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Pb and Co removal from paint industries effluent using wood ash

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ABSTRACT: The release of heavy metals into the environment is a worldwide major concern. Different studies have demonstrated that natural agents have a high removal capacity for divalent heavy metal ions. Wood ash is a natural adsorbent and, in comparison with others, has a very low price. In this study, the removal of heavy metals (Pb and Co) from Binalood paint industry (Kerman, Iran) effluent was investigated in batch condition. Pb and Co measurement in samples were done with atomic absorption equipment and test methods were adapted from standard methods for the examination of water and wastewater. The effect of pH and the amount of adsorbent was determined and different adsorption isotherms were also obtained. This study shows that the adsorption process follows the adsorption Langmuir isotherm. The amount of wood ash has a great role in the adsorption rate and adsorption rate increased as wood ash increased. In the study, the reactions reached equilibrium in 3 h contact time. The maximum Pb removal efficiency was 96.1% at pH 2 with a contact time of 3 h and 100 g/L wood ash and the maximum Co removal efficiency was 99 % at pH 2 with a contact time of 3 h and 100 g/L wood ash. According to the results, wood ash is recommended as a low cost and available adsorbent to remove Pb and Co from municipal and industrial wastewaters.

Key words: *Heavy metal, adsorption, wastewater, Langmuir isotherm, contact time*

INTRODUCTION

Heavy metals can pose health hazards to man and aquatic lives if their concentrations exceed allowable limits. Concentrations of heavy metals below these limits even have potential for long-term contamination, because heavy metals are known to be accumulative within biological systems (Quek *et al.*, 1998). Lead contamination of the environment is primarily due to anthropogenic activities, making it the most ubiquitous toxic metal in the environment. Lead readily accumulates in the humus-rich surface layer of the soils due to its complexity with organic matter and it was reported to be the least mobile heavy metal in soils under reducing and non-reducing conditions. Lead has been implicated to be the most common heavy metal contaminants in urban soils due to atmospheric deposition from automobile emission and industries (Abdus-salam and Adekola 2005). The release of industrial wastewaters to the environment causes several adverse effects . These wastewaters commonly include Cd, Pb, Cu, Ni and Co. These heavy metals are not biodegradable and their presence in streams and lakes leads to bioaccumulation in living organisms, causing health problems in animals, plants and human beings (Reviewed by staff and experts in the Programme of Chemical Safety (PCS), 2001; Gabriel, 1979; Howard *et al.*, 2002; Needlemana and Bellingerc, 2001). People are exposed to heavy metals through inhalation, water and food/ ingestion. Paint industries are among those industries that discharge effluent containing heavy metals. Paint components are pigments, solvents, blotters and auxiliary additives. Heavy metals are mainly used as pigments and blotters in the paint. The presence of these heavy metals are directly and indirectly hazardous for human and other beings (Abraham, 1982; Nergo, 1993; Clark, 1972). Several methods have been developed for decontamination of municipal and industrial waters and wastewaters. Among different heavy metal removal methods, chemical precipitation, membrane filtration (reverse osmosis and electro dialysis), electrolytic processes,

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adsorption and biological sorption could be mentioned. Adsorption techniques for wastewater treatment have become more popular in recent years with regard to their efficiency in the removal of pollutants, especially heavy metal ions, color, odor and organic pollution (Ganji *et al.,* 2005; Georg Steinhauser, 2008; Lai, 2003; Vahid dastjerdi *et al.,* 2003). Adsorption has advantages over other methods for remediation of heavy metals from wastewater because its design is simple; it is sludge-free and can be of low capital intensive (Viraraghvan and Dronamraju 1993). Activated carbon has been reported to have high and fast adsorption capacities (Sirichote *et al.*, 2002) due to its well-developed porous structure and tremendous surface area. The commonly-used procedures for removing metal ions from effluents include chemical precipitation (Ahalya *et al*., 2005). Coagulation or flocculation and ion exchange are also in use for heavy metal elimination from the environment (Juang and Shiau 2000; Amuda, and Amoo. 2006; Amuda and Alade, 2006; Amuda *et al.,* 2006). These techniques, which have been reported to be expensive, also have disadvantages such as incomplete metal removal, high reagent and energy requirements and generation of toxic sludge or other waste products that require proper disposal. Thus, preparation and use of environment-friendly materials for metal remediation is desirable. Since it is the first introduction to heavy metal removal, activated carbon has undoubtedly been the most popular and widely-used adsorbent in wastewater treatment applications all over the world. In spite of its prolific use, activated carbon remains an expensive material, since higher the quality of activated carbon, the greater its cost. Activated carbon also requires complexing agents to improve its removal performance for inorganic matters. Therefore, this situation makes it no longer attractive to be widely used in small-scale industries because of cost inefficiency. Due to the problems mentioned previously, research has been interested into the production of alternative adsorbents, especially those which have metal-binding capacities and are able to remove unwanted heavy metals from contaminated water at low cost like natural zeolite, ash, rice husk, vermicompost, peat, volcanic stones, bentonite and clinoptilolite for adsorption of heavy metal ions (Chuah, 2005, Erdem, 2004, Alessia, 2007, Babel and Kurniawan, 2003, Viraraghavan and Rao, 1991, Matos and Arruda, 2003, Naseem and Tahir, 2001, Inglezaki *et al.,* 2007, Brown *et al*., 2000). There are several surveys conducted to innovate and test low cost and efficient materials such as removing iron from groundwater by ash, multi-component adsorption of Ag (I), Cd (II) and Cu (II) by natural carbonaceous materials, adsorption of metal ions on lignin (Hanzlik *et al.,* 2004; Guo *et al.,* 2008). Parallel with other studies conducted to innovate and test efficient, low cost adsorbent for heavy metal removal. This study measured wood ash efficiency as an adsorbent for industrial discharge of heavy metal removal, considering its abundance and low cost.

MATERIAL AND METHODS

The Binalood paint industry (Kerman, Iran) effluent was selected as a source of sampling. This industry with a 70 T/M paint production approximately has 200 m^3/ mounth wastewater productions. The samples were collected from industry equalization tank effluent After in-site pH and temperature measurement, the samples were transferred to the laboratory. In order to remove supernatant, each sample was settled for one h. In order to prepare the samples, 1 M HCl was added to each one until pH decreased to less than 2. These samples kept at 4 ºC. In order to determine the effects of different pH on adsorption rate, each prepared sample was divided into three samples (100 mL volumetric) and then these samples were influenced by standard HCl and NaOH solution and their pH adjusted to 2, 7 and 10. Before the adsorption process, Pb and Co concentrations in each sample were determined and pH was defined. Then, the adsorbent (sieved wood ash with 0.9 µ sieve) was added at the rates of 15, 20, 30, 40, 50, 60, 70, 80, 90 and 100 g/L to wastewater in each vessel. The samples were centrifuged with a mechanical mixer at 100 rpm speed and then were filtered. Pb and Co measurements were done for the effluent and the settled sediments. The sediments were rinsed and filtered with deionized water and after measurement, they were used in calculations. Pb and Co measurements were done with atomic absorption equipment and test methods were adapted from standard methods for the examination of water and wastewater (Eaton *et al.,* 1998). For the control of any leaching interference during the test period, a sample was prepared by adding wood ash to 500 cc of deionized water as a blank sample. Lead and Co removals by wood ash were repeated for industrial wastewater using batch system without acid addition. Meanwhile, the amount of Pb and Co concentrations in the wood ash removed by filter paper after rinsing with deionized water was determined by sample solublizing (use of heat) and then by chemical sample decomposition. The adsorption isotherm models and equations in 25 °C ± 1, pH = 7 and fixed concentration of 2 mg/L Pb and Co were used for different amounts of adsorbent: 10, 20, 30, 40, 50, 60, 70, 80, 90, 100 g and 3 h contact time. According to result of similar study, the research was conducted in 1 to 5 h contact time (Viraraghavan and Rao, 1991). Finally, cluster analysis was used to evaluated the inter-relation amongst contact time with the adsorption of Pb and Co. Among various methods of cluster analysis, the weight pair group (WPG) method was used for its merits (Davis, 1973).

RESULTS AND DISCUSSION

The results in Table 1 show the average of ten raw wastewater samples before one hour for settling and after transferring to the laboratory. The results showed that Pb and Co concentrations were 5.4 and 1.15, respectively, which indicate that the concentration of this heavy metals are more than their MCLS for wastewater used in agricultural irrigation (5 and 0.05 mg/L). It is propounded as the most important environmental problem concerning this wastewater and it must be appointed as a specific care (ISIRI, 1999, Ayers and Westcot, 1994). The study on different amounts of wood ash show that the amount of adsorbent has a great role in adsorption of Co and Pb. As the amount of wood ash increases, the metal adsorption increases significantly. To show the effect of pH, different amounts of wood ash were considered in different pH (2, 7 and 10). The result show that the maximum Pb adsorption was achieved in 100g/L wood ash and pH = 2 about 84.2% and the maximum adsorption

Table 1: Wastewater characteristics of Binalood Paint Industries

Parameters	Unit	Mean	SD
pH	pH unit	5.5	1.5
BOD	mg/L	252.5	20.9
COD	mg/L	610	32.47
TSS	mg/L	102.5	13.9
TDS	mg/L	3325	491.05
EC	µmhos/cm	1750	217.3
Pb	mg/L	5.4	1.3
Co	mg/L	1.15	0.26
Cd	mg/L	1.6	0.29

Co reached 95% in 100 mg/L wood ash and pH = 2. By investigating the pH effect on the adsorption rate of Co and Pb by wood ash illustrated at Fig. 1 and Fig. 2, it shows that adsorption action is done within a wide range of pH, from 2 to 10 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.

Adsorption model

For modeling heavy metal adsorption from wastewater, two models (Langmuir and Freundlich) were used: where, q is the amount of metal ions adsorbed per specific amount of adsorbent (mg/g) and C is equilibrium concentration (mg/L or mmol/L); q_m is the amount of metal ions required to form a monolayer (mg/g); K_L is Langmuir equilibrium constant; K_F and n are Freundlich equilibrium constants. These models are useful in full scale applications. As Figs. 3 and 4 are shown, the adsorption of Pb and Co is better explained by Langmuir isotherm.

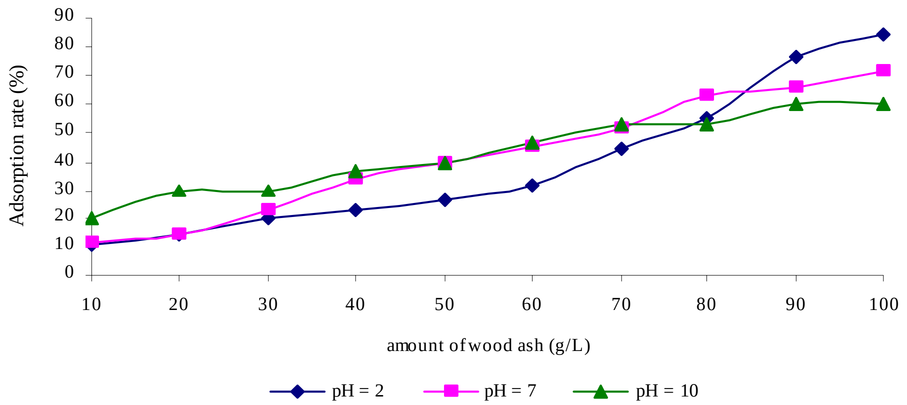

Fig. 1: Adsorption rate of Pb at different pH and different amounts of wood ash

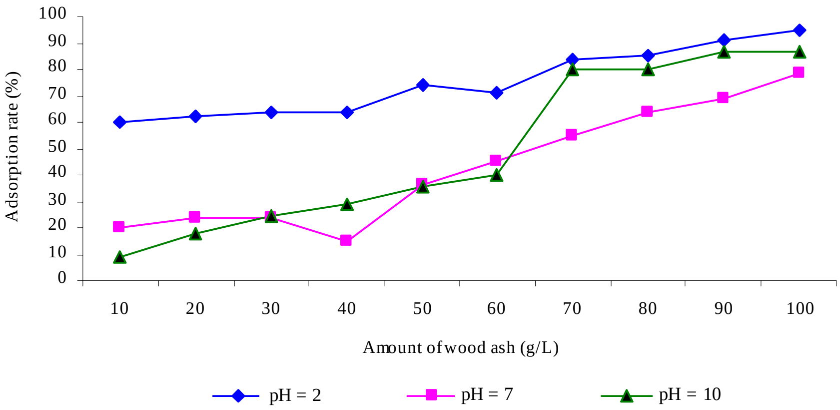

Fig 2: Adsorption rate of Co at different pH and different amounts of wood ash

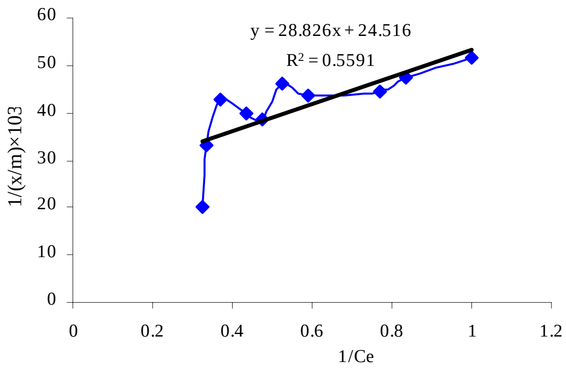

Fig. 3: Pb Langmuir isotherm

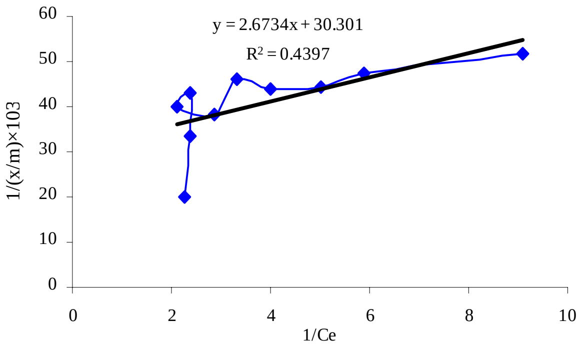

Fig.4: Co Langmuir isotherm

Original form	Linearized form
1. Langmuir model:	
$q = \frac{q_m.K_L.C}{1 + K_L.C}$	$\frac{C}{q} = \frac{1}{K_L.q_m} + \frac{1}{q_m}.C$
2. Freundlich model:	
$q = K_F.C^{\frac{1}{n}}$	$\log q = \log K_F + \frac{1}{n}.\log C$

To determine the required contact time at the same amount of metals (Co and Pb), adsorption rate was measured at different contact times with 100 g/L of adsorbent in 25 °C ± 1. The result in Table 2 shows that the adsorption of Co was 96% to 99 % in the range of 1 to 5 h contact time and adsorption of Pb was 84.2% to 96.1% in the range of 1 to 5 h, respectively. The results in Table 2 show that the reactions reached equilibrium state in 1-3 h, after which no considerable variation in adsorption rate was observed. Therefore, concerning technical and economical aspects, 3 h and 4 h contact time is recommended for Cobalt and Lead removal from wastewater by wood ash adsorption, respectively. Finally, the inter-relationship amongst adsorption of Co and Pb with that of contact time was evaluated using cluster analysis (Fig. 5). The Dendrogram of cluster analysis consists of a single branch. The best relation is found amongst Co and contact time at a similarity coefficient of about 0.97. Though Pb joins Co and contact time at lower similarity coefficient, its relation with these two parameters is about 0.85. This clearly shows the effect of contact time on the adsorption rate of Co and Pb. In other words, adsorption of both elements (Co and Pb) increases with increase in contact time.

Table 2: Optimum contact time for the removal of heavy metals

Contact time (h)	Co adsorption rate (%)	Pb adsorption rate (%)
1	96	84.2
2	97	93.4
3	98	96.1
4	99	96.1
5	99	96.1

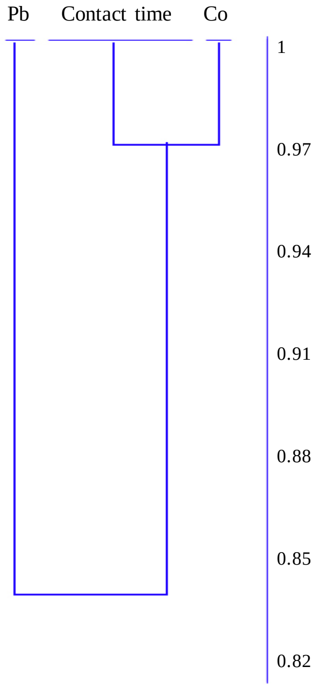

Fig. 5: Dendrogram of cluster analysis amongst contact time and trace metals

The result of this research takes into consideration the adsorption state with different amounts of adsorbent in different pH and different contact times. It shows that with the gradual increase of the adsorbent amount, the adsorption rate has been increased and finally with 100 g/L of adsorbent and pH = 2, this rate reached its maximum level of 96.1% for Pb and 99% for Cobalt. The recommended contact times were 3 and 4 h for Pb and Co, respectively. The affinity of Pb and Co for wood ash at constant and inconstant pH was Co>Pb. This study shows that the adsorption of Pb and Co is better explained by Langmuir isotherm.

The obtained results show that wood ash, as an available and low cost matter, can be considered as an alternative in the field of heavy metals removal from this type of wastewater and similar wastewater.

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