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Removal of Heavy Metals from Industrial Wastewater by Adsorption using Local Bentonite Clay and Roasted Date Pits in Saudi Arabia

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Abstract: The main objective of this study was to remove heavy metals such as Cu, Co, Zn, Pb, As, Cd and Cr from industrial wastewater by adsorption using local bentonite clay and roasted date pits. The concentration level of various heavy metals in the industrial wastewater of Riyadh City was above the permissible recommended limits. The minimum removal efficiency of the adsorption of metal ions on bentonite clay and roasted date pits was 97%. Also, the concentration level of hazardous heavy metals in the treated water was within the permissible limits for crop production. The study showed good potential for removing heavy metal ions from industrial wastewater by adsorption using local bentonite clay and roasted date pits.

Key words: Heavy metals, local bentonite clay, roasted date pits, adsorption, removal efficiency, wastewater

INTRODUCTION

Recent industrial revolution in Saudi Arabia has enormously increased the industrial wastewater production which is highly contaminated with various types of heavy metals. Heavy metal contamination exists in waste effluents of different factories such as metal plating, mining operations, tanneries, chloralkali, ceramic painting, manufacturing paints, catalysts, alloy industries, wire conducting, galvanizing iron, polymer stabilizer, storage batteries manufacturing, semiconductors, pesticides, wood preservation and pigments factories (Kadirvelu, 1998; Brezonik, 1974; Patterson and Passino, 1987; Pescod, 1992). Heavy metals have been acknowledged as potential health and environmentally hazardous materials. Many studies have shown that these metals are toxic even at low concentrations. The presence of these toxic metals can cause, in turn, accumulative poisoning, destroy liver, cancer and brain damage when found above the tolerance level (Pescod, 1992; Abdulkarim and Abu-Al-Rub, 2004).

Meena *et al.* (2005) reported that the removal of Cd (II), Pb (II), Hg (II), Cu (II), Ni (II), Mn (II) and Zn (II) by carbon aerogel is concentration, pH, contact time, adsorbent dose and temperature dependent. The adsorption isotherm studies clearly indicated that the adsorptive behavior of metal ions on carbon aerogel satisfies not only the Langmuir assumptions but also the Freundlich assumptions, i.e., multilayer formation on the surface of the adsorbent with an exponential distribution of site energy. The results indicate the potential application of this method for effluent treatment in industries and also provide strong evidence to support the adsorption mechanism proposed. Kadirvelu *et al.* (2001) studied the adsorption of toxic heavy metals from industrial wastewater onto coirpith carbon. The percent adsorption increased with increase in pH from 2 to 6 and remained constant up to 10. As coirpith is discarded as waste from coir processing industries, the resulting carbon is

expected to be an economical product for the removal of toxic heavy metals from industrial wastewater. Erdem *et al.* (2004) studied the adsorption behavior of natural (clinoptilolite) zeolites with respect to Co^{2+} , Cu^{2+} , Zn^{2+} and Mn^{2+} in order to consider its application to purity metal finishing wastewater. They found that the adsorption phenomena depends on charge density and hydrated ion diameter. According to the equilibrium studies, the selectivity sequence can be given as $\text{Co}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Mn}^{2+}$. These results show that natural zeolites hold great potential to remove cationic heavy metal species from industrial wastewater.

Presently, many techniques such as chemical precipitation, extraction, reverse osmosis and adsorption are being used for the removal of heavy metals from wastewater. Adsorption technique is an economical process especially using low cost adsorbents. Many investigators have evaluated natural clay and the date pits as a low-cost adsorbents due to their adsorption properties for heavy metals including cobalt, lead, cadmium, zinc and chromium ions (Orumwense, 1996; Yadava *et al.*, 1991; Pradas *et al.*, 1994; Singh *et al.*, 1992; Banat *et al.*, 2002, 2003; Abdulkarim and Abu-Al-Rub, 2004; Ceylan *et al.*, 2005; El-Hendawy, 2009; Al-Jlil and Alsewailem, 2009).

Extensive review of literature indicated that a very little has been accomplished on the contamination levels of various heavy metals in the industrial wastewater in Riyadh, Saudi Arabia and their removal using local bentonite clay and roasted date pits. It was, therefore, imperative to study the concentration level of different types of heavy metals in the industrial wastewater, possible sources of these heavy metals and to remove the various heavy metal ions by adsorption from the industrial wastewater by using local bentonite clay and the roasted date pits as adsorbents.

MATERIALS AND METHODS

Collection of Adsorbents

Two locally available adsorbents namely bentonite clay and roasted date pits were collected from Jeddah and Qassim City, respectively. The date pits were dried, roasted in an oven at 130°C for 4 h and ground in a Willy Mill to obtain powder for experimentation. The two adsorbents were analyzed by XRF and surface area analyzer. The chemical analysis of the two adsorbents by XRF is shown in Table 1 and by surface area analyzer is shown in Table 2.

Table 1: Mean chemical analysis of local bentonite clay and roasted date pits by XRF

Elements	Composition (% on weight basis)	
	Bentonite clay	Roasted date pits
Si	58.00	-
Al	20.00	-
Fe	5.17	-
Ca	2.00	28.02
K	1.00	56.77
S	-	11.52
Traces of other elements (Mg, Ti, Mn, etc.)	13.83	3.69

Table 2: Mean surface area and pore characteristics of bentonite clay and roasted date pits

Elements	Values	
	Bentonite clay	Roasted date pits
BJH Adsorption cumulative surface area of pores between 17.000 Å and 3000.000 Å diameter ($\text{m}^2 \text{g}^{-1}$)	47.740	0.151
BJH Adsorption average pore diameter (Å)	95.650	349.165
BJH Adsorption cumulative volume of pores between 17.000 Å and 3000.000 Å diameter ($\text{cm}^3 \text{g}^{-1}$)	0.114157	0.001320

Table 3: Mean concentration of heavy metals industrial wastewater in Riyadh City

Sample location	Sample No.	Concentration (mg L ⁻¹)						
		Cu	Co	Zn	Pb	As	Cd	Cr
Area-1	1	ND	2.33	0.65	ND	ND	0.26	1.95
	2	ND	2.61	0.57	0.89	ND	0.29	1.68
	3	ND	2.91	0.71	ND	ND	0.29	1.71
	4	ND	2.81	0.60	1.02	ND	0.35	3.50
Area-2	1	3.41	3.24	1.79	1.30	ND	8.94	1.97
	2	ND	1.50	0.35	0.36	1.11	0.35	1.64
	3	ND	3.71	0.62	ND	ND	ND	1.67
Area-3	1	ND	3.54	2.04	ND	ND	2.22	1.92
	2	ND	2.04	0.87	2.07	0.21	0.29	1.76
	3	ND	3.14	3.90	ND	2.1	6.56	3.48

ND: Not detected

The adsorbates are a mixture of different heavy metal ions such as copper (Cu), cobalt (Co), zinc (Zn), lead (Pb), arsenic (As), cadmium (Cd) and chromium (Cr) in the industrial wastewater of Riyadh City industrial areas designated as Area-1, Area-2 and Area-3 (Table 3).

Equilibrium Experiments

The Equilibrium state for bentonite clay and the roasted date pits was obtained by using a constant mass of adsorbent (3 g) in 50 mL of industrial wastewater sample in glass bottles by keeping it on a constant agitation shaker. The particle size of the adsorbent was 0.25 mm to determine the maximum adsorption of different heavy metal ions. The temperature was maintained at 25°C and the pH of the mixture was 7.67. Initially, it was observed that the adsorbed metal ions and adsorbent system reached to equilibrium after 1 h. This phenomena was based on the run experiment at different time intervals which showed that the adsorption process attained state of equilibrium after 1 h. However, the experimental process was kept for 3 h to ensure that the adsorption process obtained complete equilibrium. Later on, the samples were filtered using filter papers and the absorbance was measured using Atomic Absorption Spectroscopy (AAS). Then, the absorbance of all the samples was converted to concentration by using the calibration curve for each metal ion. The removal efficiency of different metal ions adsorption on bentonite clay and the roasted date pits was calculated by the following equation:

$$\text{Treatment efficiency (\%)} = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (1)$$

where, C_0 is the initial concentration of metal ions (mg L⁻¹) and C_e is the equilibrium concentration of the metal ions (mg L⁻¹).

RESULTS AND DISCUSSION

The concentration level of different heavy metals in the industrial wastewater in Riyadh city was above the permissible limit (Table 3) as compared to the recommended maximum concentration level of trace elements for crop production (Table 4). For example, the Cd concentration was 8.94 mg L⁻¹ which is much higher than the permissible limits for safe crop irrigation. It is well known that the Cd concentration above the permissible limits is toxic to beans and beets crops. In addition, the higher Cd concentration causes health hazards for human being such as high blood pressure, renal degradation, skeletal deformity, muscular cramps and kidney damage (Banat *et al.*, 2003).

The concentration level of heavy metals in the treated industrial wastewater was less than the permissible limits for crop production (Table 5-11) except the Co ion where the concentration of this ion after treatment by roasted date pits was 0.1 mg L⁻¹ and by bentonite clay was 0.09 mg L⁻¹ which was much higher (two times) than the permissible limits for crop production. However, these values are equal to the permissible limits for tomato plants (0.1 mg L⁻¹).

For complete removal of Co ion, the two batch adsorbers were used in series to adsorb the Co ion with 3 g adsorbent mass in each adsorber where the adsorbent and adsorbate mixture was kept together on an agitator for 3 h in the first adsorber followed by separation of solution from the adsorbent by filtration. Then this solution was put into the second adsorber with the fresh adsorbent (3 g in 50 mL of filtrate from first adsorber), mixed and kept together on an agitator for 3 h. The analysis of filtrate solution from the second adsorber

Table 4: Comparison of heavy metals concentration in the treated wastewater for crop production

Elements	Recommended maximum concentration (mg L ⁻¹)*	Maximum concentration after treatment by the adsorbents (ppm)
Cu	0.20	0.00
Co	0.05 (and 0.1 for tomato plants)	0.10
Zn	2.00	0.00
Pb	5.00	0.02
As	0.10	0.00
Cd	0.01	0.008
Cr	0.10	0.10

*Source: Pescod (1992)

Table 5: Lead (Pb) ion removal by using bentonite clay and roasted date pits

		Lead removal (ppm)					
		By	Bentonite	Clay	By Roasted	Date	Pits
Sampling location	Sample No.	Concentration before treatment	Concentration after treatment	Treatment efficiency %	Concentration before treatment	Concentration after treatment	Treatment efficiency %
Area-1	1	ND			ND		
	2	0.89	0	100	0.89	0	100
	3	ND			ND		
	4	1.02	0	100	1.02	0	100
Area-2	1	1.30	0	100	1.30	0	100
	2	0.36	0	100	0.36	0	100
	3	ND			ND		
Area-3	1	ND			ND		
	2	2.07	0.02	99	2.07	0	100
	3	ND			ND		

ND: Not deleted, Condition: Mass = 3 g, Solution volume = 50 mL, T = 25°C, pH = 7.67

Table 6: Copper (Cu) ion removal by using bentonite clay and roasted date pits

		Copper removal (ppm)					
		By	Bentonite	Clay	By Roasted	Date	Pits
Sampling location	Sample No.	Concentration before treatment	Concentration after treatment	Treatment efficiency %	Concentration before treatment	Concentration after treatment	Treatment efficiency %
Area-1	1	ND			ND		
	2	ND			ND		
	3	ND			ND		
	4	ND			ND		
Area-2	1	3.41	0	100	3.41	0	100
	2	ND			ND		
	3	ND			ND		
Area-3	1	ND			ND		
	2	ND			ND		
	3	ND			ND		

ND: Not deleted, Conditions: Mass = 3 g, solution volume = 50 mL, T=25°C, pH = 7.67

Table 7: Arsenic (As) ion removal by using bentonite clay and roasted date pits

		Arsenic removal (ppm)					
		By	Bentonite	Clay	By Roasted	Date	Pits
Sampling location	Sample No.	Concentration before treatment	Concentration after treatment	Treatment efficiency %	Concentration before treatment	Concentration after treatment	Treatment efficiency %
Area-1	1	ND			ND		
	2	ND			ND		
	3	ND			ND		
	4	ND			ND		
Area-2	1	ND			ND		
	2	1.11	0	100	1.11	0	100
	3	ND			ND		
Area-3	1	ND			ND		
	2	0.21	0	100	0.21	0	100
	3	2.10	0	100	2.10	0	100

ND: Not deleted, Conditions: Mass = 3 g, Solution volume = 50 mL, T = 25°C, pH = 7.67

Table 8: Chromium (Cr) ion removal by using bentonite clay and roasted date pits

		Chromium removal (ppm)					
		By	Bentonite	Clay	By Roasted	Date	Pits
Sampling location	Sample No.	Concentration before treatment	Concentration after treatment	Treatment efficiency %	Concentration before treatment	Concentration after treatment	Treatment efficiency %
Area-1	1	1.95	0.003	99.85	1.95	0.0013	99.93
	2	1.68	0.00	100.00	1.68	0.00	100.00
	3	1.71	0.00	100.00	1.71	0.00	100.00
	4	3.50	0.10	97.14	3.50	0.091	97.40
Area-2	1	1.97	0.004	99.79	1.97	0.002	99.89
	2	1.64	0.00	100.00	1.64	0.00	100.00
	3	1.67	0.00	100.00	1.67	0.00	100.00
Area-3	1	1.92	0.002	99.89	1.92	0.001	99.95
	2	1.76	0.00	100.00	1.76	0.00	100.00
	3	3.48	0.092	97.36	3.48	0.089	97.44

ND: Not deleted Conditions: Mass = 3 g, solution volume = 50 mL, T = 25°C, pH = 7.67

Table 9: Cadmium (Cd) ion removal by using bentonite clay and roasted date pits

		Cadmium removal (ppm)					
		By	Bentonite	Clay	By Roasted	Date	Pits
Sampling location	Sample No.	Concentration before treatment	Concentration after treatment	Treatment efficiency %	Concentration before treatment	Concentration after treatment	Treatment efficiency %
Area-1	1	0.26	0.00	100.00	0.26	0.00	100.00
	2	0.29	0.00	100.00	0.29	0.00	100.00
	3	0.29	0.00	100.00	0.29	0.00	100.00
	4	0.35	0.00	100.00	0.35	0.00	100.00
Area-2	1	8.94	0.008	99.91	8.94	0.004	99.96
	2	0.35	0.00	100.00	0.35	0.00	100.00
	3	ND			ND		
Area-3	1	2.22	0.00	100.00	2.22	0.00	100.00
	2	0.29	0.00	100.00	0.29	0.00	100.00
	3	6.56	0.007	99.89	6.56	0.007	99.89

ND: Not deleted, Conditions: Mass = 3 g, solution volume = 50 mL, T = 25°C, pH = 7.67

was free of Co ion after treatment. The experimental setup is shown in Fig. 1. The concentration of Co ion by treatment with the second adsorber was zero (0 mg L^{-1}) and the treatment efficiency was 100% both for the bentonite clay and the roasted date pits.

The minimum removal efficiency of heavy metal ions by adsorption by bentonite clay and the roasted date pits was 97% (Table 5-11). The adsorption of metal ions on the bentonite clay is the result of the electrostatic attraction between the negative sites of clay

Table 10: Zinc (Zn) ion removal by using bentonite clay and roasted date pits

		Zinc removal (ppm)					
		By	Bentonite	Clay	By Roasted	Date	Pits
Sampling location	Sample No.	Concentration before treatment	Concentration after treatment	Treatment efficiency %	Concentration before treatment	Concentration after treatment	Treatment efficiency %
Area-1	1	0.65	0	100	0.65	0	100
	2	0.57	0	100	0.57	0	100
	3	0.71	0	100	0.71	0	100
	4	0.60	0	100	0.60	0	100
Area-2	1	1.79	0	100	1.79	0	100
	2	0.35	0	100	0.35	0	100
	3	0.62	0	100	0.62	0	100
Area-3	1	2.04	0	100	2.04	0	100
	2	0.87	0	100	0.87	0	100
	3	3.90	0	100	3.90	0	100

ND: Not deleted, Conditions: Mass = 3 gm, solution volume= 50 mL, T=25°C, pH = 7.67

Table 11: Cobalt (Co) ion removal by using bentonite clay and roasted date pits

		Cobalt removal (ppm)					
		By	Bentonite	Clay	By Roasted	Date	Pits
Sampling location	Sample No.	Concentration before treatment	Concentration after treatment	Treatment efficiency %	Concentration before treatment	Concentration after treatment	Treatment efficiency %
Area-1	1	2.33	0.005	99.79	2.33	0.008	99.66
	2	2.61	0.007	99.73	2.61	0.009	99.65
	3	2.91	0.01	99.66	2.91	0.03	98.97
	4	2.81	0.009	99.68	2.81	0.01	99.64
Area-2	1	3.24	0.078	97.59	3.24	0.082	97.47
	2	1.50	0.00	100.00	1.50	0.00	100.00
	3	3.71	0.09	97.57	3.71	0.10	97.30
Area-3	1	3.54	0.088	97.51	3.54	0.093	97.37
	2	2.04	0.003	98.38	2.04	0.006	99.71
	3	3.14	0.072	97.71	3.14	0.097	96.91

ND: Not deleted, Conditions: Mass = 3 g, solution volume = 50 mL, T = 25°C, pH = 7.67

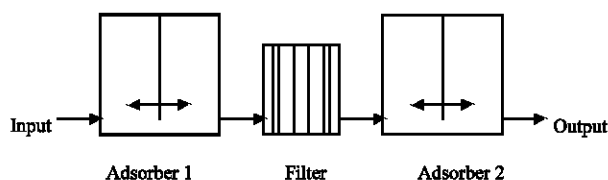


Fig. 1: Schematic diagram of two batch adsorbers in series

and the positive metal ions. The number of negative sites on the bentonite clay surface is mainly due to presence of silica (Elliott and Huang, 1981). Similar results were reported by Erdem *et al.* (2004), who studied the adsorption behavior of natural (clinoptilolite) zeolites with respect to CO^{2+} , Cu^{2+} , Zn^{2+} and Mn^{2+} in order to consider its application to purity metal finishing wastewater. Their results showed that natural zeolites hold great potential to remove cationic heavy metal species from industrial wastewater. In the case of roasted date pits, where the date pits have chemical functional groups such as carboxylic (COOH) groups. Because pH of solution affects the charge on the functional groups. Functional groups such as carboxylate are protonated at low pH values and are thus repulsive towards metal ions (Banat *et al.*, 2003). Therefore, with an increase in pH of solution, deprotonation of the functional groups might have occurred which allowed metal ion binding. Because, the metal ions has attraction with the negative charge on the functional groups of the date pits, such

as carboxylate with a pH value of 7.67 for these samples. It was, therefore, observed that both the bentonite clay and the roasted date pits have good potential to remove these heavy metal ions from the industrial wastewater. The study results agree with those of Kadirvelu *et al.* (2001), who studied the adsorption of toxic heavy metals from industrial wastewater onto coirpith carbon. They reported that the percent adsorption increased with increase in pH from 2 to 6 and remained constant up to 10.

CONCLUSIONS

The heavy metals concentration levels in the industrial wastewater in Riyadh city were above the permissible concentrations levels. The heavy metals concentrations level after treatment was within the permissible limits for crop production. In addition, the minimum removal efficiency of metal ions by adsorption using bentonite clay and the roasted date pits was 97%. The experiment showed an excellent potential of these local adsorbents for removing heavy metals from industrial wastewater in Riyadh, Saudi Arabia. Overall, the adsorption of metal ions on the negative sites of the bentonite and the functional groups of the date pits could be attributed to the electrostatic attraction between the negative charge of the adsorbents and the positive charge on metal ions.

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