

Adsorption of lead using a new green material obtained from *Portulaca* plant

A. Dubey · S. Shiwani

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Abstract In the present study the potential of a new green material obtained from *Portulaca oleracea* plant was investigated. The material was used without any chemical treatment to study the adsorption behavior of lead ions from aqueous solution. Various batch experiments were carried out using different experimental conditions such as pH, contact time, adsorbent concentration, and metal ion concentration to identify the optimum conditions. The influence of these parameters on the adsorption capacity was studied. Results showed the optimum initial pH for adsorption as 6. Adsorption equilibrium was reached in 120 min. The adsorption data were modeled using both the Langmuir and Freundlich classical adsorption isotherms. Results show ~78% removal of lead from aqueous solution. The kinetic data corresponded well with pseudo second-order equation. From the initial results, the green material obtained from the waste of *Portulaca* seems to be a potential low-cost adsorbent for removal of lead ions from water.

Keywords Adsorbent · Freundlich isotherms · Heavy metals · Kinetics · Langmuir

Introduction

Water is essential for very existence of life. Rapid industrialization is the major cause for wastewater generation.

Untreated disposal of this water into aqueous environment has increased the pollution beyond the admissible sanitary standards. Use of major 20 heavy metals has resulted in an increasing flux of metallic substance in natural source of water. Heavy metal ions are present in the effluents discharged from various industries like electroplating, battery, paint, plastic, paper manufacturing industries, and petrochemical process to name a few (Iqbal and Edyvean 2004, 2005). Heavy metal contamination may cause negative ecological effect (Micera and Dessi 1988). These are toxic even at very low concentrations. Heavy metals are stable elements; they cannot be metabolized by the body and passed in to the food chain. Lead is a major contaminant present in industrial effluents. Lead poisoning in human body can cause severe damage to kidney, nervous system, reproductive system, liver, and brain and may result in sickness or death. Severe exposure to lead has been associated with sterility, abortion, still birth and neonatal deaths, anemia, coma, mental retardation, and seizures (Zhang et al. 2005; Botkin and Keller 2000).

The removal techniques of heavy metal ions depend on the characteristic of the effluent. Different methods are used for metal removal such as coagulation, chemical precipitation, solvent extraction, electrolysis, reverse osmosis, and ion exchange. However, these techniques have certain disadvantages such as incomplete removal, high energy requirement and operational cost, use of chemicals, and generation of toxic sludge or other waste products that again require disposal. This all makes these processes impractical and adds to environmental damage (Brown et al. 2000) and (Han et al. 2006).

Adsorption is a term commonly used for several different processes involving physical as well as chemical interactions between the solid surface of a substance and a dissolved material. Adsorption is an economical and effective process

A. Dubey (✉)
Department of Chemistry, MMH College, Affiliated to CCS,
University Meerut-India, Ghaziabad 201009, India
e-mail: abhaadubey@gmail.com

S. Shiwani
Department of Applied Sciences, AKG Engineering College,
Affiliated to UP Technical University Lucknow,
Ghaziabad 201009, India



(Park et al. 2007; McKay 1996). Activated carbon is most widely used adsorbent (Dabrowski 2001; Kim et al. 2001). Due to its high cost, attempts have already been made to economize the preparation of activated carbon (Kuniawan et al. 2006). Preparation of activated carbon using natural materials also involves different type of chemical treatment, which again is not a green method. Chemically modified plant wastes were also used as adsorbents of heavy metals (Ngah and Hanafiah 2008). Among many biosorbents naturally available plant biomass (Manal 2007; Benhima et al. 2008) can be used as an inexpensive method for metal ion removal from synthetic solution and industrial effluents (Horsfall and Abia 2003; Singh et al. 2005; Zafar et al. 2007). Adsorption processes using natural adsorbents or agricultural waste products are becoming the new alternative for waste water treatment as they are cheap, simple, sludge-free, and involve small initial cost (Matheickal and Yu 1997; Chandra et al. 2003; Abdel-Ghani et al. 2007; Abdel-Ghani and El-Chaghaby 2007, 2008).

The search for innovative green ways for removal of heavy metals has forced attention on the use of new natural materials for removal of metal ions. There has been a push towards development of new environment-friendly (greener) low-cost techniques for treatment of industrial effluents. The aim of the present work was to highlight the use of a plant waste in removing lead ions from simulated samples.

This work was done at MMH College, Ghaziabad, India, and was completed in May 2010.

Materials and methods

Adsorbent

Portulaca oleracea is a herbaceous weed: phytochemical screening of plant revealed the presences of many biologically active compounds such as alkaloids, carbohydrates, flavonoids, amino acids, proteins, steroids, saponins, fixed oils, tannins, and phenolic compounds (Kokate 1986; Harborne 1998). Owing to the presence of many functional groups the plant material can be used as good adsorbents for removal of cations and anions from aqueous solutions. Plant material (leaves and stems) of portulaca plant commonly known as moss rose was collected and washed several times with tap water to remove all the dirt and any other extraneous depositions. This material was again thoroughly washed with double-distilled water, dried first in sun for 5–6 days, and then in microwave oven (LG domestic microwave oven, model no. MS-285SD, Korea, having temperature range 40–100°C) for about 15 minutes at 50°C (Magnetrons are set at a frequency of 2,450 MHz). This dried material was then ground and sieved to get uniform size particles (~355 nm). No other chemical

treatment was done. Powdered material was kept in air-tight containers, and used when required.

Adsorbate

All the chemicals used in experiments were of analytical grade. A stock solution was prepared by dissolving 1,000 mg of lead nitrate (Merck) in one liter of double-distilled water, and acidified with 10 mL of concentrated Nitric acid to prevent hydrolysis. The stock solution was diluted and used for different concentrations of lead ions required for the experiments.

Batch experiments

The experiments were carried out in the batch mode at room temperature (Abdel-Ghani et al. 2009), in 250-mL bottles. Each bottle contained 50 mL Pb(II) ion solution (1,000 ppm concentration). Fixed amount of adsorbent (0.2–1.4 g) with definite particle size (~355 nm) was added to the test solution. Bottles were shaken for a fixed period (30 min) at 100 rpm in a thermostatic shaker bath. The progress of adsorption was noted at different time intervals (20 min) till the attainment of equilibrium. Effect of contact time had been studied by many authors (Pandey et al. 2008; Selatnia et al. 2004). At definite time intervals separation of the adsorbent and solution was carried out by filtration with whatman filter paper number 41. Filtrate was stored in sample bottles in refrigerator prior to analysis. The concentration of residual lead ions was analyzed by Atomic Adsorption Spectrophotometer (GBC Avanta). The pH of the solution was adjusted to the required pH value range (2–7) by adding 0.1 M HCl or 0.1 M NaOH solution. Adsorption data obtained from the effect of contact time, pH, initial concentration of lead(II) ion, and dose of adsorbent, were employed in testing the applicability of different kinetic equations and isotherms. Blank samples were also run under similar conditions. Each experiment was repeated and the results taken as averages.

Results and discussion

Effect of contact time and adsorption kinetics

Adsorption capacities of metal ion were measured as a function of time (10–200 min) keeping the initial concentration of Pb(II) ion constant (500 mg) and varying adsorbent dosages (0.2–1.4 g). The effect of contact time on adsorption of Pb(II) ions is shown in Fig. 1. The adsorption equilibrium was obtained in 120 min. The plot shows percentage adsorption increased with increase in contact time and reached to a constant after 120 min. So the time was



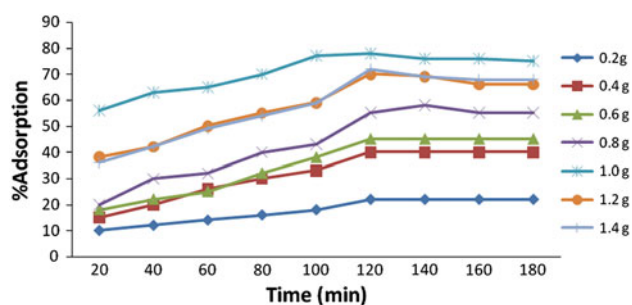


Fig. 1 Effect of contact time on adsorption

selected as 120 min for further experiments. Major adsorption was done in initial 30 min. This may be due to the fact that number of active adsorption sites on the surface of adsorbent was more initially. Adsorption rate slowed down at later stages, may be due to lesser number of available active sites; adsorbate was transported from the outer surface to the inner surface of the adsorbent particles. Similar results have been reported in literature (El-Ashtoukhy et al. 2008; Al-Anber Ahmed and Matouq Dayeh 2008). Contact time is an important factor for economical adsorption.

Kinetic studies provide the information about the mechanism of adsorption and suitable optimum conditions for batch process. Adsorption kinetics which describes the adsorbate adsorption rate is an important characteristic in evaluating the efficiency of adsorption. Figure 1 shows that kinetics of adsorption of lead occurs in two phases: first phase was rapid and the second was slower where equilibrium was achieved; first phase is related to external surface adsorption and adsorption occurs instantaneously. Second phase indicates gradual adsorption before equilibrium. According to literature (Bhattacharrya and Gupta 2006) initial high rate of metal uptake could be due to the bare surface of adsorbent. Later on available adsorption sites decreases as Pb(II) ion adsorption increases (Table 1).

Pseudo first-order and pseudo second-order adsorption kinetic models have been used to study the experimental data. Lagergren Pseudo first-order model assumes that the rate of change of solute uptake with time is directly proportional to difference in saturation concentration and amount of solid uptake with time:

Table 1 Adsorption capacity of various adsorbents for Pb(II) ions

Adsorbent	q (mg/g)	References
Leaf powder of rubber	46.73	Hanafiah et al. (2006)
Phosphatic clay	37.2	Singh et al. (2001)
NaOH-treated spent grain	35.5	Low et al. (2000)
Commercial activated carbon	5.9	Kannan and Veemaraj (2009)
Portulaca plant biomass	17.24	Present study
Typha leaf powder	0.65	Abdel-Ghani et al. (2009)

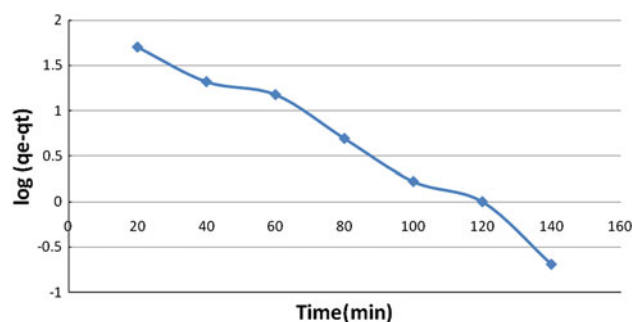


Fig. 2 Pseudo first-order kinetics plots for the adsorption

$$dq_t/dt = k_1(q_e - q_t)$$

where q_e and q_t are amount of adsorbate (mg/g) at time t and at equilibrium, respectively, k_1 is the rate constant of pseudo first-order adsorption. The integrated form of equation is

$$(q_t/q_e) = 1 - \exp(-k_1 t)$$

Linear plot of $\log(q_e - q_t)$ versus t suggests the applicability of pseudo first-order kinetic model (Lagergren 1898). The rate constant k_1 and equilibrium amount of metal ion q_e can be obtained from the slope and the intercept of plot (Fig. 2). Correlation coefficient for the pseudo first-order was 0.978. The calculated value of k_1 and q_e was 0.019/min and 8.79 mg/g, respectively.

The pseudo second-order model (Ho and McKay 1999) is based on sorption capacity of solid phase.

$$dq_1/dt = k_2(q_e - q_t)^2$$

where k_2 is rate constant of pseudo second-order adsorption (g/mg/min). The integrated linear form of equation is

$$(t/q_t) = 1/k_2 q_e^2 + t/q_e$$

This is the linear form of Ho second-order model. The plot of t/q_t versus t (Fig. 3) shows the kinetic data of adsorption of lead ions on adsorbent. The good fit of kinetic data in second-order rate expression shows excellent linearity with high correlation coefficient R^2 .

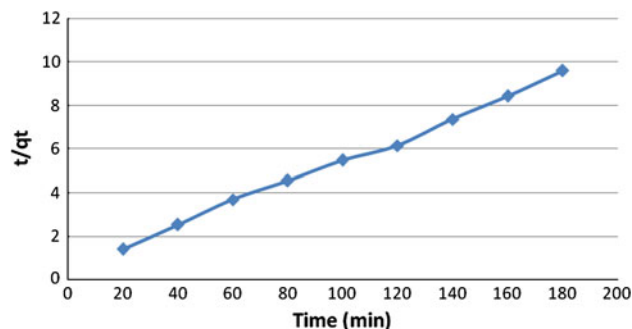


Fig. 3 Pseudo second-order kinetics plot for adsorption



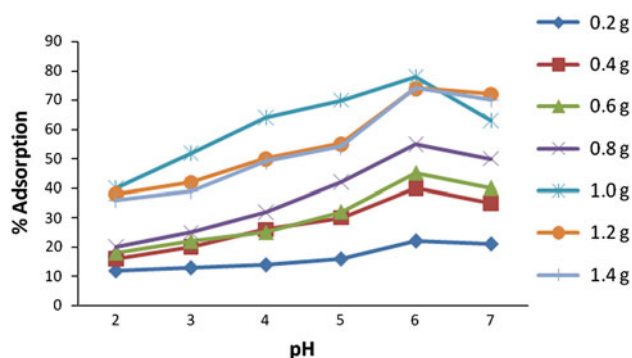


Fig. 4 Effect of pH on adsorption

The rate constant k_2 and equilibrium amount of metal ion q_e can be obtained from the slope and the intercept of plot (Fig. 3).

The value of k_2 , q_e was calculated as 0.0045 (g/mg/min), 20.408 (mg/g). The correlation coefficient for the pseudo second-order was 0.996 (Fig. 3). Indicating the applicability of the second-order model. Results are similar to previous experiments (Hanafiah et al. 2006).

Effect of pH

To study the effect of pH, experiments were done by keeping the initial Pb(II) ion concentration constant and varying the adsorbent dosages as (0.2–1.4 g). The effect of pH (range 2–7) on adsorption of Pb(II) ions is shown in Fig. 4. pH of the solution is an important controlling parameter in the adsorption process. Adsorption increased continuously with the decrease in acidity until it reached maximum adsorption at pH 6. It may be due to active adsorption sites remain protonated at low pH, and become less available for metal ion adsorption. As pH increases, the concentration of H^+ ions decreases, hence they do not compete with metal ions on the adsorption sites. The adsorbent surface with $-ve$ charge will easily attract the positively charged Pb(II) ions. Optimum pH was selected as 6 for further experiments. At higher pH lead hydroxide starts precipitating from the solution, making actual adsorption studies impossible.

Effect of adsorbent dose

Adsorbent dose has a significant influence on the percentage adsorption. Figure 5 shows the effect of adsorbent dose on adsorption of Pb(II) ions (range 0.2–1.4 g). The increase in adsorbent dose resulted in increase in adsorption up to a certain dose which then seemed to remain almost constant. Maximum adsorption occurs at an adsorbent dose of 1.0 g and this was fixed as optimum dose. Results can be explained by the fact that more surface area is available for

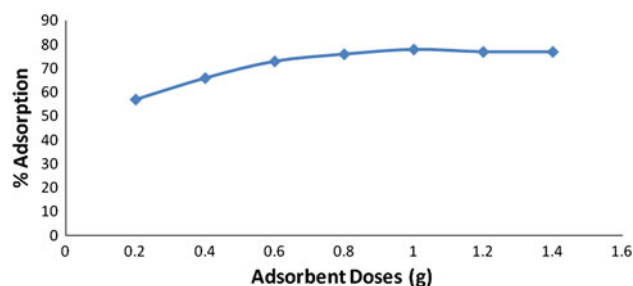


Fig. 5 Effect of adsorbent dose on adsorption

adsorption to occur, as number of available active adsorption sites increases by increasing the adsorbent dose.

Effect of initial concentration of metal ions

The effect of initial concentration on percentage removal of Pb(II) ions (range 100–600 mg/L) is shown in (Fig. 6). It can be seen that percentage adsorption of lead ion increased with increase in initial concentration up to a certain amount, and then it shows no further effect on adsorption. Maximum adsorption takes place at 500 mg/L of lead ion concentration. This can be explained as follows: at low initial concentration the ratio of number of metal ions to the number of available adsorption site was small and consequently the adsorption was independent of initial ion concentration, but as the concentration of metal ion increased, the situation changes and the competition for adsorption site becomes less. As a result, the extent of adsorption decreases, or remains constant.

Adsorption isotherms

An adsorption isotherm is characterized by certain constants; their values express the surface properties and affinity of the adsorbent. To measure the isotherm, initial lead ion concentration was changed and the weight of the adsorbent was kept fixed. The experimental data for the uptake of lead ions were processed in accordance with two most widely used Langmuir and Freundlich classical adsorption isotherms. The Langmuir expression is valid for

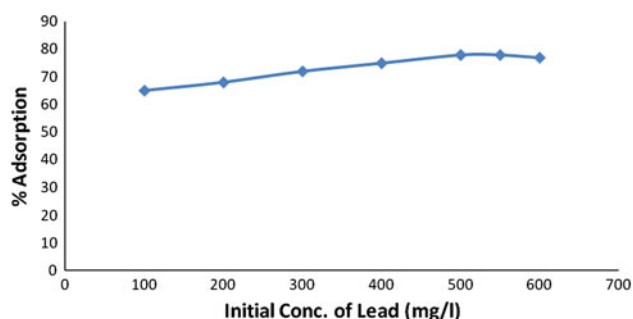


Fig. 6 Effect of initial metal ion concentration on adsorption

monolayer adsorption on to a surface with finite number of identical sites.

Langmuir isotherm: $1/Q_e = 1/(q \times bC_e) + 1/q$, where Q_e is the concentration of adsorbed metal per unit weight of adsorbent, C_e is the concentration of Pb(II) ions in the aqueous phase, q is the maximum adsorption capacity per unit weight of adsorbent, b is the adsorption equilibrium constant.

Equilibrium data for the adsorption is plotted as $1/Q_e$ versus $1/C_e$, according to the Langmuir isotherm. The two constants q and b are calculated from the slope ($1/qb$) and intercept ($1/q$) of the line, respectively.

The Freundlich expression is empirical equation based on adsorption on a heterogeneous surface. The equilibrium isotherm data were also characterized by Freundlich equation.

Freundlich isotherm: $Q_e = KC_e^{1/n}$, where K and n are empirical constants indicative of adsorption capacity and intensity, respectively. The Freundlich parameters were obtained by fitting the experimental data to the linearized equation (plot of $\log Q_e$ against $\log C_e$). Results are presented in Figs. 7 and 8. Equilibrium data obtained were fitted to both the isotherms.

The result of regression analysis for calculating the parameters of Langmuir and Freundlich equations shows that the value of q (maximum adsorption capacity per unit weight of adsorbent) for Langmuir is 17.24 mg/g, whereas the value of b (the adsorption equilibrium constant) is 0.0045 L/mg. Whereas for Freundlich equation value of K is 0.013 mg/g, the value of n is 0.658.

The co-efficient of co-relation (R^2) was found to be as high as 0.997 and 0.986 for adsorption of lead ions. These results showed that the equilibrium adsorption data of lead conformed well to both the isotherms; however, higher value of R^2 indicates Langmuir as the more favorable model. The essential characteristic of Langmuir isotherm can be shown in terms of R_L (dimensionless separation parameter) which is indicative of isotherm shape that predicts whether an adsorption system is favorable or unfavorable. R_L is defined as (Webi and Chakravort 1974)

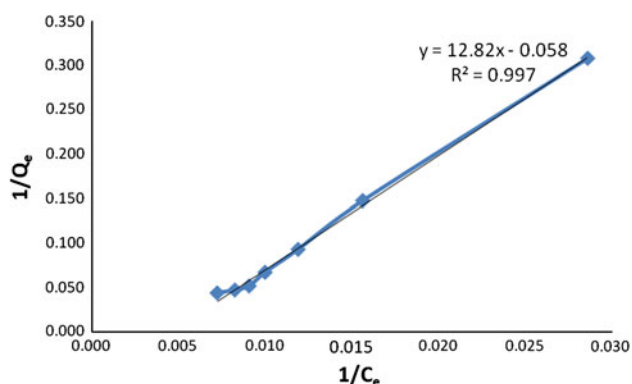


Fig. 7 Langmuir adsorption isotherm

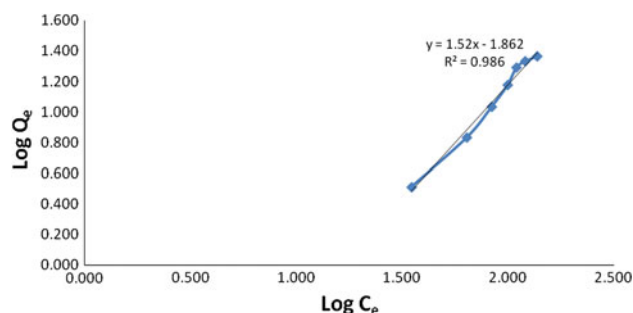


Fig. 8 Freundlich adsorption isotherm

$$R_L = 1/(1 + b \cdot C_0)$$

where b is Langmuir constant and C_0 is initial concentration of Pb(II) ion.

The adsorption process as a function of R_L may be described following Chakravarty et al. (2009): if $R_L > 1$ unfavorable, $R_L = 1$ Linear condition, $0 < R_L < 1$ favorable condition, and $R_L = 0$ irreversible condition. R_L lies between 0 and 1 which is 0.325 and which indicates the favorable adsorption of Pb(II) ions.

Conclusion

The results obtained in the present study showed that dried *Portulaca* plant material can efficiently remove lead ions present in the aqueous solution. The removal percentage of the lead ions was dependent on the contact time, adsorbent dose, concentration of lead ion, and pH of solution. The results showed that adsorption is a pH-dependent process and the maximum adsorption occurs at pH 6. Equilibrium was attained in 120 min. The kinetic study of adsorption at pH 6 and room temperature indicates that pseudo second-order model has better correlation than first-order model. Langmuir and Freundlich isotherms were found to represent well the obtained data. This new green material obtained from *Portulaca* plant was found to be a good adsorbent for the removal of lead ions from aqueous solution and may potentially be used for removal of other heavy metal ions. Use of such waste green materials represents an effective and environmentally clean way of utilization of waste water.

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