

REMOVAL OF LEAD FROM AQUEOUS SOLUTION USING WASTE TIRE RUBBER ASH AS AN ADSORBENT

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Abstract - The purpose of this study was to investigate the possibility of the utilization of waste tire rubber ash (WTRA) as a low cost adsorbent for removal of lead (II) ion from aqueous solution. The effect of different parameters (such as contact time, sorbate concentration, adsorbent dosage, pH of the medium and temperature) were investigated. The sorption process was relatively fast and equilibrium was reached after about 90 min of contact. The experimental data were analyzed by the Freundlich isotherm and the Langmuir isotherm. Equilibrium data fitted well with the Langmuir model with maximum adsorption capacity of 22.35 mg/g. The adsorption kinetics was investigated and the best fit was achieved by a first-order equation. The results of the removal process show that the Pb (II) ion adsorption on WTRA is an endothermic and spontaneous process. The procedure developed was successfully applied for the removal of lead ions in aqueous solutions.

Keywords: Removal; Pb²⁺; Waste tire rubber ash; Isotherm; Kinetics.

INTRODUCTION

Heavy metals can be introduced into the water by various industries. The heavy metals are of special concern because they pose a significant danger to human health (Babel and Kurniawan, 2003; Bayat, 2002). The safe and effective disposal of industrial wastewater is thus a challenging task for industrialists and environmentalists. The important toxic metals are Cd, Zn, Pb and Ni. These heavy toxic metals enter the water bodies through waste water from metal plating industries and mining, pigments and alloys, electroplating corrosion of galvanized piping and dezincification of brass besides other industrial wastes (Mohan and Pittman, 2006; Anthony and Alison, 2002). Heavy metal-containing water is one of the most toxic industrial wastes. Nowadays, with the exponential increase in population, measures for

controlling heavy metal emissions into the environment are essential.

Lead is a heavy, soft, malleable, bluish gray metal. Its common ore is galena, where it occurs in the form of sulphide. Most of the lead in the air comes as aerosols, fumes & sprays. It is very widely used in din storage batteries and the gasoline auto exhaust from gasoline. Motor vehicle exhaust is the major source of the atmospheric layer in the urban area. Other anthropogenic sources of lead include the combustion of coal, processing and manufacturing of lead products and manufacturing of lead additives. Some lead is also introduced into the atmosphere during incineration of residues of lead containing pesticides. Lead is a systemic poison causing anemia, kidney malfunction, brain tissue damage and even death in extreme poisoning (Acharya et al., 2009; Ho and McKay, 2000).

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Removal of pollutants such as lead from wastewater has conventionally been accomplished through a range of chemical and physical processes (Kiran et al., 2007; Cesur and Baklaya, 2007). There are traditional methods of industrial wastewater treatment, such as precipitation, adsorption and coagulation methods. However, these processes can be expensive and not fully effective. Among the available techniques, sorption has been used as one of the most practical methods and recent studies have focused on the search for an inexpensive and efficient adsorbent (Yadanaparathi et al., 2009). A wide variety of materials such as chitosan, granular red mud (Zhu et al., 2007), sugar beet pulp (Pehlivan et al., 2008), rice husk (Wong et al., 2003), rice bran Montanher et al., 2005; Ajmal et al., 2003), activated carbon (Giraldo and Moreno-Piraján, 2008), Zeolite (Stylianou et al., 2007), sawdust (Asadi et al., 2008), cocoa shells (Meunier et al., 2003), Sargassum (Silva et al., 2003) and leaves (King et al., 2006) are examples of low-cost materials used in the removal of heavy metals.

Currently, fly ash is generally dumped in landfills. Some applications of fly ash in road construction, cement production, and zeolite synthesis have been widely used. However, fly ash recycling is still not sufficient and novel applications have to be explored. In the past a few years, utilization of fly ash as a low-cost adsorbent for removal of pollutants such as heavy metals, dyes, and phenolic compounds in wastewater streams has been tested. Some scientific workers have used modified fly ash (Nascimento et al., 2009) for removal of pollutants from water and wastewater (Gitari et al., 2008; Sharma et al., 2007; Hsu et al., 2008) leading to application of fly ash as adsorbent for water and wastewater reclamation.

Waste tires have been a major management and disposal problem in many countries for decades. In 2004, over 250 million scrap tires were discarded in the United States and approximately 3 billion waste tires had accumulated in stockpiles. Some of the tires are utilized for rubber tiles and blocks or for cement materials. However, the cost of making rubber powder from a tire is very high. Waste tires are virtually non-degradable and take up landfill spaces (Weng and Chang, 2001). If not properly disposed, waste tires may accumulate water and can subsequently cause the spread of mosquito-borne diseases (Chang, 2008). Often tire fires occur and cause serious air, water, and soil pollution. Nevertheless, tire rubber has a high heat value (12,000–16,000 Btu/lb). In the United States, Canada, Germany, the United Kingdom, and Japan, waste tires have been used as a supplemental fuel for

cement kilns and in paper mills. Therefore, it is of interest to explore any new application/market for the scrap tire reclaiming industry.

This paper describes a study of the use of waste tire rubber ash (WTRA) as an adsorbent for removal of Pb^{2+} from aqueous solutions and wastewater samples. The effect of various important parameters on removal such as pH, heavy metal concentrations and fly ash dosages, contact time and temperature is also discussed. It was found that waste tire rubber ash is an excellent adsorbent for removal of lead and has several advantages over other materials.

EXPERIMENTAL

Materials

All chemicals are reagent grade and were used as received without further purification. All solutions were prepared with deionized water. Metal solutions were prepared by dissolving the appropriate amount of $Pb(NO_3)_2$ (Merck) in distilled water. 0.1 M NaOH and HNO_3 solutions were used for pH adjustment. A Metrohm pH meter (Model E-632) was used for pH measurements. A Shimadzu (AA680) atomic absorption spectrophotometer (AAS) with lead hollow cathode lamps and air acetylene flame was used for determining Pb^{2+} ion in solution. A temperature controlled water bath flask shaker was used for shaking all the solutions.

Preparation of Adsorbent

The waste tires were initially washed with detergent solution and dilute HCl in order to remove the earthen soil debris. After that, the cleaned and dried waste tire was burned and the residue placed in a porcelain crucible and burnt completely at 500°C in a muffle furnace for 2 h. After cooling, a very dilute acidic solution (such as 0.001 mol L⁻¹ HCl) was used to remove the salts of metals such as sodium, potassium and calcium. Then the mixture was filtered using Whatman grade 42 filter paper. The filtered solid was then washed with 100 mL of double distilled water and dried at 105°C for 2 h before use.

Characteristics of Adsorbent Material

The physical properties and chemical composition of the WTRA are presented in Table 1. The morphological characteristics of the adsorbent were evaluated by using a Phillips XL30 Scanning Electron Microscope. The samples of powder of

WTRA were covered with a thin layer of gold and an electron acceleration voltage of 10 kV was applied. The surface area and adsorption average pore width of the selected fraction of nano alumina was determined by the N₂ gas Brunauer-Emmett-Teller method of analysis using a Micromeritics Chemisorption ASAP 2020. The WTRA has a gray color and its specific surface area was 1.88 m²/g.

Table 1: Chemical analysis of waste tire rubber ash

Component	(%)
SiO ₂	26.5
Fe ₂ O ₃	9.3
Al ₂ O ₃	8.7
CaO	12.9
MgO	6.4
SO ₃	1.6
Na ₂ O	1.4
K ₂ O	1.1
TiO ₂	1.0
Cl ⁻	0.1
Zn	20.2
Loss on ignition	10.6

The scanning electron micrographic examination of WTRA particles (Fig.1) shows a highly porous morphology of the waste rubber fly ash with pores of different sizes and shapes. The image also reveals that the external surface is full of cavities, which suggest that WTRA exhibits a high surface area and irregular in shape.

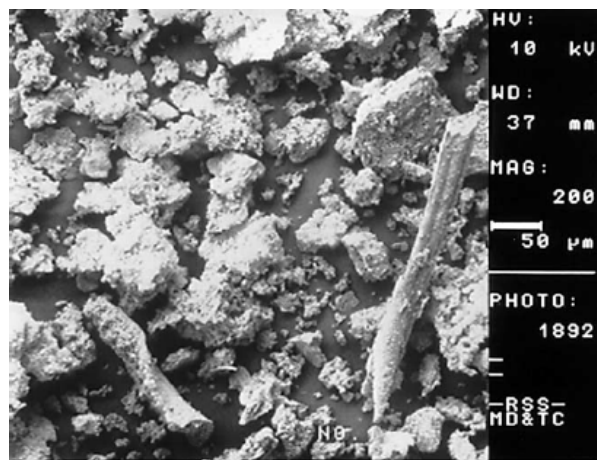


Figure 1: Scanning electron micrographs of WTRA particles

Batch Adsorption Experiments

Batch adsorption experiments were carried out by mechanically shaking a series of bottles containing 0.05 g of WTRA sample with 100 ml of an aqueous

solution of Pb²⁺ of the desired concentration, temperature and pH in different properly cleaned polythene bottles on a shaking thermostat with a constant speed of 100 rpm. The bottles were agitated for pre-determined times until equilibrium was attained. At the end of the agitation period, the mixture was centrifuged at 4200 rpm for 10 min. The progress of adsorption was assessed by determining the residual concentration of Pb²⁺ in supernatant by an atomic absorption spectrophotometer.

The percent removal of lead ions from aqueous solution was calculated by the following equation:

$$\% \text{Removal} = \frac{(C_i - C_f)}{C_i} \times 100 \quad (1)$$

where C_i and C_f are the initial and equilibrium concentrations of the adsorbate, respectively. The reported value of Pb²⁺ ions adsorbed by WTRA in each test was the average of at least three measurements.

RESULTS AND DISCUSSION

Effect of Contact Time on the Removal of Pb²⁺

The effect of contact time on the adsorption of Pb²⁺ was studied for an initial concentration of 100 - 400 mg L⁻¹. The contact time experiments were carried out at 25 °C (time interval, 15 min). It is observed from Figure 2 that the adsorption increased with increasing contact time, and the equilibrium was attained after shaking for 90 min. Therefore, for further experiments, the shaking time was set to 90 min.

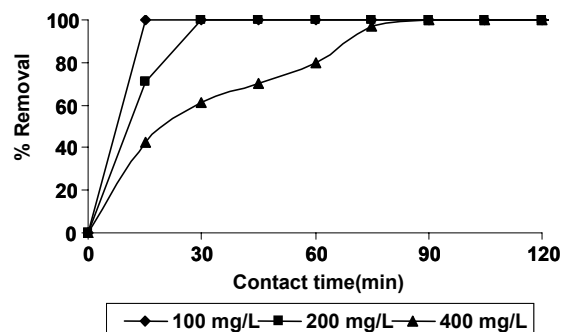


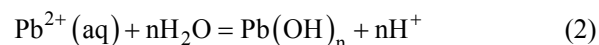
Figure 2: Effect of contact time on the removal of Pb (II), 2.0 g L⁻¹ of WTRA, 100 mL of Pb²⁺ solution, temperature 25°C.

Effect of Adsorbent Dose

A dosage study is an important parameter in adsorption studies because it determines the capacity of adsorbent for a given initial concentration of metal ion solution. The effect of adsorbent dose on the percent removal of Pb(II) at an initial concentration of 400 mg L⁻¹ is shown in Fig. 3. From the figure it can be observed that increasing the adsorbent dose increased the percent removal of Pb(II) from 28.8 % up to 99.4 % with the required optimum dose of 2 g/L. Beyond the optimum dose the removal efficiency did not change with the adsorbent dose. As expected, the removal efficiency increased with increasing the adsorbent dose for a given initial metal concentration, because, for a fixed initial adsorbate concentration, increasing adsorbent dose provides greater surface area or more adsorption sites. Further, it can be attributed to the binding of metal ions onto the surface functional groups present on the WTRA. On the other hand, when the WTRA dose increased, the adsorption capacity (the amount adsorbed per unit mass of adsorbent) decreased. The decrease in adsorption capacity with increase in the adsorbent dose is mainly due to the increase of free adsorption sites in the adsorption reaction.

Effect of pH

It is well known that the removal of heavy metals by adsorbent depends on the pH of the initial solution. Therefore, in order to establish the effect of pH on the adsorption of lead (II) ions, the batch equilibrium studies were carried out in different pH values. The pH range was chosen as 2–6 in order to avoid metal hydroxides, which has been estimated to occur at pH > 6.5 for Pb(OH)₂. Figure 4 shows the amount of lead ions removed from aqueous solution as a function of pH at a Pb²⁺ concentration of 400 mg/L. The amount of Pb²⁺ ions removed from solution increases rapidly from pH 4 to pH 6. At pH 4, 73.8% of lead ion was removed, while at pH 6, 93.1% of lead ion was removed. Above pH 6, the amount of Pb²⁺ ion removed from the solution by the WTRA, steadily increased to 100%.



At low pH, the surfaces of the WTRA are positive and there was formation of the complex [Pb(OH)₄]²⁻; hence, the complex formed will be

adsorbed on the adsorbent surfaces. Hydroxyl-metal complexes have higher affinity for adsorption than the hydrated metal ion, because the formation of an OH adduct of the metal ion reduces the free energy required for adsorption (Elliott and Denny, 1982).

Low sorption at lower pH could be ascribed to the hydrogen ions competing with metal ions for sorption sites. This means that, at higher H⁺ concentration, the adsorbent surface becomes more positively charged, thus reducing the attraction between adsorbent and metal ions. In contrast, as the pH increases, more negatively charged surface become available, thus facilitating greater metal removal. The increase in metal ion uptake by WTRA at higher pH values may be attributed to calcium content and the (SiO₂ + Al₂O₃ + Fe₂O₃) content that provides alkalinity in the system, rising the pH to strongly alkaline values. The facilitation of the uptake of Pb²⁺ ions by the WTRA at higher pH may be related not only to the formation of metal hydroxides but also to the precipitation, which caused a decrease in the rate of adsorption.

Effect of Temperature on Removal of Pb²⁺

To determine whether the ongoing adsorption process was endothermic or exothermic in nature, Pb²⁺ adsorption studies over WTRA were carried out between 1- 60°C for different initial feed concentrations and at constant adsorbent dose of 2.0 g/L. It can be seen that the adsorption of lead ions increased when the temperature was increased (Fig. 5). For example, at 1°C the amount of Pb²⁺ ion adsorbed was 15 %, whereas at 30 °C, 92.8 of Pb²⁺ ion was adsorbed by WTRA for an initial concentration of 200 mg/L of Pb²⁺. It can be seen from Figure 5 that, initially, the percentage removal increases very sharply with the increase in temperature, but beyond a certain value of ca. 30°C, the percentage removal reaches almost a constant value. The above results also showed that the sorption was endothermic in nature. The increased sorption with the rise of temperature may be diffusion controlled, which is an endothermic process, i.e., the rise of temperatures favors the sorbate transport within the pores of sorbent. The increased sorption with the rise of temperature is also due to the increase in the number of the sorption sites generated because of breaking of some internal bonds near the edges of active surface sites of the sorbent.

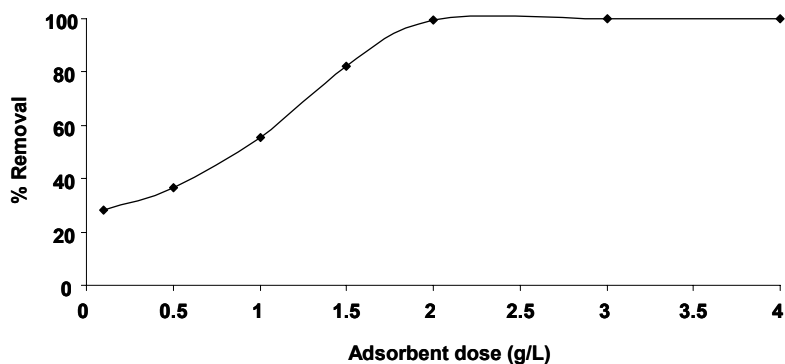


Figure 3: Effect of WTRA dosage on the removal of Pb^{2+} , 100 mL of solutions, contact time 90 min, temperature 25°C.

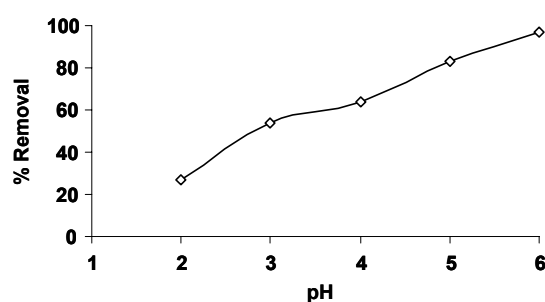


Figure 4: Effect of pH on the removal of Pb^{2+} by WTRA: 2.0 g L⁻¹ of WTRA, 100 mL of solution, temperature 25°C.

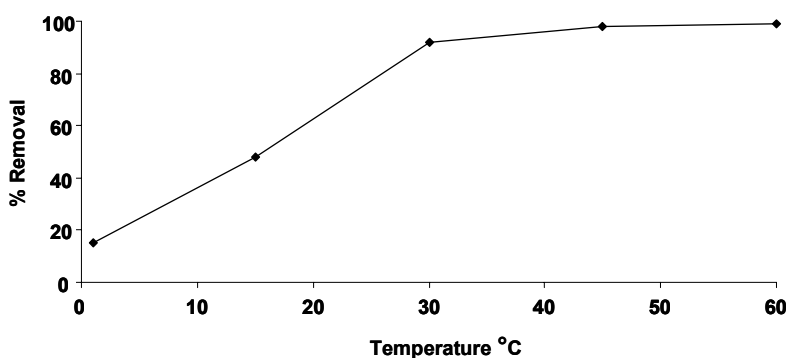


Figure 5: Effect of temperature on the removal of Pb^{2+} onto WTRA: 2.0 g L⁻¹ of WTRA, 100 mL of solution.

Isotherm Study

The relationship between the amount of a substance adsorbed per unit mass of adsorbent at constant temperature and its concentration in the equilibrium solution is called the adsorption isotherm. The equilibrium adsorption isotherms are important in determining the adsorption capacity of Pb(II) metal

ions and diagnose the nature of adsorption onto the WTRA. Two theoretical isotherm models were used to fit the experimental data: Langmuir and Freundlich models. The Langmuir and Freundlich sorption isotherms have been commonly used to describe the equilibrium behavior of adsorbate. Curves of related adsorption isotherms are regressed and parameters of the equations are provided.

Langmuir Isotherm

The general form of the Langmuir equation is (Langmuir, 1918):

$$\frac{C_e}{Q} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \quad (3)$$

where C_e is the equilibrium concentration (mg L^{-1}), Q is the amount of heavy metals sorbed, b is the sorption constant (L mg^{-1}) (at a given temperature) related to the energy of sorption, Q_0 is the maximum sorption capacity (mg g^{-1}). A linear plot of C_e/Q against C_e is employed to give the values of Q_0 and b from the slope and the intercept of the plot. These parameters, plus the correlation coefficient (R^2), of the Langmuir equation for the sorption of Pb^{2+} ions by WTRA are given in Table 2.

Freundlich Isotherm

The Freundlich isotherm is an empirical equation employed to describe heterogeneous systems. The Freundlich equation is expressed as (Freundlich, 1906):

$$Q_e = K_F C_e^{1/n} \quad (4)$$

The linear form of the equation can be written as:

$$\ln q_e = \ln K_F + (1/n) \ln C_e \quad (5)$$

where K_F and n are the Freundlich constants related to the adsorption capacity and adsorption intensity, respectively. The intercept and the slope of the linear plot of $\ln q_e$ versus $\ln C_e$ at given experimental conditions provide the values of K_F and $1/n$, respectively.

The correlation coefficient and other parameters obtained for the adsorbent are shown in Table 2, which indicate that the experimental data fitted well to Langmuir model. This suggests that the adsorption of Pb^{2+} ions by WTRA is of the monolayer-type and agrees with the observation that the metal ion adsorption from an aqueous solution usually forms a layer on the adsorbent surface.

Kinetic Study

Kinetics of adsorption is an important characteristic in defining the efficiency of adsorption. Various kinetic models have been proposed by different researchers,

where the adsorption has been treated as a first order, pseudo-first-order and pseudo-second-order process. Different systems conform to different models. The Lagergren's rate equation is the one most widely used for the sorption of a solute from a liquid solution (Lagergren, 1898). The linear form of the pseudo-first-order equation, given by:

$$\text{Log}(q_e - q_t) = \text{log } q_e - \frac{kt}{2.303} \quad (6)$$

where q_e and q_t are the amount of Pb^{2+} adsorbed at equilibrium and at time t , in mg/g and k is the pseudo-first-order rate constant, was applied in the present studies of Pb^{2+} adsorption. Fig. 6 shows that the data is well described by the Lagergren equation. The plot was found to be linear with good correlation coefficient ($R^2 = 0.998$) indicating that Lagergren's model is applicable to lead adsorption on WTRA and that the process is pseudo-first-order. The value of the corresponding pseudo-first-order rate constant k was evaluated to be 0.0023 min^{-1} .

Application of WTRA for Industrial Wastewater Treatment

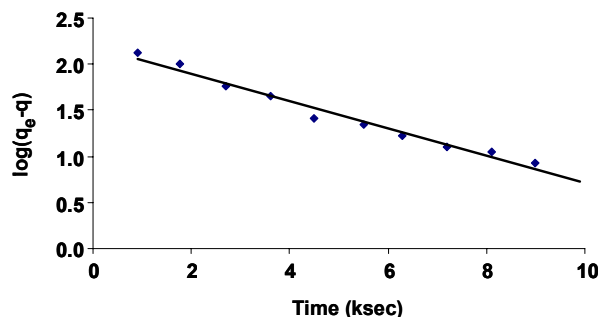
The utilization of WTRA as an adsorbent was assessed by its application in treatment of industrial wastewater samples. Electroplating industry wastewater samples containing Pb^{2+} were collected from local industries situated in the industrial belt of Semnan city (Iran). The results reveal that the treatment of metal ions in wastewater samples is not significantly different from the results predicted based on single solute batch experiments. Thus, the present study demonstrates that WTRA can be successfully used for the removal of Pb^{2+} ions from industrial wastewaters.

Comparison of Lead (II) Removal with Different Adsorbents Reported in the Literature

The adsorption capacities of the adsorbents for the removal of lead (II) have been compared with those of other adsorbents reported in the literature and the values of adsorption capacities are presented in Table 3. The experimental data of the present investigations are comparable with the reported values in some cases. We note that our material (WTRA) is more effective compared to other materials. However, the present experiments are conducted to find the technical applicability of the low-cost adsorbents to treat Pb (II).

Table 2: The Langmuir and Freundlich isotherm model constants

	Freundlich			Langmuir		
	1/n	K _F	R ²	Q ₀	b	R ²
Pb ²⁺	0.23	8.23	0.965	22.35	0.274	0.995

**Figure 6:** Plot of the pseudo-first order kinetic model for Pb(II) ion adsorption.**Table 3: Comparison of adsorption capacity with different adsorbents reported in the literature.**

Adsorbents	Maximum adsorption capacity, Q ₀ (mg/g)	Reference
Rice husk	11.0	Chuah and et al. (2005)
Baggase fly ash	2.5	Gupta and Ali (2004)
Phaseolus aureus hulls	21.8	Madhava Rao et al.(2009)
Waste tea leaves	9.0	Ahluwali and Goyal (2005)
This study	22.35	

CONCLUSIONS

The present study shows that waste tire rubber ash is an effective adsorbent for the removal of lead ions from aqueous and wastewater solutions. The adsorption of Pb²⁺ by waste tire rubber ash is a function of the adsorbent dosage, initial concentration of metal ions, pH and time of contact. Increase in adsorbent dosage leads to an increase in Pb(II) adsorption due to the increased number of adsorption sites. The kinetic study shows that equilibrium is reached for Pb²⁺ ions at 90 minutes. The adsorption isotherm studies showed that the Langmuir adsorption isotherm model fits well with the experimental data. The maximum adsorption capacity was obtained for WTRA (22.35 mg/g). Thermodynamic studies indicated the adsorption process increases with an increase in temperature and the sorption was endothermic in nature. The adsorbent has a high capacity for removal of lead ions from contaminated water and wastewaters and it can be used for removal of Pb²⁺ from moderately acidic aqueous solutions. The cost of removal is expected to be quite low, as the adsorbents are cheap and easily available in large quantities. The WTRA would be useful in treatment of wastewater containing lead ions.

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