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Removal of Cadmium Ions from Industrial Waste Water Plants Around Cairo

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Toxic elements occur naturally at trace or ultra trace levels in the aquatic environment. However, waste waters from mining activities, electroplating factories or chemical laboratories contain very high concentrations of a wide variety of toxic heavy metals, including cadmium. Release and dispersal of this toxic element to aquatic system can have disastrous consequences for living organisms. Cadmium attacks the kidney and may produce lung cancer (Fergusson 1990). It also inhibits a large number of enzymes because it replaces zinc in enzymes and thus interferes with cellular metabolism (Cooke et al. 1990). Removing of cadmium ions from industrial waste water samples is of great significance from the environmental view point.

Treatment proceses for removing of cadmium ions from water and waste water through adsorption or ion exchange were recently studied. Wilson and Edyvean (1994) studied the removal of cadmium and mercury ions from industrial waste water by some biological sorbents. Snowden et al. (1993) used colloidal microgels for the absorption of lead and cadmium ions from aqueous solution. Denizli et al. (1998) studied the removal of copper (II), cadmium (II) and lead (II) ions from waste water by magnetic sorbents. Viraraghavan and Rao (1993) studied the removal of cadmium and chromium ions by adsorption on peat at pH range 4-5 from waste water. Ferro-Garcia et al. (1988) studied the adsorption of zinc, cadmium and copper ions on activated carbon obtained from agricultural by-products. Haklits et al. (1988) studied the removal of cadmium ions from waste water by ion exchange. Vecchio et al. (1998) studied the removal of copper, lead and cadmium ions by biosorption on bacterial cells. Faghihian et al. (1999) used clinoptilolite and its sodium form for removal of lead, nickel, cadmium and barium ions from waste water. Hilmi et al. (1990) used titanium dioxide deposited on glass plates for removal of metals including cadmium ions from aqueous wastes. Park et al. (1999) studied the removal of cadmium and lead ions in water by Sargassum. Liu et al. (1999) studied the removal of copper (II), zinc (II), cadmium (II) and mercury (II) ions from waste waster by poly(acrylamino-phosphonic)- type chelating fiber. Murata (1998) studied the removal of heavy metals including cadmium (II) by plants. Namasivayam and Ranganathan (1995) used iron (III)/ chromium (III) hydroxide as adsorbent for removal of cadmium(II)

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from waste water. Reed et al. (1994) used granular activated carbon columns in removing lead and cadmium ions from aqueous waste streams.

The aim of this work is to study the adsorption capacity of bone powder, active carbon, plant powder and commercial carbon for removal of cadmium ions. The factors affecting adsorption process of cadmium ions such as contact time, pH, amount of adsorbent and concentration of cadmium solution were also studied.

MATERIALS AND METHODS

The bone powder was prepared by burning the animal bone sample at 600°C, then grinding, washing over night with distilled water, drying at 100°C and mechanically sieved to suitable grain size (0.2 mm). The plant powder was prepared by washing the roots of the Nile rose plant (water hyacinth), then cutting and grinding to suitable size (0.2 mm). The commercial carbon was obtained from the burning of Qafuor tree by the national incinerators, then drying at 100°C to remove moisture and finally grinding to suitable size (0.2 mm). The active carbon (BDH) was dried at 100°C and mechanically sieved to suitable grain size (0.2 mm).

The capacity of different types of natural materials such as bone powder, active carbon, plant powder and commercial carbon for cadmium ions were determined by batch experiment technique, where a constant V/m ratio was used and chosen to be 500 ml/g. In this technique a certain weight of each adsorbent (0.1 g) is mixed with a known volume (50 ml) of certain concentration of cadmium nitrate solution. The mixture is then agitated at 300 rpm till equilibrium is reached. The liquid phase was separated by decantation or filtration. A known volume (1.0 ml) of the liquid phase was used for analysis by using atomic absorption spectrometry. The capacity (mol/g) of cadmium ions adsorbed from nitrate solution by different natural materials was calculated from Equation (1).

$$Capacity = \frac{\%\, uptake \times C_o}{100} \times V/m \text{ ....Eq. (1)}$$

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

The uptake percent of cadmium ions on different types of natural materials was calculated from Equation (2).

$$\%\, uptake = \frac{C_o - C_w}{C_o} \times 100 \text{ ....Eq. (2)}$$

where C_W = the final concentration of cadmium (mg/l) and C_o = the initial concentration of cadmium (mg/l).

Table 1. Synthetic sample contents.

Sample	pH	Contents mg/l				
		Pb^{2+}	Cd^{2+}	Zn^{2+}	Fe^{3+}	F^{-}
(1)	3.0	2.0	1.5	2.0	10.0	3.5
(2)	3.5	2.5	2.0	3.0	12.5	4.5
(3)	4.0	3.0	2.5	4.0	15.0	5.0

Table 2. The concentration of cadmium mg/L in industrial waste water samples during six months.

	Conc. of cadmium (mg/L)									
	Samples from Abu Zabaal					Samples from Ahlia				
	1	2	3	4	5	6	7	8	9	10
April										
Concentration (mg/l)	1.48	0.05	0.02	0.05	0.03	1.09	0.03	0.02	0.04	0.02
pH	2.9	7.2	7.3	7.1	7.2	7.1	7.3	7.2	7.2	7.1
May										
Concentration (mg/l)	1.62	0.06	0.03	0.06	0.02	1.17	0.04	0.03	0.05	0.03
pH	3.0	7.5	7.4	7.3	7.2	7.2	7.3	7.2	7.2	7.3
June										
Concentration (mg/l)	1.61	0.06	0.03	0.06	0.03	1.23	0.04	0.02	0.05	0.03
pH	4.0	7.8	7.8	7.4	7.4	7.4	7.8	7.7	7.6	7.7
July										
Concentration (mg/l)	1.49	0.05	0.02	0.05	0.03	1.20	0.03	0.02	0.04	0.02
pH	3.8	7.7	7.7	7.3	7.3	7.3	7.6	7.6	7.4	7.4
August										
Concentration (mg/l)	1.58	0.06	0.03	0.06	0.03	1.29	0.04	0.02	0.05	0.03
pH	3.6	7.6	7.6	7.3	7.3	7.2	7.7	7.6	7.4	7.4
September										
Concentration (mg/l)	1.50	0.05	0.02	0.05	0.03	1.30	0.03	0.02	0.04	0.02
pH	3.1	7.5	7.4	7.3	7.2	7.3	7.6	7.5	7.4	7.6
Mean Cd^{2+} (mg/l)	1.55	0.055	0.025	0.055	0.03	1.21	0.035	0.02	0.045	0.025

Locations: 1,6: End of pipe effluent into Ismalia Canal 2,7: Up-stream plant (150 m from side of Ismailia canal), 3,8: Up-stream plant (150 m from middle of Ismailia canal), 4,9: Down-stream plant (150 m from side of Ismailia canal), 5,10: Down-stream plant (150 m from middle of Ismailia canal).

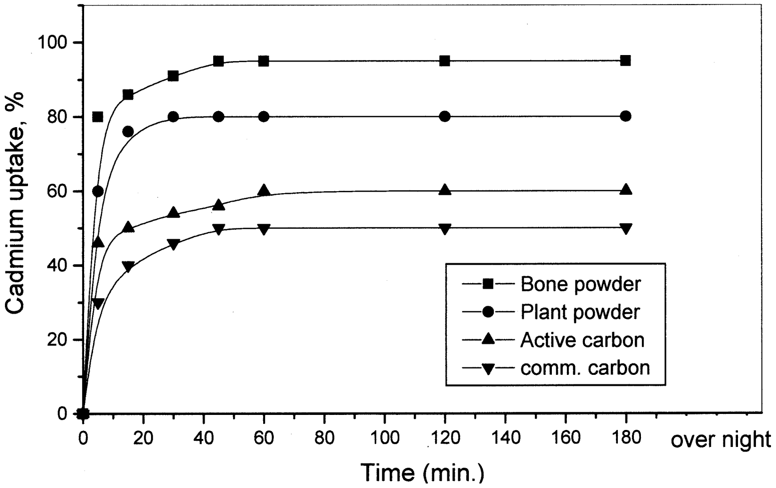

Figure 1. Effect of contact time on uptake percent of cadmium adsorbed from cadmium nitrate solution (3.0 mg/l Pb^{2+}) by bone powder, plant powder, active and commercial carbon at pH = 4.0.

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

The cadmium ion concentration was determined using Unicam model PU 9100 Atomic absorption spectrometry. Test sieve shaker No. 990 and flask shaker, Gallen Kamp with timer No. SGL 700w were used. Muffle furnace, Heareaus type Mir 170E and electrical furnace, type 50 No. 139 were also used.

RESULTS AND DISCUSSION

The cadmium concentrations in industrial waste water samples collected from Abu Zabaal and Ahlia area around Cairo during six months were determined (Table 2). The mean concentration of cadmium varies from 0.02 to 1.55 mg/L in industrial waste water samples during six months (Table 2).

Different weights of powdered animal bone were shaken with 50 ml of cadmium nitrate solution (3.0 mg/L Cd^{2+}) for two hours. The results showed that the

Table 3. Effect of pH and Cd^{2+} concentration on uptake percent of cadmium by bone powder, plant powder, active and commercial carbon, where adsorbent dose = 0.1 g and V/m = 500 ml/g.

Natural materials	conc. of cadmium mg/l	uptake % of Cd					
		pH					
		1	2	3	4	5	6
Bone powder	3.0	0	0	86.9	95.0	95.5	96.0
	10.0	0	0	74.1	90.2	91.0	92.0
	30.0	0	0	63.3	80.5	85.3	86.8
	60.0	0	0	48.8	61.2	65.6	68.8
	160.0	0	0	18.4	23.6	25.1	26.3
Plant powder	3.0	30.7	62.5	73.4	80.0	81.2	81.5
	10.0	20.5	41.8	59.6	74.8	76.1	76.6
	30.0	10.6	32.7	50.0	56.6	59.7	61.2
	60.0	0	5.9	36.6	40.5	43.8	44.6
	160.0	0	5.0	14.2	15.7	16.8	17.3
Active carbon	3.0	27.3	51.7	58.6	60.0	61.3	63.0
	10.0	15.8	32.3	45.8	50.1	56.3	62.0
	30.0	0	4.5	35.6	39.5	41.0	42.0
	60.0	0	3.9	27.5	30.0	33.0	34.6
	160.0	0	1.2	10.5	11.7	12.9	13.2
Commercial carbon	3.0	20.1	40.2	48.3	58.0	61.0	62.0
	10.0	10.8	22.2	37.7	39.8	41.0	42.6
	30.0	7.0	12.6	23.2	29.7	30.5	31.9
	60.0	2.0	4.6	14.9	20.9	21.9	23.6
	160.0	1.9	2.3	6.0	8.0	8.8	9.2

cadmium nitrate solution at pH = 4 had the highest uptake percent at 0.1 g bone powder (95%). The V/m ratio was chosen to be 500 ml/g.

The adsorption process of cadmium ions by bone powder, active carbon, plant powder and commercial carbon was affected by various parameters such as contact time, pH and concentration of cadmium solution.

The effect of contact time on adsorption process of cadmium ions by the different natural materials was studied using cadmium nitrate solution of 3.0 mg/L Cd^{2+} at pH = 4.0 with V/m = 500 ml/g. The relation between the shaking time and the uptake percent of cadmium ions by the different natural materials is shown in (Fig.1). The cadmium percent uptake reaches equilibrium state after 45 minutes, 30 minutes, 60 minutes and 45 minutes for bone powder, Nile rose plant powder, active carbon and commercial carbon, respectively (Fig.1). The percent uptake of cadmium ions is 95% for bone powder, 80% for plant powder, 60% for active carbon and 50% for commercial carbon.

The effect of pH on the uptake percent of cadmium ions adsorbed from different concentrations of cadmium nitrate solutions by bone powder, plant powder, active carbon and commercial carbon is shown in (Table 3). The highest uptake percent of cadmium ions at pH = 6 but the lowest uptake percent of cadmium ions at pH = 1, i.e. the uptake percent of cadmium ions increased by increasing pH value (Table 3). It is apparent that the sequence of cadmium uptake percent (% adsorption) from certain concentration of cadmium nitrate solution at constant pH by the different natural materials is in the order: bone powder > plant powder > active carbon > commercial carbon (Table 3).

The effect of cadmium concentration on uptake percent of cadmium ions on the different adsorbents were studied at constant pH. The results recorded in (Table 3) show also the effect of concentration on the uptake percent of cadmium ions adsorbed from nitrate solution at constant pH by the natural materials. It is apparent that the cadmium uptake percent is increased by decreasing the concentration of cadmium ions (Table 3). The uptake percent of cadmium ions by bone powder at pH 1 and 2 was negligible because the bone powder was completely dissolved at these pH values.

Capacity (mol/g) of cadmium ions which adsorbed from nitrate solution by bone powder, plant powder, active carbon and commercial carbon was calculated (Eq. (1)). The cadmium adsorption capacity (mol/g) of each adsorbent could be determined from adsorption isotherms at pH 3, 4, 5 and 6 (Fig. 2-5). The adsorption isotherms made by using the experimental data in (Table 3), where V/m = 500 ml/g. The capacity of cadmium ions (mol/g) adsorbed from nitrate solution by the different natural materials increased by increasing pH value (Fig.2-5). The sequence of cadmium capacity at constant pH by the different natural materials is in the order: bone powder > Nile rose plant powder > active carbon > commercial carbon.

The synthetic and industrial waste water samples were treated by using the bone powder, plant powder, active carbon and commercial carbon to remove cadmium ions. The treatment process was carried out at contact time (3 hours) and pH = 4. A good results were obtained where cadmium ions was removed (95%) by bone powder, (80%) by Nile rose plant powder, (60%) by active carbon, but only 50% by commercial carbon.

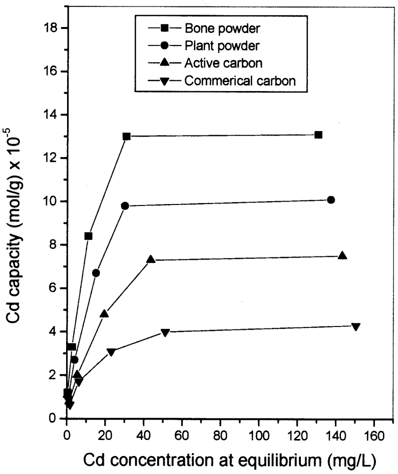

Figure 2. Adsorption isotherm at pH = 3, V/m = 500 ml/g

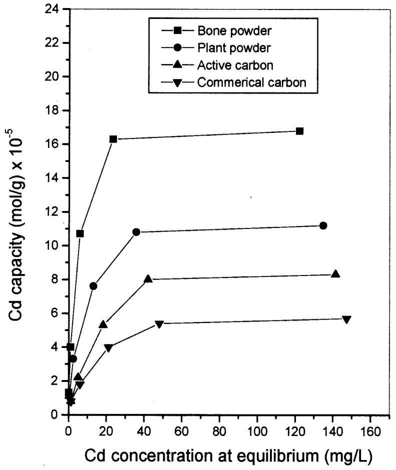

Figure 3. Adsorption isotherm at pH = 4, V/m = 500 ml/g.

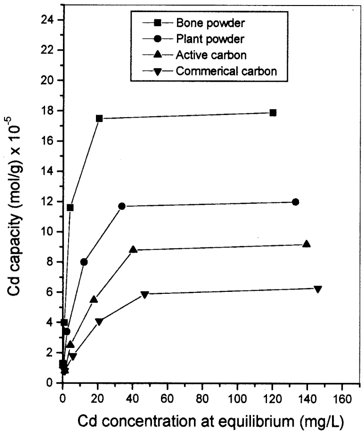

Figure 4. Adsorption isotherm at pH = 5, V/m = 500 ml/g.

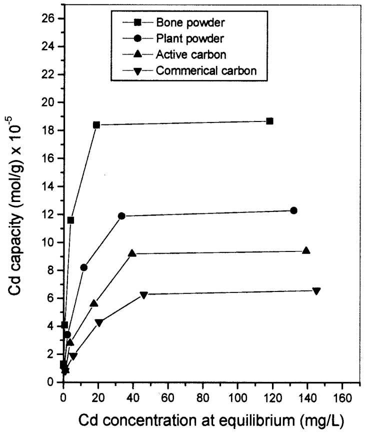

Figure 5. Adsorption isotherm at pH = 6, V/m = 500 ml/g

REFERENCES

Fergusson JE (1990) The heavy elements, chemistry, environment impact and health effects. Pergamon Press, New York

Cooke JA, Andrewa SM, Johnson MS (1990) The accumulation of lead, zinc, cadmium and fluoride in the wood mouse. Water Air Soil Pollut 51: 55-63.

Wilson MW, Edyvean RG (1994) Institution of Chemical Engineers, Symposium Series, Publ by Inst of Chemical Engineers, Rugby, England: 89-91.

Snowden MJ, Thomass D, Vincent B (1993) Use of colloidal microgels for the absorption of heavy metal and other ions from aqueous solution. Analyst 118:11: 1367-1369.

Denizli A, Tanyolac D, Salih B, Ozdural A. (1998) Cibacron Blue F_3 GA-attached polyvinylbutyral microbeads as novel magnetic sorbents for removal of copper (II), cadmium (II) and lead (II) ions. J Chromatog. A 793:1: 47-56.

Viraraghavan T, Rao GAK (1993) Adsorption of cadmium and chromium from waste water by Peat Proc Ind Waste Conf, 47th: 677-689.

Ferro-Garcia MA, Rivera-Utrilla J, Rodriguez-Gordillo J, Bautista-Toledo I (1988) Adsorption of zinc, cadmium and copper on activated carbons obtained from agricultural by-products. Carbon 26:3:363-373.

Haklits I, Nagy A, Kiss Lu, Simon P. Nagy O (1988) Reactive Polymers, Ion Exchange, Sorbents V7.

Vecchio A, Finoli C, Di Simine D, Andreoni V (1998). Heavy metal biosorption by bacterial cells. Fresenius J Anal Chemistry 361:4:338-342.

Faghihian H, Ghannadi-Margeh M, Kazemian H (1999) The use of clinoptilolite and its sodium form for removal of radio active cesium and strontium from nuclear waste water and lead (II), nickel (II), cadmium (II), barium (II) from municipal waste water. Appl Rad Isotopes 50:4:655-660.

Hilmi A, Luong JHT, Nguyen AL (1990) Utilization of TiO_2 deposited on glass plates for removal of metals from aqueous wastes. Chemosphere 38:4:865-874.

Park KH, Park MA, Jang H, Kim EK, Kim YH (1999) Removal of heavy metals, cadmium (II) and lead (II) ions in waster by sargassum horneri. Anal Sci Technol 12:3:196-202.

Liu R, Tang HX, Zhang B (1999) Removal of copper (II), zinc (II), cadmium (II) and mercury (II) from waste water by poly (acrylamino-phosphonic)-type chelating fiber. Chemosphere 38:13:3169-3179.

Murata K (1998) Accumulation of heavy metals using plants. Bunseki 5:364-365.

Namasivayam C, Ranganathan K (1995) Removal of Cd (II) from waste water by adsorption on waste Fe III/Cr III hydroxide. Water Res 29:7:1737-1744.

Reed BE, Arunachalam S, Thomas B (1994) Removal of lead and cadmium from aqueous streams using granular activated carbon columns. Environ Prog 13:1:60-64.