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Wood Ash Effectiveness in Cadmium Removal from Paint Industrial Effluent

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Abstract: This study was conducted in order to present more information and evidence to authorities to make them capable of making better decisions. Survey was done in batch conditions on wastewater of Binalood paint industries using different amount of wood ash as adsorbent and in variable pH from acidic to alkaline and different contact times. Cadmium measurement in samples was done with atomic absorption equipment and test methods were adapted from standard methods for the examination of water and wastewater. This investigation showed that wood ash has high effectiveness in cadmium removal and this effectiveness raises with the increase of the amount of adsorbent substance to 100 g L^{-1} wastewater, where adsorption rate reaches 97-98% in acidic, neutral and alkaline pH. Data concerning adsorption isotherms indicates that, adsorption process follows Freundlich model. Concerning the results of this research and other investigations, the use of fly ash and wood ash is recommended as a low cost and available material to remove cadmium from municipal and industrial wastewater.

Key words: Wood ash, paint industries effluent, cadmium removals, adsorption

INTRODUCTION

Disposal of industrial wastewater containing heavy metals in the environment has caused several problems (Gabriel, 1979). The discharge of low amounts of heavy metals in the environment will result in severe and bad effects on the vital ecosystems (Mahvi *et al.,* 2002; Manshouri *et al.,* 1999). These metals are highly soluble in water and cause pollution of surface and ground water resources and finally soil pollution (Ahmadkhan, 2001). Concerning the cumulative characteristics of heavy metals and their ability to enter into the food chain, these materials will gradually reach to the head of the pyramid and will cause different hazards (Tabatabaei et al., 2001; Masoudinegad and Rezazadeh, 2001; Mosaferi and Mahvi, 2001). The use of polluted water containing these metals for agricultural irrigation, vegetable growing, aquatic life and finally the use of these products by animal and human will provide an affliction field to known or unknown diseases (Pourmoghaddas and Yazdankhah, 2003; Tam and Vong, 1994). Between different industries discharging wastewater containing heavy metals, paint industries can be mentioned. Generally paint is defined as a cover used on the surface or a context for decoration, protection or both of them (Virvaghava *et al.,* 1991). Paint components are pigments, solvents, blotters and auxiliary additives (Abraham, 1982). Heavy metals are mainly used as a pigment and blotter in the paints (Clark, 1972). Presence of heavy metals in the paints is directly and indirectly hazardous for human and other beings (Nergo 1993). Exposure to this type of paints and the contamination of hand, water and food by it will cause the direct transmission of these pollutants. Also the discharge of wastewater from these industries to water bodies and soil resources will lead to the indirect transmission of pollution to human (Otte, 1993).

Hazards from the presence of these metals in the environment, has inevitably brought the attention to different heavy metals removal methods. Among heavy metals removal methods, chemical precipitation, membrane filtration (reverse osmosis and electrodialysis), electrolytic processes, adsorption and biological sorption can be mentioned (Ganji *et al.,* 2005; Dastjerdi *et al.,* 2003). Most of these methods have high capital, operation and maintenance costs. Despite of the effective use of activated carbon in heavy metals adsorption from wastewater, its application has been limited by its high costs (Clark, 1972). In recent decades several surveys such as application of oat essence in heavy metals removal (Masoudinegad and Rezazadeh, 2001), application of natural fibers in cadmium removal from industrial wastewater (Mahvi *et al.,* 2002), heavy metals

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removal by artificial wetlandsn (Manshouri *et al.*, 1999), cadmium and chromium adsorption from wastewater by fly ash (Clark, 1972) and other studies were conducted to innovate and test low cost and efficient adsorbents. One of these materials was wood ash which its utilization is relatively cheap and feasible in Iran. Therefore this research was conducted to provide recommendations and application methods for heavy metals removal such as cadmium from paint industries wastewater and other industries using wood ash.

MATERIALS AND METHODS

The effluent of Binalood paint industries in the Kerman City of Iran was selected as a sample during 2003-2004 in 6 month period. This industry produces 30 tons of paint products per month. The estimation of monthly discharged wastewater from this industry is about 200 m^3, which is discharged in the environment without any treatment unit. Wastewater sample used in this research has been the raw wastewater from the equalization tank of the industry. Collected samples after pH and temperature measurement, were transported to the laboratory immediately. After one hour of settling, supernatant was removed and 1 M HCl was added to samples until pH decreased to less than 2, then the samples were placed at 4°C. These samples were used to measure the Cd adsorption rate by the selected adsorbent (wood ash). In this investigation wood ash was used after being sieved with 0.9 µ Sieve. From each prepared sample, three samples with 100 cc volume were selected separately and them with the addition of standard HCl and NaOH, the pH of samples were adjusted to 2, 7 and 10, respectively. At first, cadmium concentration in each sample was determined before adsorption process and the pH was defined. Then with the addition of adsorbent (wood ash) at the rate of 15, 20, 30, 40, 50, 60, 70, 80, 90 and 100 g L^{-1} to wastewater in each vessel, samples were mixed with a mechanical mixer to 100 rpm speed, centrifuged and filtered and cadmium measurement was done for the effluent and the settled sediments. Sediments were rinsed and filtered with deionized water and were used in calculations after measurement.

Cadmium measurement was done in accordance with the standard methods for the examination of water and wastewater (Eaton *et al.*, 1998). For each sample, one blank sample was obtained without wood ash for controlling the possibility of cadmium adsorption on the walls of glass vessel. For the control of any cadmium leaching during the test period, a sample was prepared by the addition of wood ash to 500 cc of deionized water as a blank sample. Cadmium removal by wood ash was repeated for industrial wastewater using batch system without acid addition. In addition the amount of cadmium concentration in the wood ash removed by filter paper after rinsing with deionized water, was determined by sample solubilizing (use of heat) and then by chemical sample decomposition. For the determination of adsorption isotherm models and equations in 25°C±1 and pH=7 and fixed concentration 2 mg L^{-1} of cadmium was used for different amounts of adsorbent: 10, 20, 30, 40, 50, 60, 70, 80, 90, 100 g and 3 h contact time. In this study, some results obtained from similar research conducted by Virvaghavan and Ganesh in Regina University, were used. On the basis of mentioned research, the reaction of fly ash adsorption was reached to the equilibrium state after 3 h and therefore surveys in this research were conducted in 1 to 5 h contact time (Clark, 1972).

RESULTS AND DISCUSSION

Results in Table 1 are the mean values for ten samples of raw wastewater before one hour settling and after transmission to the laboratory. The results showed that Pb, Cd and Co concentration were 5.87, 1.98 and 1.05, respectively which indicate that the concentration of this heavy metals are more than their MCL_S for wastewater used in agricultural irrigation (0.5 mg L^{-1}) and is propounded as most important environmental problem concerning this wastewater and must be appointed as specific care (IISIR, 1999).

As the Table 2 shows the removal of Cd by different amounts of adsorbent in various pH indicated that, there was a significant differences between adsorption percent that was from 20 to 98.3%. Results showed that amount of adsorbent was more important and most adsorption was achieved in the 100 g L^{-1} and pH equal to 2.

Also for determining the required contact time, the amount of cadmium adsorption was measured at different contact times with 100 g L^{-1} of adsorbent in 25°C±1. Table 3 shows that adsorption of Cd was 98.2 to 99.3% in the range of 1 to 5 h contact time, respectively.

Table 1: Wastewater characteristics of Binalood paint industries

Parameters	Mean	Range	SD
pH	6.60	2.00-9.50	2.36
BOD (mg L^{-1})	261.50	220-280	20.36
COD (mg L^{-1})	635.70	535-690	59.47
TSS (mg L^{-1})	105.70	75-130	19.57
TDS (mg L^{-1})	3550	2740-4050	513.23
EC (µmhos cm^{-1})	1793	1300-2100	270.60
Pb (mg L^{-1})	5.87	2.00-7.50	1.94
Co (mg L^{-1})	1.05	0.50-1.60	0.38
Cd (mg L^{-1})	1.98	0.80-2.80	0.58
Turbidity NTU	535.50	350-620	74.90

Table 2: Cd adsorption of raw wastewater from Binalood paint industries by different amount of wood ash in various pH and in 25°C ±1

	Cd concentration in raw wastewater before the contact to wood ash (mg L^{-1}) pH			Cd concentration in effluent (filtered and rinsed water) (mg L^{-1}) pH			Adsorbed Cd by wood ash(mg L^{-1}) pH			Adsorption percent by adsorbent (mg L^{-1}) pH		
wood ash added (g L^{-1})	2	7	10	2	7	10	2	7	10	2	7	10
10	3	2	1.5	2.1	1.5	1.3	0.9	0.5	0.2	33	30	20
20	3	2	1.5	2.7	1.4	1.1	1.3	0.6	0.4	50	40	33.3
30	3	2	1.5	1.5	1.3	1	1.5	0.7	0.5	56.6	50	46.6
40	3	2	1.5	1.3	1	0.6	1.7	1	0.9	63.3	60	66.6
50	3	2	1.5	1	0.7	0.4	2	1.3	1.1	70	70	80
60	3	2	1.5	0.9	0.7	0.2	2.1	1.3	1.3	76.6	70	93.3
70	3	2	1.5	0.5	0.4	0.1	2.5	1.6	1.4	90	90	94
80	3	2	1.5	0.3	0.2	0.08	2.7	1.8	1.42	96.6	95	95.3
90	3	2	1.5	0.1	0.1	0.07	2.9	1.9	1.43	97	95.5	96.6
100	3	2	1.5	0.07	0.07	0.05	2.93	1.93	1.45	98.3	97.5	97.3

Table 3: Percentage of Cd adsorption by wood ash in acidic condition at different contact times for 100 g L^{-1} of adsorbent in raw wastewater (t=25°C ±1)

Contact time (h)	Cd concentration in raw wastewater (mg L^{-1})	Cd concentration in effluent after contact with adsorbent (mg L^{-1})	Adsorbed Cd by wood ash (mg L^{-1})	Adsorption %
1	3	0.05	2.95	98.2
2	3	0.04	2.96	98.6
3	3	0.03	2.97	99.0
4	3	0.02	2.98	99.3
5	3	0.02	2.98	99.3

Table 4: Adsorption isotherm related data in 25°C±1

Cd concentration in raw wastewater, C_o(mg L^{-1})	Cd concentration in filtered) effluent, C_e(mg $L^{-1)}$)	Aborted Cd, X (mg)	Wood ash, (g)	x/m	log x/m	Log C_e	$1/x/m$	$1/C_e$
2.000	1.500	0.500	10	0.050	-1.301	0.176	20.000	0.667
2.000	1.400	0.600	20	0.030	-1.523	0.146	33.333	0.714
2.000	1.300	0.700	30	0.023	-1.632	0.114	42857	0.769
2.000	1.000	1.000	40	0.025	-1.602	0.000	40.000	1.000
2.000	0.700	1.300	50	0.026	-1.585	-0.155	38.462	1.429
2.000	0.700	1.300	60	0.022	-1.664	-0.155	46.154	1.429
2.000	0.400	1.600	70	0.023	-1.641	-0.398	43.750	2.500
2.000	0.200	1.800	80	0.023	-1.648	-0.699	44.444	5.000
2.000	0.100	1.900	90	0.021	-1.675	-1.000	47.368	10.000
2.000	0.070	1.930	900	0.019	-1.714	-1.155	51.813	14.286

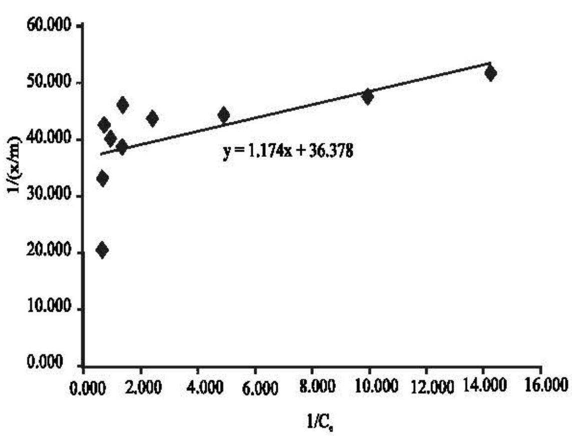

Fig. 1: Variation of longmuir equation parameters for Cd adsorption by wood ash in 25°C ±1 an pH =7

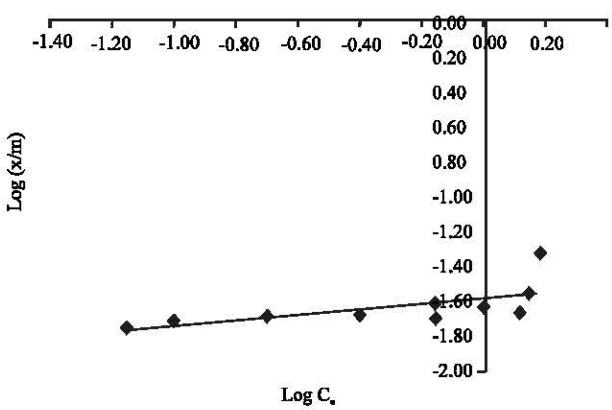

Fig. 2: Variation of freundich equation parameters for Cd adsorption by wood ash in 25°C ±1 an pH =7

The results of this research concerning the adsorption state with different amounts of adsorbent in different pH, showed that at 10 g L^{-1} of wood ash in different pH, adsorption rate was about 20% and with the gradual increase of the adsorbent amount, adsorption rate has been increased and with 70 g L^{-1} of adsorbent matter, adsorption rate reached about 90% and finally with 100 g L^{-1} of adsorbent, this rate reached its maximum level of 97-98% (Fig. 1).

Investigation about pH effect on the adsorption rate of cadmium by wood ash as shown in Table 2 showed that adsorption action is done at extent range of pH, from 2 to 10 nicely and that pH variations have relatively low effect on the adsorption rate. If pH is lowered, the increase in adsorption rate was small and not considerable. Considering these results and the limitations concerning the discharge of acidic and alkaline effluents to the environment, neutral pH is logical and acceptable in the removal process.

Whereas industrial wastewaters have an extent range of pH from acidic to alkaline and municipal wastewater has a neutral pH, therefore mentioned method is applicable for the removal of cadmium from both wastewaters. With regard to the high efficiency of cadmium removal by wood ash, cadmium concentration could be reduced to acceptable level for effluent reuse in irrigation (IISIR, 1999).

Results from Table 1 and Fig. 1 showed that the reactions reached equilibrium state in 1-2 h after which no considerable variation in adsorption rate was observed. For example by use of 100 g L^{-1} wood ash in acidic pH, during 1 h contact time, 98.3% of cadmium adsorption was accomplished while adsorption rate is reached 98.6% during 5 h contact time. Therefore concerning technical and economical aspects, 1 h contact time is recommended for Cd removal from wastewater by wood ash adsorption.

Results of the cadmium adsorption tests with different amounts of wood ash for the adsorption isotherm models are shown in Table 4, Fig. 1 and 2.

Figure 1 and 2, drawn based on the adsorption isotherm data, showed that adsorption process by wood ash is followed by Freundlich isotherm and this model explained better the adsorption data than other isotherm equations.

RECOMMENDATIONS

To pay attention to investigations, following recommendations are presented:

- From environmental point of view, principal problem of Binalood paint industries wastewater and similar industries is the presence of heavy metals such as Cd, Pb and Co these industries should be plan and design to remove it.
- Wood ash as an available and low cost matter in Iran can be considered as an alternative in the field of Cd removal from this type of wastewater and similar wastewater.
- Using 70-100 g L^{-1} of wood ash leads to 90-98% of cadmium removal efficiency, so use of wood ash is not recommended for lower than 70 g L^{-1} for this purpose.
- For leaching equilibrium state, contact time should be about 1 to 2 h.
- Wood ash have been proved to be effective for acidic to alkaline pH, therefore considering environmental limitations of receiving water, use of neutral pH is recommended for this purpose, meanwhile in addition this method is applicable for the cadmium removal from municipal sewage mixed with industrial wastewater.

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