Influence of Operating Conditions on Adsorption of Lead (II) Ions From Contaminated Water Using Different Adsorbents

Areej Dalf Abbas
Chemical Engineering Department, University of Technology/ Baghdad
Email: uot_magaz@yahoo.com

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ABSTRACT
Removal of heavy metals from water and wastewater has received a great deal of attention. Adsorption is one of the most technologies being used for treatment of polluted water. This study records lab scale experiments to test efficiency of activated carbon as an adsorbent and comparing it with low-cost naturally occurring materials (sand & egg shells) in removing lead ions from wastewater.

The adsorption of lead ions from solutions containing different initial lead concentrations (100, 150 and 200 ppm pb as lead nitrate) using different particle size (140, 300 and 500 µm) and different doses of activated carbon, sand and egg shells at different pH (4, 7 and 10) was examined. Also the metal concentration retained in the adsorbent phase (mg/g) was calculated. This method of heavy metals removal proved highly effective as removal efficiency increased with increasing adsorbent dose while it decreased with increasing metals concentration.

The results revealed that of the studied adsorbents, the activated carbon showed the highest adsorption capacity and the maximum adsorption can be obtained by using particle size of 140 µm in neutral media (pH 7). This technique might be successfully used for the removal of lead ions from liquid industrial wastes and wastewater.

Keywords: lead removal, adsorption, heavy metals, wastewater treatment, activated carbon.

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INTRODUCTION

Toxic metals are often discharged by a number of industrial processes and this can lead in turn to the contamination of freshwater and marine environment [1]. Heavy metals are major pollutants in marine, ground, industrial and even treated wastewaters [2]. Industrial waste constitutes the major source of various kinds of metal pollution in natural waters. The important toxic metals i.e. Cd, Zn, Ni, and Pb find its way to the water bodies through waste waters [3]. The release of large quantities of heavy metals into the natural environment e.g. irrigation of agricultural fields by using sewage has resulted in a number of environmental problems [4-6].

Lead is one of major pollutants in wastewater. It is known to damage the kidney, liver and reproductive system, basic cellular processes and brain functions. The toxic symptoms are anemia, insomnia, headache, dizziness, irritability, weakness of muscles, hallucination and renal damage [7]. The main sources of human exposure to lead include the uses of leaded gasoline, industrial sources such as lead mining, smelting and coal combustion, the use of lead-based paint and lead containing pipes in water supply systems. According to the World Health Organization, the accepted range of Pb$^{+2}$ in water is 0.01 ppm.

There are many conventional processes for the removal of lead and the different heavy metals from industrial wastewater streams such as precipitation, coagulation, ion exchange etc [8]. These processes have many disadvantages such as incomplete removal, high energy and reagents costs and disposal of toxic sludge.

Adsorption methods were found to be more effective and attractive due to its lower costs and the higher efficiency of heavy metal ions removal from wastewater. It is a physico-chemical technique which involves mass transfer between liquid and solid phase [9]. Activated carbon is a potential adsorbent for the removal of several organic and inorganic pollutants [10]. Zeolites were used for the purification of wastewater from heavy metals [11]. Removal of lead from water by adsorption on a kaolinite clay was investigated [12].

Vazquez et al [13] reported the ambient temperature adsorption of the metal cations Zn$^{2+}$, Cu$^{2+}$ and Pb$^{2+}$ on Pinus pin aster bark pretreated with acidified formaldehyde solution. They investigated the influences of the pretreatment conditions and of the pH of the cation solution on the adsorption capacity of the bark. They found that the bark was an excellent adsorbent for removal of toxic ions from wastewater with efficiency comparable to commercially available adsorbents, but at a reduced cost. Under favorable conditions, the fractions of dissolved ion adsorbed 85-95% for Pb$^{2+}$, 55-85% for Cu$^{2+}$ and 51-57% for Zn$^{2+}$.

De Vasconcelos and Beca [14] investigated the feasibility of using pine bark for the decontamination of waste waters from heavy metal ions, Pb (II), Cd (II) and Cr (III). It was concluded that the adsorbent’s fraction size and ‘concentration’ as
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well as the solution’s pH and metal ion concentration, reached significant levels that should be considered. They believed that with optimal operating conditions, pine bark may be successfully used to solve the pollution problems of industrial wastewaters.

The objective of this study is to screen and evaluate a series of adsorbents, including activated carbon and low-cost naturally occurring materials (sand & egg shells), for the removal of lead ions from aqueous media. This study compares multiple adsorbents exposed to one pollutant (lead) under the same conditions.

EXPERIMENTAL WORK

Adsorbents collection and preparations

Granular activated carbon (GAC) of industrial grade was supplied from local markets. Activated carbon was used directly without any treatment. Ordinary sand was collected from Al-Ekhaider/Karabalaa in the south of Iraq (specific gravity 2.61). It was washed with dilute HCl then washed twice with distilled water and air dried. Egg shells were washed with water and air dried. Activated carbon and egg shells were ground to a powder. The size distribution of the adsorbents samples was found by the dry sieving method using impact test sieves mesh model BS410, brass frames and mesh (London, England) to obtain various sizes (140, 300 and 500 µm). The surface areas of the adsorbents were measured in the laboratory of Petroleum Research and Development Center using surface area analyzer. These values are presented in Table (1).

MATERIALS

All chemicals used in the study were of analytical grade. Lead nitrate was selected as a source of lead ions in the synthetic wastewater sample. Lead nitrate was dried in oven at 110°C for two hours. A standard solution of 1000 ppm was prepared using 1.59 g of extra pure oven dry lead nitrate in a one liter flask, dissolved in 200 ml of water and 1.5 ml of 15% HNO₃ and then diluted up to the liter with double distilled water. From this 1000 ppm standard solution different concentrations of lead nitrate solutions were prepared by dilution. The pH of the adsorption mixture was adjusted to various pH values (4, 7 and 10) by using buffer solutions of boric acid/borax. All solutions were prepared in distilled water to avoid errors in the results.

ANALYSIS

Lead-ion concentration in the aqueous solutions was determined by atomic absorption flame emission spectrophotometer (AA-680) and atomic absorption spectrophotometer graphite furnace atomizer flameless (GFA-48).

ADOsorption EXPERIMENTS

Batch adsorption experiments were carried out in a glass column. The dimensions of column for samples are taken as, 2.2 cm diameter, 17.9 cm bed height, and 68 cm³ volume. The column was packed with adsorbents to the desired level from the top. For adsorption treatment, a known volume of the particular sample was then introduced at the top and the effluent was collected from the
bottom at the end of each run in plastic bottles and analyzed for concentration of lead.

The percent lead removal efficiency was calculated as follows:

\[
\text{Removal \%} = \left(\frac{C_i - C_t}{C_i}\right) \times 100 \quad \ldots \quad (1)
\]

Where, \(C_i\) and \(C_t\) are the initial concentration and the concentration of lead (ppm) after treatment.

The metal concentration retained in the adsorbent phase (mg/g) was calculated by using:

\[
q_e = \frac{V}{w}[C_i - C_t] \quad \ldots \quad (2)
\]

Where, \(V\) is the volume of the solution (l) and \(w\) is the weight (g) of the adsorbent.

**RESULTS AND DISCUSSIONS**

Various adsorption parameters for the effective removal of lead using different materials naturally occurring and others as adsorbents from aqueous solution were studied and optimized. At the same experimental conditions, different adsorbents had different removal rates.

Activated carbon showed highest removal rate reached 100% of lead from the sample solution while the low-cost naturally occurring (sand & egg shells) showed lower removal rate as compared with activated carbon. Overall, the order of lead removal efficiency for the various materials was as follows: Activated carbon \(>\) sand \(>\) egg shells.

**EFFECT OF PARTICLE SIZE**

The experimental data for the adsorption of pb ions for different sizes of activated carbon and egg shells (140, 300 and 500 \(\mu\)m) with a fixed adsorbent dose and at a pH value of 4 are shown in Figures (1) and (2). The plots between percent pb removal versus adsorbent size reveals that for a fixed adsorbent dose, the maximum adsorption of pb on activated carbon (99.99 percent) is at size 140 \(\mu\)m. So the fine particles showed almost complete removal of the unwanted metals. This adsorption decrease with increase in both activated carbon and egg shells sizes. This is because adsorptions being a surface phenomenon, the smaller particle sizes have large surface area per unit weight and so provide more adsorption capacity than the larger particle size of the adsorbent, as reported in references [15-17].

**EFFECT OF pH**

Experiments with solution pH as a variable were also conducted to determine the optimum pH range for maximum pb adsorption by activated carbon, sand and egg shells.

The adsorption of lead on the activated carbon, sand and egg shells was studied over a pH range of (4-10) for a fixed adsorbent dose at particle size of 500 \(\mu\)m and influent concentrations of lead ions of 100 ppm and 150 ppm. The results are shown in Figures (3) and (4) where an increase in adsorption with increasing pH of
solution for both initial pb ion concentrations (100 and 150 ppm ) up to a pH value of 7. Beyond this pH the adsorption decrease with increasing pH, so the maximum adsorption is at pH 7 for all adsorbents, i.e. in acidic or basic solutions the adsorption was lower as compared to neutral solution. A similar behavior has been reported by many authors [18-21] for the uptake of metal ions on various adsorbents.

The removal of lead by adsorbents was highly dependent on the pH of the solution which affects the surface charge of the adsorbents, and the degree of ionization and speciation of the adsorbates. The change in adsorption efficiency with change in pH of samples was found to be significant.

The variation in removal efficiency due to the solution pH was attributed to the precipitation of metal hydroxide [M(OH)] at a higher pH. The simple hydrolysis of most divalent metal ions especially Cu^{2+} and Pb^{2+} can be written as follows:

$$\text{M}^{2+} (\text{aq}) + \text{H}_2\text{O} (\ell) \rightarrow \text{M(OH)}^+ (\text{aq}) + \text{H}^+ (\text{aq}) \quad (3)$$

As the pH increases there is an increasing trend in concentration of hydroxide ions [OH−] in solution, causing disturbance of equilibrium. Therefore the system adjusts to counter this effect (Le Chatelier principle) by more precipitation of hydroxide out of the solution. Precipitates are not permanently adsorbed by the sorbent particles; therefore washing of sorbents will certainly remove the hydroxide and bring the lead into direct contact with external environment.

At low pH values the surface of the adsorbent, would be closely associated with hydronium ions (H_3O^+) which hinder the access of the metal ions to the surface active groups. Consequently, the percentage of metal ion removal may decrease at low pH showing that sorbents have negatively charged surface.

**EFFECT OF Pb ION CONCENTRATION**

To evaluate the effect of the pb ions concentration on the adsorption behavior of lead on the activated carbon, egg shells and sand, studies were conducted with initial pb ions concentrations ranging from 100 to 200 ppm , fixed adsorbent dose of 500 µm particle size for each adsorbent at a pH value of 4. Plots were prepared between the pb removal % versus initial concentration at particle size of 500 µm (Figure. 5). The adsorption data indicates that the maximum adsorption occurred with the lowest initial lead concentration (100 ppm) and the percentage pb ions adsorbed decreased with increasing initial pb concentration while the total amount of pb adsorbed per g-adsorbent, q_e, increased as shown in Figure (6) where before 120 ppm pb ion concentration, sand showed higher adsorption than egg shells and after 120 ppm egg shells higher. Even at a very high concentration of 200 ppm, the removal efficiency rarely falls below85%.

This can be explained by the fact that as the concentration of lead ions increases so does the metal surface loading. For example, a concentration of 200 ppm will have a higher surface loading as compared to a concentration of 100 ppm. The number of ions coming into contact with the adsorbent particles in the same amount of time increases. Since the number of available adsorption sites is constant
for all concentrations, at higher influent concentrations, more ions go through without being adsorbed. These results agree with the references [22-24].

**ADSORBENT DOSE EFFECT OF**

After obtaining the suitable adsorbent size (140 µm), optimum pH (7), initial Pb concentration (100 ppm) for Pb adsorption, it was decided to obtain the suitable dose of the adsorbent that will bring about a better decontamination of Pb contaminated effluent. The effect of adsorbent dose on adsorption of lead was studied at constant adsorbate concentration (150 ppm). The results are shown in Figure (7) where the adsorption of Pb indicates change with the amount of adsorbent. It may be observed that for a fixed initial Pb ions concentration, the adsorption of Pb ions increased with an increasing adsorbent dose for each adsorbent. Smaller amount of adsorbent means availability of lesser adsorption sites for Pb and therefore less removal efficiency. The adsorption of Pb ions per unit weight of adsorbent decreased with increasing adsorbent dose as shown in Figure (8) for each adsorbent [15, 16, 23, 27].

**CONCLUSIONS**

A simple and cost effective treatment procedure was proposed for the removal of heavy metals through the adsorption on activated carbon and low cost naturally occurring materials such as sand and egg shells. Adsorption is a strong choice for removal of heavy metals as it is operationally simple and can adapt to changing wastewater conditions. Removal efficiencies were found to fall within the range of 69-100%, depending on the type of adsorbent, solution composition and other adsorption conditions.

Activated carbon was proved to be the best adsorbent for removal of lead from aqueous solutions under certain physicochemical conditions. Sand and egg shells are also good adsorbents for removing lead ions from aqueous solutions, in the range of concentrations used. For example, at adsorbent dose of 35 g for each adsorbent, removal efficiencies were, 96% for activated carbon, 84% for sand and 72% for egg shells.

Egg shells are disposed in nearly all parts of the world and have no commercial value therefore their utilization as an adsorbent of lead or of other metal ions may represent an attractive strategy for the effective reduction and reuse of this type of waste.

The adsorbents studied are very effective in removing lead from wastewater even at very high concentration e.g. 200 ppm. The percent Pb ions removal increases with increasing adsorbent dose, and such removal increases with decreasing size of the adsorbent material. The maximum adsorption can be obtained by using particle size of 140 µm in neutral media (pH 7).

**REFERENCES**

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Figure (1): Effect of particle size on removal of lead (II) ions at initial concentration of 150 ppm & pH 4.

Figure (2): Effect of particle size on removal of lead (II) ions at initial concentration of 100 ppm & pH 4.
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Figure (3): Effect of pH on adsorbent performance at initial concentration of 100 ppm.

Figure (4): Effect of pH on adsorbent performance at initial concentration of 150 ppm.

Figure (5): Effect of initial concentration on the percentage of Pb ion removal at a pH 4
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Figure (6): Effect of initial concentration on lead (II) ions adsorbed per g-adsorbent at a pH 4.

Figure (7): Effect of adsorbent dose on adsorption of lead (II) ions at initial concentration of 150 ppm.

Figure (8): Effect of adsorbent dose on lead (II) ions adsorbed per g-adsorbent at initial concentration of 150 ppm