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Biosorption Of Lead (Pb^{+2}) From Aqueous Solution On Cordia Dichotoma L Biomass

Panchanana Gouda, A.J.Pattanayak, Prachi Pragyan Gouda, Chakrapani Patnaik

Post Graduate Department of Chemistry, Khallikote University, Berhampur, Odisha, India 760 001
Department of Chemical Engineering, BITS, Pilani, India
Email: pngouda18@gmail.com

ABSTRACT: A method is described for the Biosorption of Pb^{+2} from aqueous solution as well as natural water samples by using biomass prepared from the seed powder of Cordia dichotoma. Parameter such as pH, bio-adsorbent dose, contact time and concentration of the metal ion in the solution were investigated. The adsorption equilibrium data were tested by the commonly used two parameter equations such as the Langmuir and Freundlich adsorption isotherms. The results indicated that the data of Pb^{+2}adsorption on to biomass of Cordia dichotoma fits to the Freundlich model. The adsorption capacity (Qm) calculated from the Langmuir adsorption isotherm was 0.02 mg Pb^{+2} g-1 at a pH of 7. Adsorption kinetics data were analysed using the pseudo first order and pseudo second order equations. The graphs showed that the experimental data suited well to pseudo second order model. XRD spectrum of the Cordia dichotoma powder showed the presence of the fine crystals which help for the best adsorption of Pb^{+2} ions. The FT-IR spectral analysis revealed the presence of hydroxyl and carbonyl functional groups which are chelated in the bioadsorbent. It is very much effective in removing Pb+2 ion from water in presence of common metal ions like Na^{+} , K^{+}, Ca^{+2} and Mg^{+2} etc.

Keywords : *Cordia dichotoma*; bioadsorbent; Langmuir and Freundlich adsorption isotherms; adsorption capacity; chelation.

1 INTRODUCTION

Toxic metals enter surface water from a variety of sources including industrial discharges, domestic sewage, non-point runoff, urban storm runoff and atmospheric precipitation. Due to their toxicity, accumulation in food chain & persistence even at low concentrations these metals are harmful to living organisms and cause biological disorders [1]. The elements having atomic weight in the range of 63.5 to 200.6 and specific gravity greater than 5.0 are referred as heavy metals [2]. Many heavy metal ions are known to be toxic or carcinogenic. Toxic heavy metals of particular concern include zinc, copper, nickel, mercury, cadmium, lead and chromium [3]. Lead (Pb) is a toxic heavy metal that can cause serious damage to the liver, brain, kidney, reproductive and nervous system. Severe exposure to Pb(II) has been associated with sterility, abortion and neonatal deaths [4],[5],[6]. The major source of Pb(II) pollution in natural waters is due to discharge of waste from acid battery manufacturing, metal plating and finishing, printing, metallurgical alloying, lead mining, ceramics and glass industries [7],[8],[9],[10]. The permissible limit (mg/L) for Pb(II) in wastewater given by Environmental Protection Agency (EPA) is 0.05 mg/L and by Bureau of Indian Standards (BIS) is 0.1mg/L [11]. Owing to the toxic effects, the industries are advised that the waste waters be treated systematically to remove or minimize the metal contents in their wastes. The removal of Pb(II) from wastewaters by traditional processes includes its precipitation with lime or alkali hydroxide, coagulation, electrolytic deposition, reverse osmosis and ion exchange. Moreover, there are concentration limits to which these methods are economical and become ineffective or too expensive to treat wastes having metal ions in concentrations of 100 mg/L or below [12]. Hence, there is a constant need to search for an optimal technology while considering its cost, materials employed and its efficiency. Removal of toxic heavy metals to an environmentally safe level in a cost effective and environment friendly manner assumes great importance [13]. Biosorption of heavy metals from aqueous solution can be considered as an alternative technology in industrial waste water treatment [14]. This process uses organic materials as biosorbents. Biosorption of contaminants by sorbents of natural origin has gained popularity recently due to its good performance, high uptake capacity and low cost. Various plant materials such as waste tea leaves [15], sphagnum moss peat [16], sago waste [17], Medicago sativa [18], peat [19], Quercus ilex leaf, stem and root phytomass [20], sawdust [21], rice polish [22], Azadirachta indica leaf powder [23], Caladium bicolor biomass [24], Oryza sativa husk [25],maize bran [26], palm shell activated carbon [27], olive pomace [28], maize leaf [29], saw dust [30], coconut and seed hull [31], Strychnos potatorum seeds[32] have been studied for Pb+2 removal from aqueous system. Similarly coconut shell [33], dry cells of Rhizopus arrhizus [34], brown sea weeds [35], dried algae [36] and amine based ligand [37] have been reported for Cd removal from aqueous system. Cordia dichotoma is a plant species in the genus Cordia. It is called gunda or tenti in Hindi and lasura in Nepali [38]. Cordia dichotoma L. (Family: Boraginaceae) is a tree of tropical and subtropical regions. It is a medium sized tree with short crooked trunk, leaves simple, entire and slightly dentate, elliptical-lanceolate to broad ovate with round and cordate base, flower white, fruit drupe, yellowish brown, pink or nearly black when ripe with viscid sweetish transparent pulp surrounding a central stony part [39]. It is used as immunomodulator, antidiabetic, anthelminitic, diuretic and hepatoprotective in folklore medicine. Cordia dichotoma seeds have disclosed the presence of α-amyrins, betulin, octacosanol, lupeol-3-rhamnoside, β-sitosterol, β-sitosterol-3-glucoside, hentricontanol, hentricontane, taxifolin-3,5-dirhmnoside and hesperitin-7-rhamnoside [40]. The seed contains α- amyrin and toxifolin-3,5-dirhamnoside which shows significant anti-inflammatory activity by an oral dose of 1gm/kg in albino rats [41]. The seeds of this plant reported to contain fatty acids and flavonoids [40]. In addition to its medicinal properties the seed powder is being used for clearing muddy water by the rural community. They are reported to be very effective as coagulant aids. This property is attributed because of the presence of polyelectrolyte, proteins, lipids, carbohydrates and alkaloids containing the –COOH and free –OH surface groups in the seed [42]. Having established the coagulating properties of the Cordia dichotoma seeds there has been a recent interest in the metal binding property [43]. The aim of the present study is to determine the efficiency of Cordia dichotoma seed powder in removal of heavy metal Pb(II). The influence of pH, biomass dose, contact time and initial concentration of metals on biosorption of Pb(II) ions were studied in aqueous solutions.

2 Materials & Methods

2.1 Preparation of Pb(II) stock solution

All the chemicals used in the experiments were of analytical grade. Stock Pb(II) solution (1000 mg/L) was prepared by dissolving 1.5984 g of $Pb(NO_3)_2$ (Qualigens Fine Chemicals, Mumbai; minimum assay 99%) in 100mL of Milli-Q (Millipore) water and the final volume was made quantitatively to 1000 mL. Pb(II) solutions of different concentrations were prepared by adequate dilution of the stock solution with Milli-Q water. pH of the solutions was adjusted with 1N HNO3 or 1N NaOH. All the glassware and polypropylene flasks used were washed with 10% (v/v) HNO3 and rinsed several times with deionized distilled water. All the glassware and polypropylene flasks used were washed with 10% (v/v) HNO3 and rinsed several times with deionized distilled water.

2.2 Plant material

Cordia dichotoma seeds were collected from forests of Odisha and were dried at 40 ◦ C for 2 days in hot air oven. Seeds were made into powdered form, sieved and used as a biosorbent.

2.3 Batch Experiments

The influence of pH on Pb^{2+} ion biosorption was studied by introducing 0.5g of adsorbent into 250 mL conical flasks containing 50 mL of 50 ppm lead solution. 0.1M NaOH and 0.1M HCl were used to adjust the pH during the study. The pH range of interest was 4 – 8 and three hours was the duration of the agitation at 200 rpm. After agitation, the solution was filtered using Whatman-42 filter paper and centrifuged. Then they were refrigerated until the metal ion analysis was done.

2.4 Effect of biosorbents dosage

Different amount of biosorbent dose ranging from 0.3 g/L – 0.7 g/L of biosorbent were added to each Pb(II) solution in 100 mL Erlenmeyer flask, while keeping the pH 7.0, contact time 180 minutes and concentration of the Pb(II) ions 50 mg L−1. The samples were subjected to constant shaking using orbital shaker at 175 rpm for 180 minutes.

2.5 Effect of pH

For effect of pH experiment, concentration 50 mg L−1 each of Pb (II) ions, 0.5 g/L of biosorbent dose in 100 mL metal solution with varying pH from 4.0 to 8.0. The sample was shanked using orbital shaker with 175 rpm for 180 minutes.

2.6 Effect of contact time

Effect of contact time was studied at optimum pH 7.0; constant metal concentration 50 mg L−1, biosorbent dose 0.5 g/L in 100 mL of the solution. The samples were subjected to constant shaking using orbital shaker at 175 rpm and fixed volumes were taken after 30, 60, 90, 120 and 180 minutes for analysis.

2.7 Effect of initial concentration

Concentrations ranging from 20 ppm – 70 ppm were used for the pH study. Time for agitation was 3 hours while aqueous solution was maintained at pH 7. The percentage adsorption was determined using the equation:

[C0 - Ca/ C0] X 100
Where Co = is the initial concentration of solution, Ca = concentration of solution after adsorption.

2.8 FT-IR Analysis

The FT-IR of the powdered sample was taken before and after adsoption of Pb+2. Strong absorption peaks were obtained at1680 cm-1 and 3596 cm-1 of the fresh sample but the intensity of the peaks diminished after adsorption. XRD of the sample was taken before and after the adsorption, Fig.1 and Fig.2.

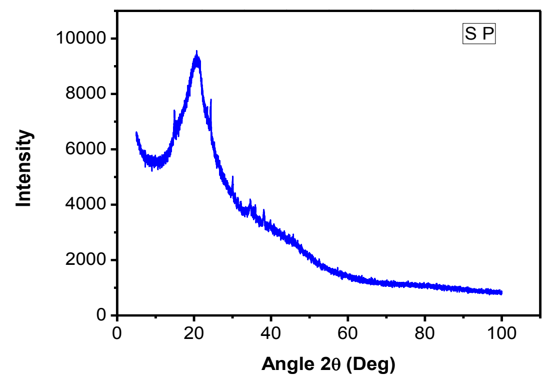

Fig.1. *XRD of unloaded seed powder of Cordia dichotoma L.*

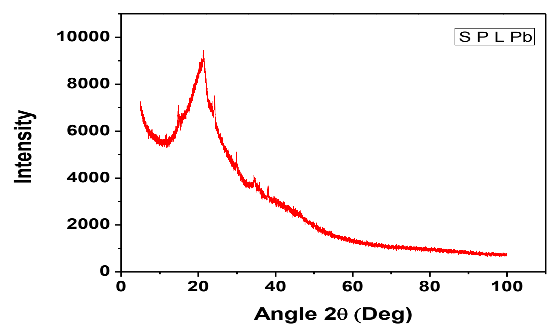

Fig.2. *XRD of lead loaded seed powder of Cordia dichotoma L.*

3 Results and Discussion

3.1 Effect of pH on metal ion binding

The pH of the aqueous solution plays an important role in the adsorption process [46]. In order to establish relation bet. Effect of pH on Pb(II) adsorption onto Cordia dichotoma seeds, the pH of solution was varied from 4.0 to 8.0. From Fig. 3, it is observed that the adsorption of Pb(II) varies with pH and there is a gradual increase in Pb(II) uptake with varying in the pH from 4.0 to 8.0. The maximum uptake of these ions was obtained at pH 7.0 (94.58% for Pb^{+2}) at 180 minutes. At pH below 5.0 uptake of ions were less probably because the H_3O^+ ions may compete with the metal ions for the exchange sites in the sorbent. One of the reasons for the metal ions adsorption behavior of the biosorbent is that the biomass

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contains a large number of active functional groups [44 - 45] as well as on the nature of the metal ions in solution. When pH is increased (above pH 7), the metal ions get precipitated due to formation of metal hydroxides. For this reason, the optimum pH was selected to be 7.0 for further experiments.

3.2 Effect of biomass

Biomass is a significant factor to be considered for effective metal sorption. When Pb(II) removal at different adsorbent doses (0.300 to 0.700 mg/L) was studied at pH 7.0 while keeping the volume and concentration of the metal solutions constant. The results have been presented in Fig. 4. It is evident that percentage adsorption of Pb(II) ion increased with increase in adsorbent dose. The resulting effect can be easily explained by an increase in surface area (more availability of active adsorption sites) with the increase in biosorbent mass which is evident from the XRD. Similar behaviour for the effect of sorbent concentrations on metal sorption capacity was observed and discussed in the literature for a variety of sorbents and metals [47-50].

3.3 Effect of contact time

The effect of contact time on the adsorption of Pb(II) at 50 mg/L is shown in Fig.5. The maximum removal of Pb(II) occurs at 360 minutes.

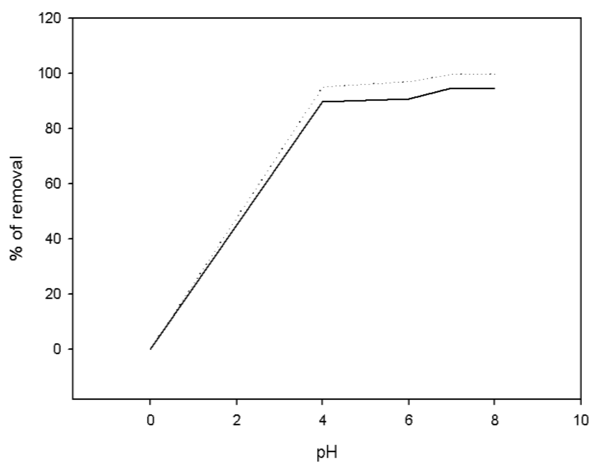

Fig.3. *Variation of adsorption with pH.*

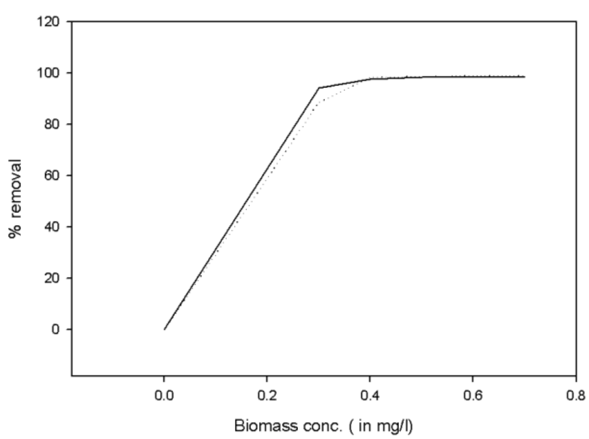

Fig.4. *Variation of adsorption with biomass concentration*

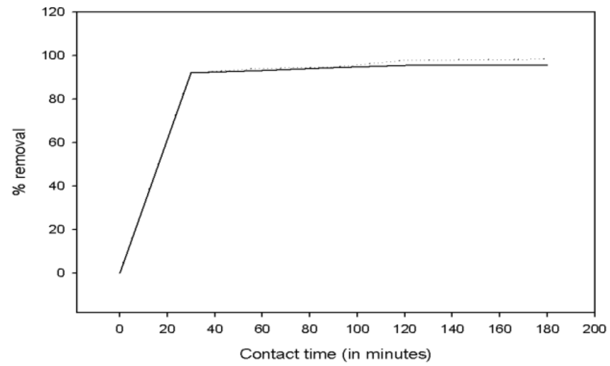

Fig.5. *Variation of adsorption with contact time*

4 CONCLUSION

From the present study it is concluded that the biomass of Cordia dichotoma seeds serve as a good bioadsorbent of Pb^{+2} ions from the aqueous solution. With the variation of pH, Contact time, Biomass concentration and increase in the concentration of the metal ion in the test solution the degree of adsorption increased.

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