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Adsorption of Lead by Bentonite Clay

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Abstract
Removal of heavy metals from industrial waste water is a worldwide challenge. Inorganic pollutants are difficult to treat as they are non-biodegradable, hence they remain in nature. Such pollutant when enters the food cycle, affect human, plant, animal lives and aquatic systems. Therefore, their removal becomes critical from the environmental point of view. In this study lead is being used as a pollutant in water and unmodified bentonite clay is used as adsorbent material. The bentonite clay was characterized using technique XRD. The results of XRD show that montmorillonite is the main clay mineral. The applicability of the bentonite clay from Bhawnagar area for removal of lead from aqueous solution was tested using the batch process. Experimental parameters affecting the adsorption process like pH value, initial metal concentration, dose of adsorbent (clay), agitation time, and speed were analyzed to get optimum conditions for maximum removal of lead. Experimental data were fitted well to the Langmuir adsorption isotherm with maximum adsorption capacity of 26.3 mg/gram at correlation coefficient of 0.955. It was found that Langmuir adsorption model is fit well with experimental data. Successful application of bentonite clay from Bhawnagar area for removal of lead from aqueous solution greatly supports its field application.

Keywords: Adsorption, bentonite clay, heavy metal, Langmuir adsorption isotherm, Lead removal.

1. INTRODUCTION

Industrialization in all sectors is at peak throughout the world. Industries are using different type of chemicals as a part of their manufacturing process. Effluents released from these industries contain chemical pollutants. Some of them are mentioned here as lead, cadmium, zinc, arsenic, chromium, copper, etc. Another source responsible for water and soil contamination is effluents discharged from dying industries (Kadirvelu K et al., 2003) like textile, leather, printing, painting, plastic, fertilizer and pesticide, mining and smelting ferrous ores, energy and fuel production and food (Wan Ngah and Hanafiah, 2008). Textile finishing industries are the main contributors to environmental pollution by way of releasing waste water containing the heavy metals and dyes (Tangsathitkulchai, M. et al., 2012). Dye is the first noticeable contaminant in the effluent. In Maharashtra, Rajasthan and Gujarat there are a large number of small scale industries using dyes for jeans and other clothes. These industries were discharging their waste water without any treatment into river or water bodies around. As per McMullan et al., 2001, and Pearce et al., 2003, approximately 100,000 units of textile dyes used and their annual production worldwide is more than 7×10^{-5} metric tons

These pollutants may be organic or inorganic in nature. Soil and waste water polluted with organic pollutants are easy to purify as they are biodegradable. However, soil and waste water polluted with inorganic pollutants are difficult to treat as they are non-biodegradable and therefore they will remain in the environment. These pollutants are known as heavy metals and dyes. Different type of dyes used in textile industry is chemically resistant to light, heat, oxidizing agents and non-biodegradable.

Plants uptake the heavy metals when grown in the heavy metals polluted environment. This way it leads to accumulation of metals in tissues of human and other livings on earth (Kumar, P. S. et al., 2012). Heavy metal contaminated effluents are also affecting the aquatic life. Further, it is not the end the contamination of ground water might occur if contaminated effluents allowed to infiltrate to groundwater aquifer.

Effects on human health

Most of the heavy metals are hazardous and they have adverse effects on human health. They may cause the serious health problems like upsets on kidneys and brain cells thereby disturbing their regular function (Asli Baysal et al., 2013). Further, they can accumulate in the body and results in additional disturbance to health. Lead(Pb) is one of the hazardous element which is present in industrial effluents. Consumption of trace amount lead concentration may result in permanent adverse health effects of brain development.

Heavy metal removal from effluents can also be achieved using conventional processes like chemical precipitation, coagulation and Ion-exchange, etc. (Ming Qin J., et al. 2009).

Recently, a lot of research work has been done using physiochemical processes for decontamination of soil and water and same is known as adsorption (Kurniawan T. A. et. al, 2006). Adsorption of heavy metals using some adsorbent material is an example of physiochemical process. Physiochemical process is a mass transfer process in which a substance moves from liquid phase to surface of solid via physical and chemical reaction. Most commonly used adsorbent material is the activated carbon (Shim et al., 1996; Ouki et al., 1997; Leyva-Ramos et al., 1997; Monser and Adhoum, 2002 and Leyva-Ramos et al., 2002) but it proves to be expensive. Other adsorbent materials were also used e.g. volcanic ash, fly ash, bentonite clay. Bentonite found to be most economical adsorbent material because of its high efficiency in removing heavy metals and availability (Boyd et al., 1998; Brigatti et al., 1995; Gutierrez and Fuents, 1996; Lo et al., 1997).

2. Materials and Methods

Materials and methods used to study the adsorption of lead are described here.

2.1 Adsorbent

Bentonite received from Bhawnagar, Gujarat was used as an adsorbent. The mineralogical composition of which determined by XRD test and detail is given in Table 1.

Table 1: Mineralogical Composition of Bentonite

S. No.	Minerals	(%)
1.	Kaolinite	3.90
2.	Montmorollonite	48.60
3.	Hematite	26.7
4.	Anatase	4.10
5.	Dolomite	16.60

2.2 Chemicals

Lead nitrate ($Pb(NO_3)_2$) is used in adsorption study. pH adjustment was carried out using the 0.1 N hydraulic acid (HCl) and 0.1 N sodium hydroxide (NaOH). The chemicals used all are of analytical regent were supplied from Merck.

2.3 Instrumentation

Lead analysis is carried out using the Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES), make Spectro Analytical Instruments GmbH, Germany (Model ARCOS) at Sophisticated Analytical Instrument Facility (SAIF) Department of IITB, Mumbai. pH adjustment was carried out using digital pH hydrotester (Model: PH-80). A magnetic stirrer (Model-1 ML) supplied from REMI Laboratory Instrument, Goregaon was used for shaking the mixture of metal solution and bentonite.

2.4 Procedure

Adsorption of lead is carried out in a batch reactor. A stock solution of 100 mg/litre of lead is prepared by dissolving 1.6 g $Pb(NO_3)_2$ in 1 L deionized water. Metal solution of required lower concentration is prepared by diluting the stock solution. The volume of sample is determined to be 50 ml (Ahmed Marzoog et.al, 2014). pH adjustment for this study was carried out using 0.1 N HCl and 0.1 N NaOH. The amount of clay is taken in the range of 0.1 g to 1 g. The mixture of clay and metal solution is shaken for 2 hours at 200 rpm on magnetic stirrer. Whatman's filter paper was used to separate the clay from the solution. The concentration of lead remains in solution after adsorption is analyzed by Inductively Coupled Plasma –Atomic Emission Spectrometer (ICP-AES) at IITB. In this study, the effect of parameters like pH value, metal concentration, amount of clay, agitation time and speed were examined.

2.5 Adsorption Model

Batch adsorption studies were performed to obtain the equilibrium isotherms for lead. A metal solution of 50 mg/l concentration was used to optimise the pH value and amount of dose of clay ranging from 0.1 g to 1 g. The amount of heavy metal adsorbed per gram of adsorbent mass was calculated as follows:

$$q_e = \frac{(C_o - C_e) \times V}{m} \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Where C_o is the initial heavy metal concentration, C_e is the final concentration remains in solution after adsorption (mg/L), m is the clay mass (g), and V is the volume of solution (L).

Calculations were made using the equation (1) to obtain the adsorption isotherm curve for parametric study.

3. Results and Discussion

An experimental parametric study is carried out to determine the efficiency of bentonite clay in removing the lead. Results and discussions for the adsorption study presented here.

3.1 Effect of pH

To study the effect of pH on lead adsorption with Bhawnagar bentonite, metal solution 50 ml in volume and 50 mg/L in concentration were used at pH ranging from 2 to 10. The mass of clay is taken as 1 g. Agitation speed and contact time is fixed as 200 rpm and 2 hours respectively. Figure 1 shows that adsorption increases with increase in pH value and remains constant after pH value of 4. The adsorption phenomenon of bentonite is well explained by ion exchange/adsorption and precipitation (Altin et. al. 1999). Cations present in structure of bentonite with exchangeable ability are exchanged for Pb^{2+} cations in metal solution. At high pH there is formation of hydroxyl complexes of lead, they participate in adsorption and precipitates on bentonite. The optimized pH value is used for study of effect of other parameters like amount of clay, agitation time and speed. Figure 1 shows the effect of pH on removal of Pb^{2+} by bentonite.

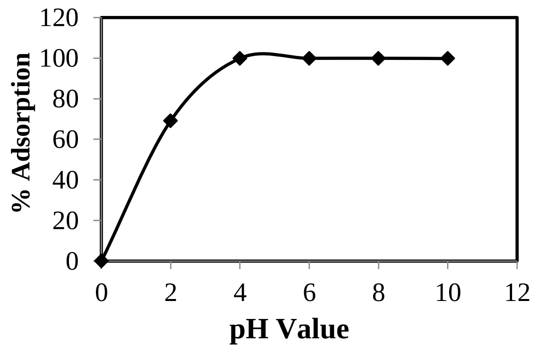

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Fig. 1 Effect of pH on adsorption [Dose = 1 g, Vol. = 50 ml, Speed: 200 rpm, Agitation time: 2 Hours, Initial Concentration = 50 mg/L]

3.2 Effect of clay dosage

This experimental study is carried out in order to determine the optimum amount of clay. At optimum pH of 6, initial metal concentration of 50 mg/L by varying the clay amount 0.1 g to 0.9 g. Results are presented in Figure 2.

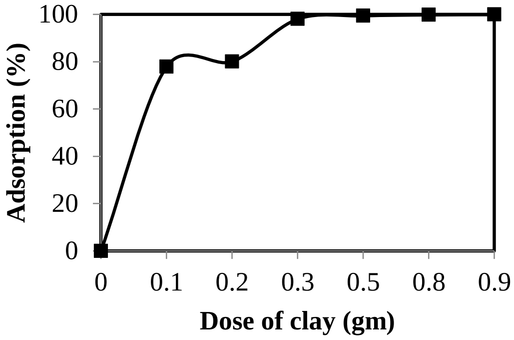

Fig. 2 Effect of dose of clay on adsorption [Vol. = 50 ml, Speed: 200 rpm, Agitation time: 2 Hours, Initial Concentration = 50 mg/L]

It is seen from the Figure 2 that as the clay dose increases the adsorption efficiency increases and this is due to increase of surface area of the adsorbent. The optimum dose of clay that can be used in removal of lead (Pb) is 0.3 gram/50 ml.

Table 2. Absolute experimental capacities for Pb^{2+}

Clay dose (g)	$q_{e\ (experimental)}$ (mg/gram)
	Pb^{2+}
0.1	19.45
0.2	10.43
0.3	8.24
0.5	4.97
0.8	3.12
0.9	2.77

Experimental capacities for lead (Pb) are given in Table 2. Further experiments were carried out using these selected values.

3.3 Effect of Initial Concentration

The optimization of metal concentration is determined by varying the lead concentrations from 1 mg/L to 180 mg/L. 1 g of bentonite clay added in 50 ml solution and it was shaken for 2 hours at 200 rpm. Figure 1 shows that lead removal efficiency increases due to adsorption effect to some extent. The lead removal efficiency slightly decreases from 35 mg/L. After attaining the saturation level, adsorption decreases as no more ions can be adsorbed. In this study we found that optimum value of metal concentration is 36.5 mg/L.

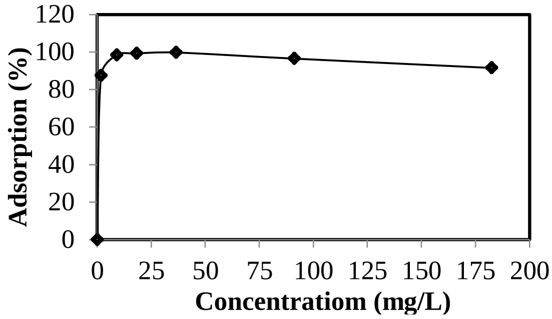

Fig.3 Effect of metal concentration on adsorption [pH= 6.7, dose = 1 g, Vol. = 50 ml, Speed: 200 rpm, Agitation time: 2 Hours]

3.4 Effect of agitation time

Agitation time is very important factor affecting the efficiency of adsorption. To study the removal efficiency of Pb^{2+} using bentonite, a analysis is carried out using the previously determined optimum value of pH, clay dose and initial concentration. In this batch study samples were taken at different interval ranging from 1 minute to 60 minutes. The results are shown in Figure 4. It is clear from Figure 4 that maximum adsorption occurs within 5 minutes. The optimized value of agitation time is 5 minutes after which the adsorption becomes constant.

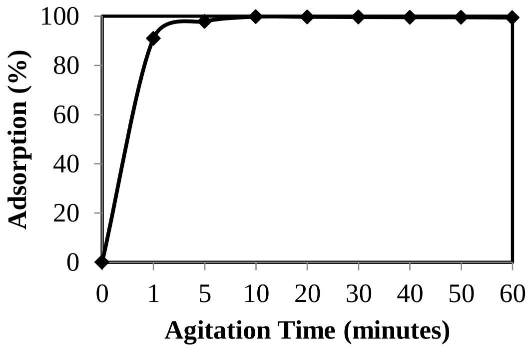

Fig. 4 Effect of agitation on adsorption [Dose = 0.3 gram, pH = 6, Vol. = 50 ml, Speed: 200 rpm, Initial concentration = 50 mg/L]

3.5 Adsorption isotherms

The process of adsorption is usually studied through a graph known as adsorption isotherm. It is the graph between amount of adsorbate (x) adsorbed on (m) mass of adsorbent and equilibrium concentration at constant temperature.

3.5.1 Langmuir isotherm

In 1916 Irvin Langmuir presented a adsorption model based on kinetic theory of gas with two basic assumption. This is based on assumption that a fixed number of accessible sites are available on the adsorbent surface and all of which have the same energy further adsorption is reversible. At the equilibrium, the rate of adsorption is equal to the rate of desorption. On the basis of this background he derived one mathematical equation and same is known as Langmuir equation as written below.

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Where C_e is the equilibrium concentration of the adsorbate, q_e is the adsorption capacity adsorbed at equilibrium, q_m is the maximum adsorption capacity and K_L is the Langmuir adsorption constant.

Langmuir equation can also be written in the following form:

$$\frac{1}{q_e} = \frac{1}{q_m K_L C_e} + \frac{1}{q_m} \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

The Langmuir constants can be determined from a plot of $1/q_e$ versus $1/C_e$

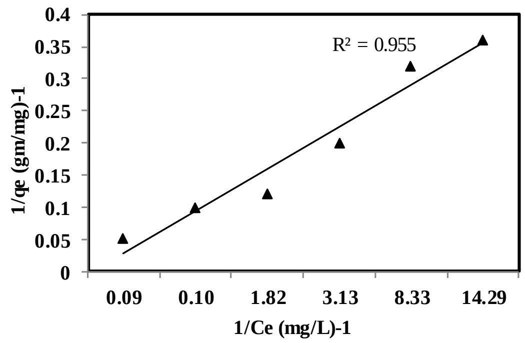

Fig. 5 Langmuir adsorption model for adsrption of lead (Pb) on bentonite.

The linear form of Langmuir adsorption model for lead adsorption on clay is given by the following equation 4.

$$\frac{1}{q_e} = \frac{0.065}{C_e} - 0.038, \quad R^2 = 0.955 \ldots\ldots\ldots\ldots\ldots (4)$$

From this equation (4), maximum adsorption capacity (q_m) of bentonite clay for lead (Pb) is 19.45 mg/gram and K_L is the 0.58.

Conclusions

Bentonite clay from Bhawnagar area can be utilized for lead removal from aqueous solution. The optimal experimental conditions for maximum lead removal was achieved at 6 g/L of bentonite clay and solution pH of 4. It has been observed that maximum adsorption occurs in within 5 minutes. Therefore, it can be said that adsorption is a spontaneous phenomenon. The kinetics study reveals that maximum adsorption capacity obtained from Langmuir adsorption model is 26.3 mg/gram and constant K_L is 0.58 with regression coefficient of 0.955. It was found that Langmuir adsorption model is fit well with experimental data.

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