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Removal of Zinc and Fluoride Ions from Industrial Waste Water Plants Around Cairo

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Removing of zinc and fluoride ions from industrial waste water is of particular interest from the environmental view point. Zinc and fluoride ions are toxic when certain level are exceeded. Zinc ions have a great affinity towards replacing iron in red cells and plasma proteins and may cause anemia (Jones et al. 1983). Fluoride ions may attack the bone and cause dental and bone steoporsis (Cooke et al. 1990).

Treatment process for removing of zinc and fluoride ions from water and waste water through adsorption or ion exchange were recently studied. Liu et al. (1999) studied the removal of Cu, Zn, Cd and Hg ions from waste water by chelating fiber. Muratak (1998) and Srivastav et al. (1993) used aquatic plants for removal of heavy metals including zinc ions from water and industrial waste water. Mishra et al. (1997) used sodium titanate for removal of zinc ions from aqueous solutions. Pascucci (1993) studied the removal of Zn ions from aqueous solution by an algal biomass. Leinonen et al. (1994) studied the purification of Ni and Zn ions from waste waters of metal-plating plants by ion exchanger. Sanciolo et al. (1992) studied the removal of Cr (III), Ni (II) and Zn (II) from chromium stream electroplating waste water by adsorbing colloid floatation. Moosa et al. (1991) studied the adsorption of zinc ions on titanium oxide. Gudushauri et al. (1989) studied the sorption extraction of zinc ions from industrial waster water. Micera et al. (1989) used $Al(OH)_3$ for removal of Zn ions from aqueous solution. Ferro-Garcia et al. (1988) studied the adsorption of Zn, Cd and Cu ions on activated carbons obtained from agricultural by-products. Buffle et al. (1985) studied the purification of fluoride ions from waste waters.

The purpose of this work was to study the adsorption ability of bone powder, active carbon, plant powder and commercial carbon for removal of zinc and fluoride ions from industrial waste waters. The factors affecting adsorption process of zinc ions such as contact time, pH and concentrations were also studied.

MATERIALS AND METHODS

The samples of waste water were collected from Abu Zabaal area and Ahlia area around Cairo. Then, they were filtered, acidified with HNO_3 (0.5% V/V) and stored in polyethylene bottles.

The synthetic samples which have similar qualifications to waste water discharging from Abu Zabaal area were prepared. The qualifications of synthetic samples are shown in (Table 1) .

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The bone powder was prepared by burning the animal bone sample at 600°C, then grinding, washing overnight with distilled water, drying at 100°C and mechanically sieving to suitable grain size (0.2 mm). The plant powder was prepared by washing the roots of the Nile rose plant (water hyacinth) which is called Echornia Speciosa, then cutting and grinding to suitable grain size (0.2 mm). The active and commercial carbon were prepared by drying the sample at 100°C and mechanically sieving to suitable grain size (0.2 mm).

The capacity and the uptake percent of zinc ions adsorbed from nitrate solution by bone powder, active carbon, plant powder and commercial carbon was determined by batch experimental technique, where a constant V/m ratio was used and chosen to be 500 ml/g. The analysis of the liquid phase was carried out using a Unicam model PU 9100 atomic absorption spectrometry.

The total fluorides (gaseous and particles) were determined by using the ion selective technique. Particles were collected by means of membrane filter and gaseous fluorides were absorbed by an alkali impregnated cellulose pad placed immediately behind the membrane filter. The membrane filter and collected solids were made alkaline, then ashed and the residue fused with additional alkali. The fluoride was determined in a solution of the melt using the fluoride selective electrode.

RESULTS AND DISCUSSION

The detection limits of the proposed methods calculated from three times standard deviation of the blank was 0.01 and 0.05 mg l^{-1} for zinc and fluoride, respectively. The relative standard deviation S_r (%), for the determination of 1.0, 2.0 and 5.0 mg l^{-1} fluoride and 0.5, 1.0 and 2.0 mg l^{-1} zinc ions were ≤ 2.8 (n = 7). The reproducibility of the proposed methods was tested by repeating the analysis of solutions containing 1.0, 2.0 mg l^{-1} fluoride and 0.5, 1.0 mg l^{-1} zinc ions (n = 7) on three different working days. The values of relative standard deviation, S_r (%) were ≤ 2.6. Moreover, the percentage recoveries and the relative standard deviation (n = 7) for the analyzed waste water samples were determined. Significantly high recoveries were obtained (97-100%) with relative standard deviation, S_r (%) of ≤ 2.7. This indicated the high accuracy and precision of the proposed method of analysis of fluoride and zinc ions.

The zinc and fluoride concentrations in industrial waste water samples collected from Abu Zabaal and Ahlia area around Cairo during six months were determined (Table 2). The mean concentrations of zinc and fluoride vary from 0.49 to 2.57 mg/l and 1.13 to 7.10 respectively, in industrial waste water samples during six months (Table 2).

Different weights of powdered animal bone were shaken with 50 ml of zinc chloride solution (4.0 mg l^{-1}) for two hours. The results showed that the zinc nitrate solution at pH = 4 had the highest uptake percent at 0.1 g bone powder (80%). The V/m ratio was chosen to be 500 ml g^{-1}.

The different factors affecting adsorption process of zinc ions by bone powder, active carbon, plant powder and commercial carbon, such as contact time, pH and concentration were studied. In such experiments the uptake percent was measured spectrophotometrically by atomic absorption spectroscopy. Also the capacity of zinc ions was calculated on the different natural materials at different pH and at constant concentration.

Table 1. Qualification of synthetic samples

Sample	pH	Contents mg/l				
		Pb^{2+}	Cd^{2+}	Zn^{2+}	Fe^{3+}	F^-
(1)	3.5	2.5	2.0	3.0	12.0	4.0
(2)	4.0	3.0	2.5	3.5	14.0	6.0
(3)	4.5	3.5	3.0	4.0	16.0	8.0
(4)	5.0	4.0	3.5	4.5	20.0	10.0

Table 2. The concentration of zinc and fluoride ions in industrial waste samples (from Abu zabaal (AZFC) and Ahlia areas) during six months.

Months	Conc. of Zn (mg/l)						Conc. of fluoride (mg/l)					
	Samples from AZFC			Samples from Ahlia			Samples from AZFC			Samples from Ahlia		
	1	2	3	4	5	6	1	2	3	4	5	6
April	2.50	1.05	0.90	1.90	0.60	0.46	7.01	2.85	2.45	2.95	1.39	1.20
May	2.60	1.10	0.95	2.05	0.80	0.50	6.50	2.60	2.25	2.65	1.20	1.00
June	2.30	1.00	0.80	1.65	0.56	0.40	6.10	2.56	2.20	2.56	1.30	0.96
July	2.30	0.96	0.75	1.70	0.60	0.45	7.90	2.90	2.60	3.14	1.50	1.25
August	2.40	1.06	0.90	1.80	0.65	0.50	6.80	2.65	2.30	2.69	1.25	1.05
Sept.	2.70	1.20	1.05	2.10	0.90	0.60	8.50	3.10	2.80	3.20	1.60	1.30
Mean	2.57	1.06	0.89	1.87	0.69	0.49	7.10	2.78	2.40	2.87	1.37	1.13

Locations: 1, 4: Up-stream plant (150 m side Ismalia Canal), 2, And 5: Up-stream plant (150 m middle the canal), 3, And 6: Down-stream plant (150 m side the canal).

The time effect of adsorption of zinc on the different natural materials was studied using zinc chloride solution of 4.0 mg l^{-1} at pH = 4 with V/m = 500 ml/g. The relation between the shaking time and uptake percent of zinc by the natural materials is shown in (Fig.1). The zinc uptake percent reaches equilibrium state after 60 min., 180 min., 60 min., and 120 min. for bone powder, plant powder, active carbon and commercial carbon, respectively (Fig.1). The percent uptake of zinc is 80% for bone powder, 50% for plant powder, 40% for active carbon and 20% for commercial carbon.

The effect of pH on the uptake percent of zinc ions adsorbed from different concentrations of zinc chloride solutions by bone powder, plant powder, active carbon and commercial carbon is shown in (Table 3). The pH range was chosen from pH 1-6.The results indicated that the uptake percent of zinc ions increased by increasing pH value (Table 3). It is apparent that the uptake percent of zinc is negligible at pH = 1, 2 for bone powder, plant powder and active carbon and at pH = 1, 2 and 3 for commercial carbon. The sequence of the uptake percent of zinc ions is in the order: bone powder > plant powder > active carbon > commercial carbon (Table 3).

The capacity (m mol/g) of zinc ions adsorbed from nitrate solution by different natural materials was calculated from this equation:

$$Capacity = \frac{\%\ uptake \times C_o}{100} \times V/m$$

where C_o = the initial concentration of zinc (m mol/ml), V = total solution volume (ml), m = weight of the material (g)

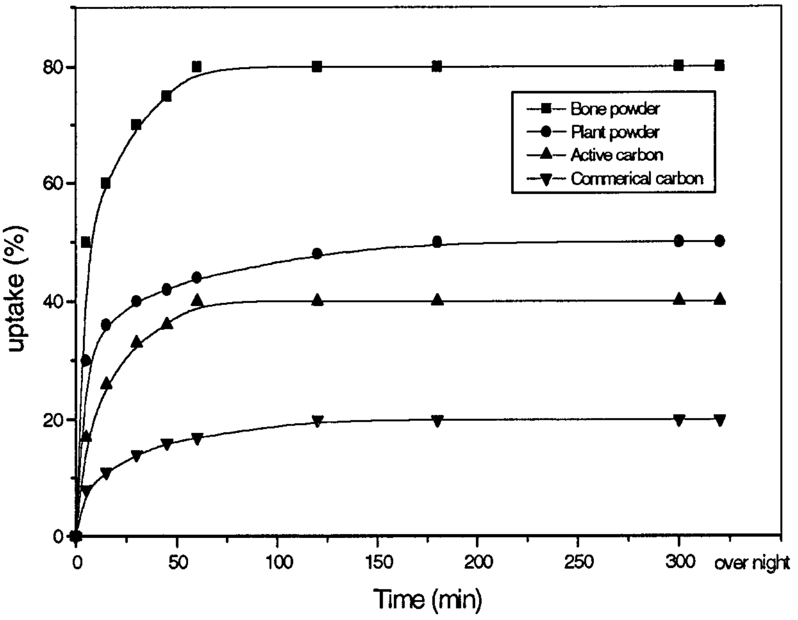

Figure 1. Effect of contact time on uptake percent of zinc adsorbed from zinc chloride solution (4.0 mg/l) by bone powder, plant powder, active and commercial carbon at pH = 4.0

The effect of zinc concentration on uptake percent of zinc ions on the different natural materials were studied at constant pH. The results recorded in (Table 3) show also the effect of concentration on the uptake percent of zinc ions adsorbed from chloride solution at constant pH by the natural materials. It is apparent that the zinc uptake percent is increased by decreasing the concentration of zinc ions (Table 3).

The effect of pH on the capacity of zinc ions adsorbed from chloride solution (4.0 mg l^{-1}) by bone powder, plant powder, active carbon and commercial carbon is shown in (Table 4). The capacity of zinc ions adsorbed from chloride solution by the different natural materials increased by increasing pH value. The sequence of zinc ions capacity is in the order: bone powder > plant powder > active carbon > commercial carbon (Table 4).

In order to check the success of the method, the synthetic and industrial waste water samples were treated by using the bone powder, plant powder, active carbon and commercial carbon to remove zinc and fluoride ions. The treatment process for zinc ions was carried out at contact time (4 hours) and pH = 4. A good results were obtained where zinc ions were removed (80%) by using bone powder, (50%) by using Nile rose plant powder, (40%) by using active carbon and (20%) by using commercial carbon. The treatment process for fluoride ions was carried out at contact time (4 hours) and pH = 4. A good results were obtained only by using bone powder where fluoride ions were removed (85%) but no removing was obtained by the other natural materials.

Table 3. Effect of pH on uptake percent of zinc on different concentrations by bone powder, plant powder, active and commercial carbon.

Natural materials	Conc. of zinc mg/l	Uptake % of zinc					
		pH					
		1	2	3	4	5	6
Bone powder	4.0	0	0	69.5	80.0	82.0	82.5
	10.0	0	0	59.1	68.7	70.2	73.0
	30.0	0	0	47.8	56.3	57.2	58.0
	60.0	0	0	21.6	27.5	29.0	30.1
	120.0	0	0	9.9	15.5	16.0	18.2
Plant powder	4.0	0	0	39.3	50.0	52.0	53.6
	10.0	0	0	27.6	36.7	38.6	40.5
	30.0	0	0	17.6	25.8	27.1	28.3
	60.0	0	0	4.6	7.8	8.6	9.9
	120.0	0	0	2.0	3.2	3.5	4.0
Active carbon	4.0	0	0	29.5	40.0	42.6	43.0
	10.0	0	0	17.6	24.3	26.0	26.5
	30.0	0	0	6.4	9.9	10.2	12.0
	60.0	0	0	1.2	2.8	3.2	3.5
	120.0	0	0	0	0.6	0.80	0.85
Commercial carbon	4.0	0	0	0	20.0	22.3	24.0
	10.0	0	0	0	10.7	16.9	18.0
	30.0	0	0	0	2.5	4.9	5.8
	60.0	0	0	0	1.1	1.6	1.7
	120.0	0	0	0	0.3	0.4	0.5

Table 4. Effect of pH on capacity of zinc adsorbed from chloride solution (4.0 mg/l) by natural materials

Natural materials	Capacity (m mol/g) x 10^{-3}					
	pH					
	1	2	3	4	5	6
Bone powder	0	0	21.2	24.4	25.1	25.2
Plant powder	0	0	12.0	15.3	15.9	16.4
Active carbon	0	0	9.0	12.2	13.0	13.2
Commercial carbon	0	0	0	6.1	6.8	7.3

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