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Research Article

Uptake Capacity of Pb^{2+} by Sulphonated Biomass of *Cicer arietinum*: Batch Studies

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Fundamental investigation on the removal of heavy metal Pb^{2+} from aqueous solutions by sulphonated biomass (S-III) of *Cicer arietinum* is conducted in batch mode. The effect of different parameters such as contact time, sorbent dose, pH and temperature has been studied. Adsorption kinetic modeling data were found. The kinetics of biosorption results shows that sorption process is well explained by pseudo-second-order model with determination coefficients 0.998 for S-III under all experimental conditions. The sorption mechanism was determined by Weber and Morris intraparticle diffusion model. Thermodynamic parameters, namely, K_D and ΔG, have also been calculated to determine the spontaneity of the process.

1. Introduction

The process adsorption is found to be, highly effective, cheap, and easy method. Active carbon in most cases has been used as adsorbent for reclamation of municipal and industrial wastewater for almost the last few decades, but the high cost carbon has inspired investigation to search for low cost agriculture waste as adsorbents. A batch study was carried out by Ncibi et al. on biosorption of textile dyes [1] from aqueous solutions using *Posidonia oceanica* leaf sheath fibres. The uptake capacity of chromium(VI) by nitrated and sulphonated Coconut shell carbon [2] was studied by Selvi and Jeyanthi. A sorption study of Al^{3+}, Co^{2+}, and Ag^{+} in aqueous solutions by Fluted pumpkin [3] waste biomass was carried out by Jnr and Spiff. Girgis and Ishak have been worked on activated carbon from cotton stalks [4] by impregnation with phosphoric acid. Farooqui et al. reported the use of leaves of cauliflower [5] for removal of iron from wasterwater. Removal of Fe^{2+}, Zn^{2+}, and Mg^{2+} from polluted water using thioglycolic modified oil-palm fibre [6] was done by Akaniwor et al. who worked on adsorption of dyes, chromate, and metallic ions by poly(ethyleneimine) [7]. Adsorption behavior of Cd^{2+}, Pb^{2+}, Ni^{2+}, Cd^{2+}, and Zn^{2+} from aqueous solutions by *Mangifera indica* [8] seed shell was reported by Ajmal et al. Choy and Mckay studied the rate of adsorption of cadmium [9], copper, and zinc ions onto bone char in three single component systems using an agitated batch adsorbent rice straw, soybean hull, sugar bagasse. The biosorption of cadmium and lead ion from artificial aqueous solution using waste baker's yeast biomass [10] was investigated by Goksungur et al. Akar et al. carried out a study on Pb^{2+} accumulation on the surface of Botrytis cinerea [11]. Padmavathy et al. worked on the biosorption of nickel(II) ions by deactivated protonated yeast [12]. Partially converted crab shell waste which contains chitosan was used by Pradhan et al. to remove nickel from water [13]. Mirtezky et al. studied the mechanism of simultaneous metal removal Cd(II), Ni(II), Cu(II), Zn(II), and Pb(II) by three macrophyte biomass . Biosorption of nickel(II) and copper(II) ions from aqueous solution by dried *Streptomyces coelicolor* Al(II) [14] was studied by Ozturk et al. as a function of concentration, pH, and temperature. Tarley and Arruda characterized the rice milling byproducts [15] used for removing Cd(II) and Pb(II) ions from effluents. Li et al. worked on comparison between biosorption of Pb^{2+} ions and Cd^{2+} by the biomass of *P. chrysosporium* [16]. Othman and Amin have used the *Rhizopus oligosporus* biomass for the biosorption of Cu^{2+}, Mn^{4+}, and Zn^{2+} at the maximum adsorption rate [17].

Marshall and Johns evaluated the sorption properties of deflated rice bran, soya bean, and cotton seed hulls and their resistance to mechanical abreation [18]. Periasamy and Namasivayam used the agricultural waste activated carbons and reported that the carbon prepared from the waste is successfully employed for the removal of Ni(II) from wastewater [19]. Subramaniam and Cooner have reported lead [20] contamination of drinking water and utilization of fly ash and waste tea leaves as decolorizing agent for dye effluents. Ahalya et al. have studied adsorption of heavy metal ions on carbonaceous material developed from waste slurry of fertilizer plants, biosorption of chromium(VI) from aqueous solutions by the husk of Bengal gram [21] (*Cicer arietinum*). The toxicity of hexavalent chromium from the discharge of various industrial wastes is well studied by Singh and Lal [22]. The heavy metal Pb^{2+} present in high concentration in the waste of industries like pharmaceutical, paint, pigment, insecticide, cosmetics, and polymer, and so forth causes serious problems to the environment. The Pb^{2+} reported by the World Health Organization is highly toxic to human life, and other heavy metals are reported to be bioaccumulated into flora and fauna creating ecological problems.

2. Experimental

2.1. Preparation of Biosorbent. The sieved biomass of *Cicer arietinum* was taken in a beaker and soaked in AR concentrated sulphuric acid (Loba Chemicals) for 2 hours. It was then washed thoroughly with distilled water till the black mass was acid free. The black mass was then dried at 110°C in the oven for 3 hours. The material sieved through 63 mm mesh to get particles of uniform size of S-III. The present work deals with the study of adsorption of heavy metals Hg^{2+} ions on chemically treated biomass of *Cicer arietinum* S-III.

2.2. Adsorption Experiments. A standard solution of $Pb(NO_3)_2$ (Loba Chemicals) of strength 0.00202 gm Pb^{2+}/mL was prepared (solution A). The 50 mL of solution A and 50 mL of distilled water were taken in a conical flask maintained at constant temperature in a thermostat. To this 500 mg of the appropriate sorbent S-III was added; it was stirred for 2.5 minutes and then filtered. The same procedure was followed for time intervals 5.0, 7.5, 10, 15, 30, 90, 120, and 180 minutes. Similar experiments were repeated using different material doses 1.0 g, 2.0 g, and 5.0 g. Amount of lead in the filtrate was determined by titrating against standardized EDTA (Loba Chemicals). The effect of contact time, temperature, pH of solution, and material dose on removal of the Pb^{2+} ion was studied.

3. Results and Discussion

3.1. Effect of Time on Adsorption of Pb^{2+} by S-III. A study of effect of time on adsorption of lead shows that with increase in time the adsorption increases and equilibrium is attained after 2 hours (Figure 1). Uptake of lead at equilibrium time, two hours for 500 mg S-III, is 40.0%. The percentage of adsorption of Pb^{2+} ion from its solution of concentration 200 mg/dm^3 was found to be 71.10%.

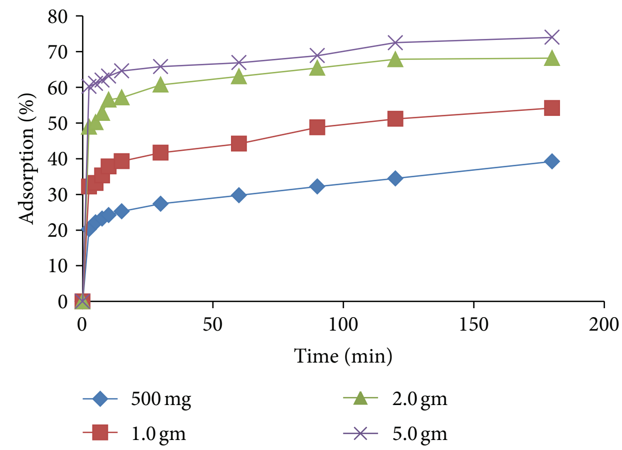

FIGURE 1: Effect of time on percentage of adsorption of Pb^{2+} by S-III.

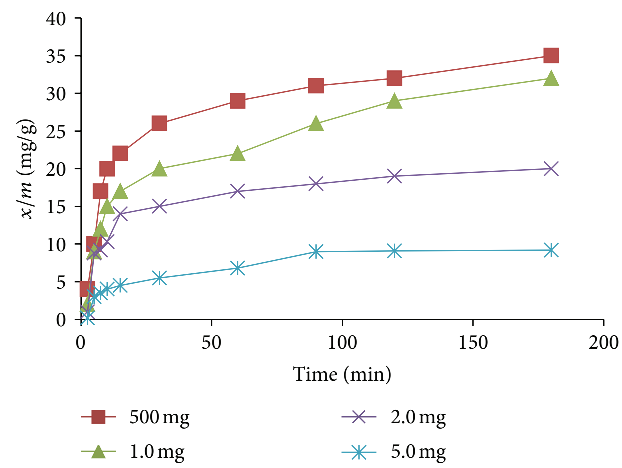

FIGURE 2: Plot of adsorption capacity versus time for Pb^{2+} by S-III.

3.2. Effect of Material Dose. The adsorption capacity decreases with material dose. S-III shows a decrease in x/m from 32 mg/g to 6.1 mg/g. Increase in the material dose from 500 mg to 5 g/100 mL shows increase in percentage of age adsorption but a decrease in adsorption capacity (Figure 2). A fixed amount of sorbent has a fixed number of sites for adsorption; amount increases the total number of sites available for adsorption increase. When a solution comes in contact with the larger mass of sorbent, the Pb^{2+} ions rapidly interact with maximum sites on the surface. This leads to a reduced population of the metal ions per unit mass of the sorbent compared to that when a smaller mass of sorbent is used. Effectively we find that percentage adsorbed has increased but the amount adsorbed per unit mass of sorbent has reduced.

Table 1

Temperature in K	K_D	ΔG (J/mole)
288	1.61	−1124
298	2.29	−2023
308	3.46	−3131
318	3.8	−3468

3.3. Effect of pH. pH of the solution influences electrostatic binding of the ions to the corresponding sites. It also influences the site dissociation and also the solution chemistry of the heavy metals such as hydrolysis, binding by organic and inorganic ligands, and redox reactions. The extent of functional groups on the sorbent and the nature of the cationic species are also affected by changes in the pH of the solution. The adsorption of the Pb^{2+} on S-III increases as the pH is increased from 2 to 6 thereafter decreases when pH is raised to 7; the % adsorption decreases from 74% (pH = 6) to 70% (pH = 7) (Figure 3). At low pH protons would compete with metal ions for the active sites responsible for the biosorption and decrease the metal sorption. At pH less than 2.0 all the binding sites may be protonated and thereby even desorb all metal bound to the biomass. As pH increases, the concentration of protons decreases, allowing more metal to be adsorbed. As a general rule, the acidic dissociation constant of an aquometal ion is greater; greater is its oxidation state. The hydroxide/hydrous oxides of metal in 2+ oxidation state [16] have a tendency to undergo hydrolysis beyond pH = 6, effect of pH on percentage of adsorption of Pb^{2+} by S-III.

3.4. Effect of Temperature. The study of adsorption of Pb^{2+} under optimum conditions which revealed that with increase in temperature there is a substantial increase in percentage of adsorption by S-III also shows an increasing trend in adsorption with rise in temperature. Sorbent III shows enhancement in adsorption from 54% to 76% as the temperature is increased from 15°C to 45°C (Figure 4). These results indicate that the process of adsorption of the metal ion on S-III is endothermic in nature. In addition to the endothermic nature of the process, another reason for this enhancement in uptake could be an increase in the pore size with rise in the temperature, similar enhanced ion exchange capacity with rice as biosorbent is also reported in the literature [17]. This could also be due to the centers developed on the surface by treatment of the raw material with sulphuric and nitric acid during preparation. The optimum temperatures for working with S-III appear to be 35°C.

3.5. Thermodynamic Studies of Adsorption of Pb^{2+} on S-III. The equilibrium constant K_D for adsorption on S-III was calculated from the experimental data. From the values of K_D at different temperatures (Table 1), it can be concluded that adsorption is an endothermic and temperature activated process. ΔG values for adsorption are negative indicating

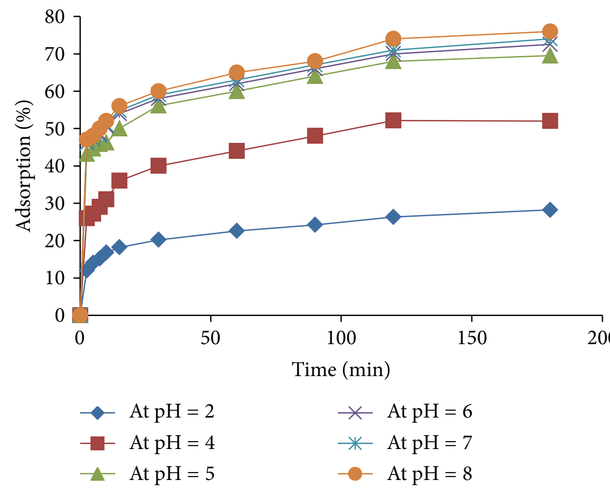

Figure 3: Effect of pH on percentage of adsorption of Pb^{2+} by S-III.

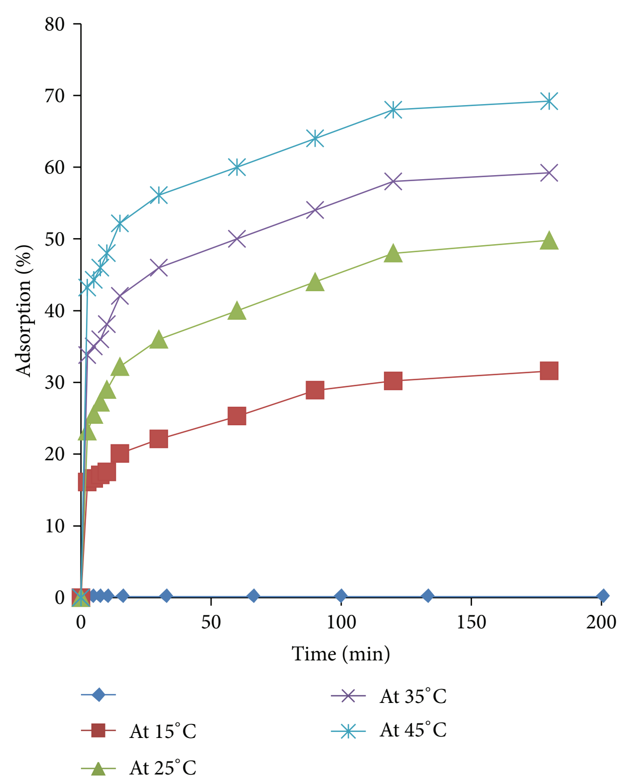

Figure 4: Effect of temperature on percentage of adsorption of Pb^{2+} by 2.0 g, S-III.

spontaneity of the process. The isosteric heat of adsorption for Pb^{2+} was calculated using the following

$$\Delta H \text{ adsorption} = \frac{R \ln C_2/C_1}{1/T_1 - 1/T_2}. \quad (1)$$

The value of ΔH adsorption was found to lie between 8.16 kJ/mole and 3.022 kJ/mole over the temperature range studied. An increase in the value of K_D from 1.61 to 3.8 J/mole with rise in temperature indicates that at higher temperature

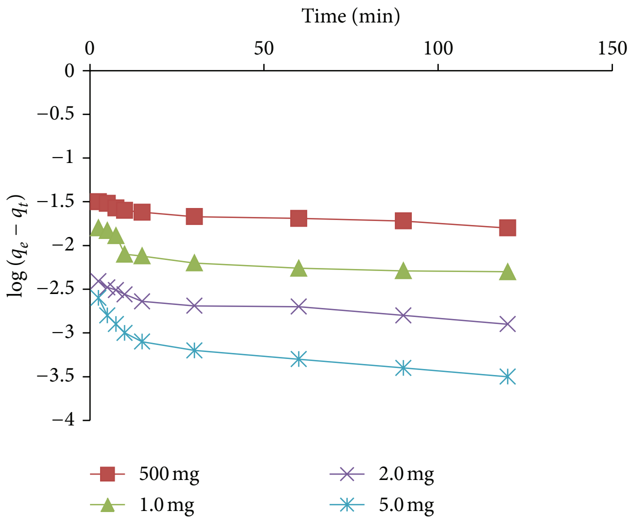

FIGURE 5: Plot of $\log(q_e - q_t)$ versus time for adsorption of Pb^{2+}.

the mobility of the Pb^{2+} ions is enhanced resulting in the effective interaction between the sorbent and sorbate.

3.5.1. Adsorption Isotherms. To explain the adsorption of Pb^{2+} on treated *Cicer arietinum* stalks, the data obtained from the adsorption experiments was fitted into Langmuir and Freundlich adsorption isotherm models. The applicability of the models was checked by plotting graphs of C_e/q_e versus C_e and $\log C_e$ versus $\log x/m$, respectively. The plots of C_e/q_e versus C_e for adsorption on sorbent S-III were straight lines; however, the values of Langmuir constant were negative indicating the no applicability of this model. The Freundlich equation gave plots with $K = 46.03$ and $1/n = -0.451$, $R^2 = 0.996$ for data obtained using S-III as sorbent. From this data one can conclude with caution that the sorption of Pb^{2+} cannot be explained completely by this model. The adsorption of metal cations on the modified surface of stalks of *Cicer arietinum* appears to be governed not by any single mechanism but by different mechanisms [23] such as ion-exchange and complexation in addition to adsorption.

3.5.2. Kinetic Studies. Kinetics of adsorption of Pb^{2+} on S-III was modeled by the pseudo-first-order equation proposed by Lagergren. The plots of $\log(q_e - q_t)$ versus t yielded plots as shown in Figure 5, using various sorbent doses. For the sorbent S-III, the plots of $\log(q_e - q_t)$ versus t are expected to yield straight lines if adsorption follows pseudo-first-order reaction. The plots in Figure 5 indicate that this model cannot describe the sorption kinetics. The data was also fitted in the pseudo-second-order model proposed by Ho and McKay. The plots of t/q_t versus t yielded straight lines as shown in Figure 6 with linear regression coefficient of 0.99 and second-order-rate constant $K_2 = 0.2466$. It can thus be concluded that the adsorption of Pb^{2+} on S-III obeys the second-order kinetics.

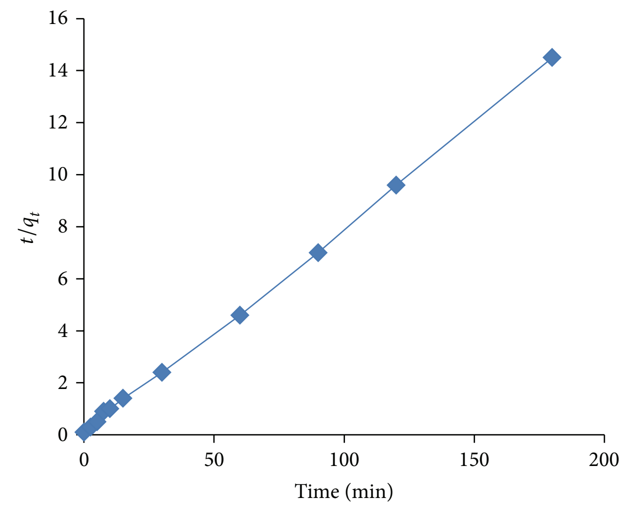

FIGURE 6: Plots of t/q_t versus time for adsorption of Pb^{2+} by S-III.

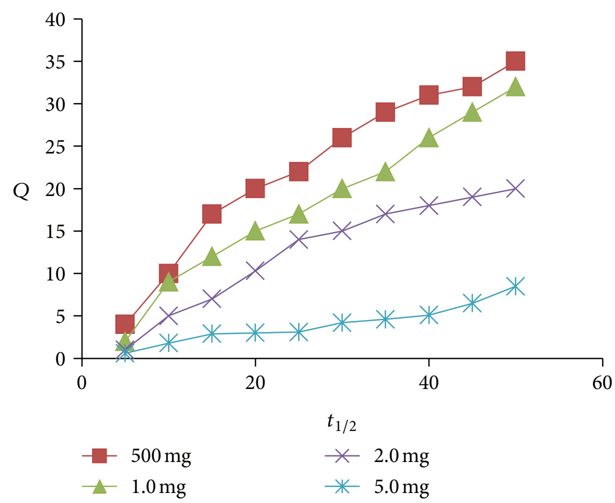

FIGURE 7: Plots of Q versus $t_{1/2}$ for S-III.

3.5.3. Webber-Morris Intraparticle Diffusion Model. Adsorption kinetics is usually controlled by different mechanisms, the most limiting mechanism being the diffusion mechanism. The plots of Q versus $t_{1/2}$ show three portions. The initial curve portion is attributable to rapid external diffusion or boundary layer diffusion. The plot in Figure 7 indicates that the major contribution to adsorption can be attributed to intraparticle diffusion [24]. For all material doses studied the contribution of boundary layer diffusion is insignificant.

4. Conclusions

The results of adsorption studies of Pb^{2+} on S-III: important conclusions of this work are that equilibrium time for adsorption of Pb^{2+} is 120 minutes. The percentage removal on S-I is 76% A 5 g dose of shows a maximum adsorption of 76%. Optimum pH for adsorption of lead is 6 on S-III. The percentage of adsorption decreases from 74% (pH = 6) to

70% (pH = 7). ΔG values for adsorption on S-III are negative at the temperatures studied at 15°C, 25°C, 35°C, and 45°C indicating the spontaneity of the reaction. Increase in K_D values is observed on S-III from 15°C to 45°C. The adsorption follows the Freundlich model with K_f values of 46.03 for S-III, indicating good adsorption. Kinetic modeling indicates that the adsorption follows pseudo-second-order kinetics. K_2 values for S-I 0.2466, with $R^2 = 0.99$.

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