are fitted in the linear form of Langmuir isotherm equation [Tahir et al., 1998). The Langmuir isotherm equation is

$$C_e / (X/m) = 1/ Vm\,K + C_e / K. \quad (5)$$

The parameters Vm and K give the adsorption capacity of

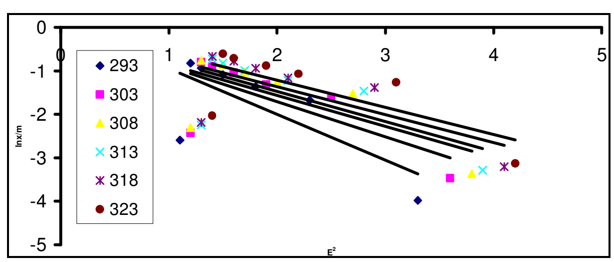

Figure 4. D-R plots for the removal of Na from water sample W50 using Al_2O_3 adsorbent at different temperatures.

the adsorbents. It is evident from Figures 6, 7 and Table 8 that adsorption capacity increases with increase in tem-

Table 3. Statistical multiple co-relation between paired water samples collected from various area of Karachi.

Metals	F	K	Na	Mn	Li	Cd	Co	Ni	Cu
F	-								
K	-0.047								
Na	-0.043	0.037	-						
Mn	0.126	0.062	0.033	-					
Li	-0.078	0.688	0.637	0.121	-				
Cd	-0.1312	0.352	0.377	0.147	0.588	-			
Co	0.133	0.0040	0.100	-0.072	0.083	-0.069	-		
Ni	0.222	-0.135	0.190	0.166	0.069	0.023	0.406	-	
Pb	-0.102	0.576	0.489	0.117	0.788	0.479	-0.073	0.125	
Fe	-0.216	0.441	-0.05	0.0251	0.311	0.240	.136	-0.128	
Zn	-0.133	0.915	-0.034	0.059	0.676	0.381	-0.011	-0.157	
Cu	-0.124	0.933	-0.041	0.078	0.682	0.393	0.0181	-0.108	-

Table 4. Optimization of amount of Al_2O_3 adsorbent for the removal of Na metal from the water samples W50.

S/No.	Amount of Al_2O_3(g)	Ci (g/l)	Cf (g/l)	Ce (g/l)	% Removal	K_D
1	0.1	500	245	255	51.0	510
2	0.2	500	240	260	52.0	260
3	0.3	500	200	300	60.0	199
4	0.4	500	150	350	72.0	175
5	0.5	500	105	395	79.0	158
6	0.6	500	105	395	79.0	131
7	0.7	500	105	395	79.0	112
8	0.8	500	105	395	79.0	98
9	0.9	500	105	395	79.0	87
10	1.0	500	105	395	79.0	79.0

Table 5. Optimization of stay time of Al_2O_3 adsorbent for the removal of Na from drinking water samples W50.

S/N	Stay time (min)	Ci (g/l)	Cf (g/l)	Ce (g/l)	% Removal	K_D
1	10	500	410	90	18.0	25.7
2	20	500	400	100	20.0	28.0
3	30	500	385	115	23.0	32.0
4	40	500	365	135	27.0	38.0
5	50	500	240	260	52.0	74.0
6	60	500	210	290	58.0	82.0
7	70	500	125	375	75.0	107
8	80	500	125	375	75.0	107
9	90	500	125	375	75.0	107
10	100	500	125.5	374.5	74.9	106
11	110	500	125.5	374.5	74.9	106
12	120	500	125.5	374.5	74.9	106

perature. The slope and intercept gives the values of Vm and K from which the monolayer capacity and binding constant can be computed. The values of monolayer capacity increase with the increase in temperature and

Table 6 Freundlich parameters for the removal of Na metal from standard NaCl and water sample W50 using Al_2O_3 adsorbent and Al_2O_3-Pb $_{0.1}$ and Al_2O_3-Pb $_{0.01}$ doping system at different temperatures (293 - 323).

S/N	Temperature (K)	NaCl			W50		
		N	K (L/g)	R^2	n	K (L/g)	R^2
1	293	1.358	8.627	0.476	2.211	3.430	0.382
2	303	1.908	3.291	0.422	2.249	3.461	0.393
3	308	1.880	3.485	0.444	2.292	3.461	0.403
4	313	1.927	3.534	0.453	2.443	3.212	0.391
5	318	2.010	3.441	0.424	2.610	2.951	0.373
6	323	2.169	3.019	0.462	2.833	2.650	0.355
S/N	Temperature (K)	Al_2O_3-$Pb_{0.01}$			Al_2O_3-$Pb_{0..1}$		
		N	K (L/g)	R^2	n	K (L/g)	R^2
1	293	1.922	4.027	0.415	1.422	7.974	0.517
2	303	2.013	3.733	0.403	1.602	5.768	0.487
3	308	2.082	3.574	0.398	1.766	4.539	0.471
4	313	2.247	3.135	0.382	1.930	3.766	0.452
5	318	2.358	2.968	0.390	1.986	3.607	0.456
6	323	2.655	2.456	0.386	2.046	3.493	0.453

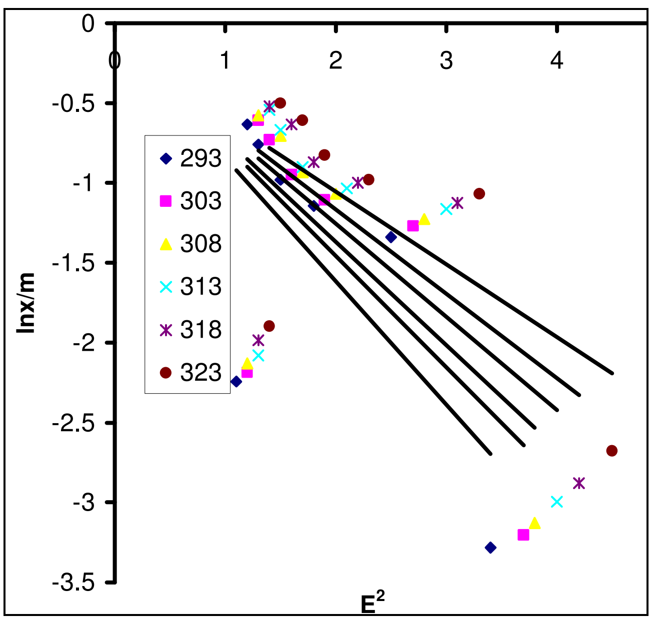

Figure 5. D-R plots for the removal of Na metal from water sample W50 using Al_2O_3 - $Pb_{0.01}$ doping system at different temperatures.

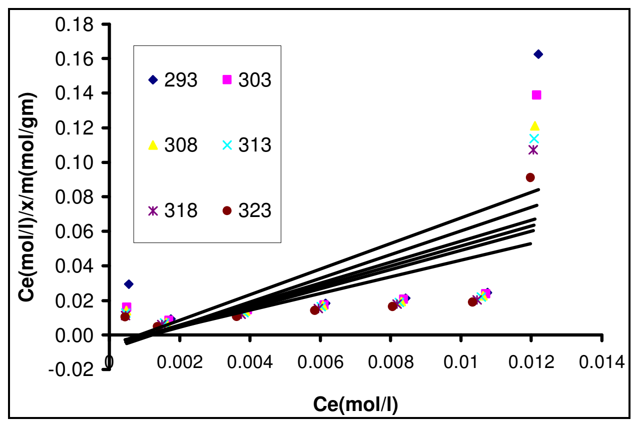

Figure 6. Langmuir plots for the removal of Na metal from water sample W50 using Al_2O_3 adsorbent at different temperatures

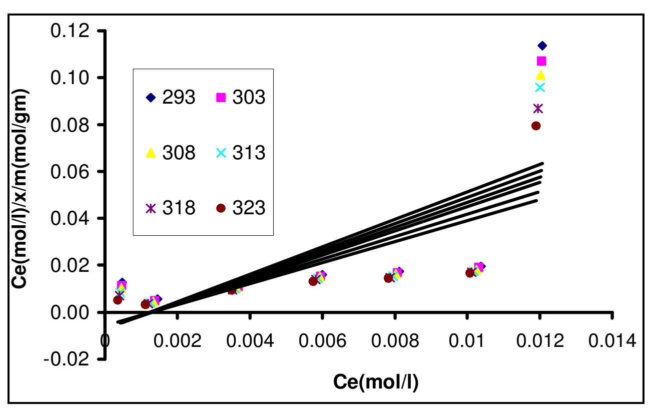

Figure 7. Langmuir plots for the removal of Na metal from water sample W50 using Al_2O_3 – $Pb_{0.01}$ doping system at different temperatures.Top of Form

indicate the strengthening of the adsorbate-adsorbent interaction at high temperature.

Thermodynamic parameters such as free energy (ΔG^o), enthalpy (ΔH^o) and entropy (ΔS^o) of adsorption are calculated from the distribution constant K_D. Table 9 Show the values of thermodynamic parameters. The values of ΔH^o and ΔS^o were calculated from the slope and intercept of the linear variation of ln K_D with the reciprocal of temperature (1/T) using the relation:

Table 7. D-R Parameters for the removal of Na metal from standard NaCl and from water sample (W50) using Al_2O_3 adsorbent, Al_2O_3-Pb 0.01 and Al_2O_3-Pb $_{0.1}$ doping system at different temperature (293-323).

S/N	Temperature (K)	NaCl				W50	
		Al_2O_3-$Pb_{0.01}$				Al_2O_3-$Pb_{0.1}$	
		K (mol^2Kg^{-2})	X_m ($mol.g^{-1}$)	E ($KgJ.mol^{-1}$)	K. (mol^2Kg^{-2})	X_m ($mol.g^{-1}$)	E ($KgJ.mol^{-1}$)
1	293	-0.772	1.072	0.804	-1.066	1.155	0.684
2	303	-0.698	1.059	0.845	-0.892	1.058	0.748
3	308	-0.647	1.075	0.878	-0.748	1.102	0.817
4	313	-0.583	1.095	0.926	-0.684	1.095	0.854
5	318	-0.528	1.115	0.972	-0.623	1.141	0.895
6	323	-0.455	1.152	1.040	-0.614	1.076	0.901
S/N	Temperature (K)	Al_2O_3-$Pb_{0.01}$				Al_2O_3-$Pb_{0.1}$	
		K (mol^2Kg^{-2})	X_m ($mol.g^{-1}$)	E ($KgJ.mol^{-1}$)	K (mol^2Kg^{-2})	X_m ($mol.g^{-1}$)	E ($KgJ.mol^{1}$)
1	293	-0.772	1.072	0.804	-1.066	1.155	0.684
2	303	-0.698	1.059	0.845	-0.892	1.058	0.748
3	308	-0.647	1.075	0.878	-0.748	1.102	0.817
4	313	-0.583	1.095	0.926	-0.684	1.095	0.854

Table 8. Langmuir parameters for the removal of NA metal from water sample w50 using al_2o_3-$pb_{0.01}$, al_2o_3-$pb_{0.1}$ doping system at different temperature (293-323) at the steps of ($5^oC \pm 0.2$)

S/N	Temperature (K)	Al_2O_3-$Pb_{0.01}$			Al_2O_3-$Pb_{0.1}$		
		V_m ($mol.L^{-1}$)	K ($mol^1.L$)	R^2	V_m ($mol.L^1$)	K ($mol^1.L$)	R^2
1	293	0.170	801.9	0.462	0.173	2877	0.376
2	303	0.178	799.3	0.475	0.173	1748	0.426
3	308	0.186	799.7	0.487	0.176	1228	0.459
4	313	0.193	761.9	0.503	0.181	1018	0.485
5	318	0.209	796.1	0.524	0.189	1032	0.498
6	323	0.223	784.1	0.550	0.197	1011	0.509

$$\ln K_D = \Delta S^o / R - \Delta H^o / (RT) \quad (6)$$

The values of ΔG^o was calculated using equation:

$$\Delta G^o = \Delta H^o - T\Delta S^o \quad (7)$$

The values of ΔG^o at different temperatures are negative for all the systems as expected for spontaneous process. The values of ΔH^o are negative and ΔS^o values are positive. The negative values of ΔH^o indicates that the adsorption of Na on alumina and metal doped alumina is exothermic in nature. The decrease in ΔG^o values with increasing temperature show that the adsorption of metal ion on Al_2O_3, and Al_2O_3 – Pb $_{0.1}$ and Al_2O_3 – $Pb_{0.01}$ doping systems is favorable at high temperatures. This may be due to the desolvation of metal ions at higher temperatures (Fahim-Uddin and Tahir, 2002)

Conclusion

The investigations in the present study on water pollution aspects were carried out especially in reference to the level of fluoride and other metal ions level in the drinking water samples. The study has amply evidenced that the status of local metal pollution situation is quite alarming. If the level of fluoride is insufficient, dentists recommend that fluoride tablet (dentifluor) which contains about 0.553 mg of sodium fluoride must be use. The results also show that the Na metal, under optimized conditions can be removed (about 79.00 %). The use of demineralised purified water for the home is a good option. The minerals they contain are in the form of metallic inorganic

Table 9. Thermodynamic parameters for the removal of Na metal from standard NaCl and water sample W50 using Al_2O_3, and Al_2O_3 $Pb_{0.01}$ and Al_2O_3-$Pb_{0.1}$ dopping systems at different temperatures.

Concentration ($mol.L^{-1}$ X 10^3)	ΔH^0 (KJ mol^{-1})	ΔS^0 (KJ deg^{-1} mol^{-1})	ΔG^0 (KJ mol^{-1})					
			293 K	303 K	308 K	313 K	318K	323K
NaCl	**Al_2O_3**							
12.5	-0.281	2.1914	-642.4	-6640	-6750	-6862	-697.2	-708.2
10.1	-0.308	2.414	-707.7	-7310	-7439	-7560	-768.1	-780.2
7.5	-0.925	2.556	-749.3	-7877	-7877	-8005	-813.3	-826.1
5.0	-1.533	7.004	-2053	-2159	-2159	-2194	-2229	-2264
2.5	-1.667	8.57	-2512	-2641	-2641	-2684	-2727	-2770
1.3	-1.693	8.726	-2631	-2645	-2645	-2650	-2652	-2655
0.62	-1.705	9.271	-2701	-2740	-2740	-2768	-2785	-2801
12.5	-0.373	2.54	-7448	-7700	-7829	-7956	-8083	-8210
10.1	-0.395	2.801	-8211	-8490	-8631	-8771	-8911	-9051
7.5	-0.419	3.106	-9105	-9410	-9571	-9726	-9881	-1003
5	-0.755	4.529	-13279	-1373	-1395	-1418	-1441	-1463
2.5	-2.067	10.03	-2941	-3041	-3091	-3142	-3192	-3242
1.25	-2.15	10.73	-2152	-2230	-2260	-2300	-2336	-2373
0.62	-2.778	11.53	-2202	-2285	-2322	-2360	-2398	-2435
	Al_2O_3 -$Pb_{0.01}$							
12.5	-0.329	2.694	-7898	-8168	-8302	-8437	-8572	-8707
10.1	-0.417	3.169	-9290	-9607	-9765	-9924	-1008	-1024
7.5	-0.373	3.157	-9256	-9571	-9729	-9887	-1004	-1020
5	-0.713	4.934	-1446	-1495	-1520	-1545	-1569	-1594
2.5	-2.419	12.99	-3809	-3938	-4003	-4068	-4133	-4198
1.25	-0.135	0.754	-2210	-2290	-2330	-2360	-2402	-2440
0.62	-2.353	10.37	-3040	-3144	-3196	-3248	-3300	-3352
	Al_2O_3 -$Pb_{0.1}$							
12.5	-0.241	2.077	-6090	-629	-6401	-6505	-6609	-6713
10.1	-0.301	2.31	-6772	-7003	-7119	-7235	-7350	-7466
7.5	-0.391	2.906	-8520	-881	-8956	-9101	-9247	-9392
5	-0.882	5.319	-1559	-1612	-1639	-1665	-1692	-1719
2.5	-1.471	8.185	-2399	-2481	-2522	-2563	-2604	-2645
1.25	-0.106	0.626	-1835	-1900	-1930	-1960	-1992	-2023
0.62	-2.245	8.938	-2621	-2710	-2755	-2800	-2844	-2889

minerals and human body utilizes them in the form of organic minerals.

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