IOSR Journal of Environmental Science, Toxicology and Food Technology (IOSR-JESTFT)
e-ISSN: 2319-2402,p- ISSN: 2319-2399.Volume 10, Issue 2 Ver. I (Feb. 2016), PP 01-05
www.iosrjournals.org

Kinetics and Thermodynamic Study of Uptake of Pb^{2+} by Nitrated biomass of stalks Bengal gram

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Abstract: *Investigation of uptake capacity of by nitrated biomass of Cicer arientinum(Bngal gram) is conducted in batch conditions. The effect of different parameters such as contact time, sorbent dose, pH and temperature has been studied. Adsorption kinetic modeling data were found out. The kinetics of biosorption results shows that sorption process is well explained by pseudo–second order model with determination coefficients higher than 0.98 for sorbent under all experimental conditions. The value Kp is found to be 0.652 to 2.43 for initial and final concentrations. The Weber and Morris intraparticle diffusion model show liquid-film, mass transfer is effective sorption mechanism. Thermodynamic parameter via KD,ΔG has also been calculated to determine the spontaneity of the process. The low value of activation energy indicates that sorption is an activated and physical process. Thus nitrated biomass of Cicer areintinum is a low cost and easily available efficiently used as an excellent sorbent for the removal of Pb^{2+} from wastewater. It can be safely concluded that biomass of Cicer arientinum is much economical effectual, viable and can be an alternative to more costly adsorbents.*

Key words: *E.D.T.A., biosobent, adsorbent, adsorption, Nitrated biomass (sorbent S-IV)*

I. Introduction

Acidic water contain large quantity of mercury, when the pH between 5 to 7 increase mobilization of mercury present in the ground and convert it to methyl mercury, which can be absorbed fastly by organisms like fish to cause nerve damage. The methyl mercury accumulated in fish can transfer to animals by food chain and causes are kidneys, stomach, intestines, reproductive failure and DNA alteration. Sugarcane bagasse is a cheap and abundantly available biomass, and adsorption is an eco-friendly and economically feasible dye removal technique (Churchleyet al. 2000). The US Environmental Protection Agency (USEPA) has classified textile wastes into four groups: (1) dispersible, (2) hard-to-treat, (3) high volume, and (4) hazardous and toxic wastes (Arami et al. 2005) [4]. The batch experiments have been carried out by Raghuvanshi et al. (2004), [20] to study the kinetics of adsorption of methylene blue dye on bagasse with two different forms, like raw and chemically activated forms. Spectrometric studies have been accomplished by Rasheed Khan et al. (2005),[21] for adsorption of dye methylene blue from an aqueous solution on the surface of sheep wool and cotton fiber under optimal conditions of temperature, concentration, pH, stay time duration, and amount of adsorbent. Adsorption characteristics of these materials have been widely investigated for removal of organic matter, such as organic acid dyes, phenol, refractory organic, and heavy metals(Arami et al. 2006) [6]. The biosorption is an alternative to the remediation of industrial effluents as well as recovery of metals reported by Igwa et al. Ahalya, N. and Kanamadi R.D. (2006) worked on biosorption of Chromium (VI) husk of Cicer arientinum [1]. Akar et.al. (2005). worked on sorption of $Pb2^{+}$ by Botrytis cinerea [2]. The effect pH has been reported for dye sorption on to banana peels by Annudurai et.al. (2002), [3]. Choy and McKay (2005) reported adsorption of cadmium copper zinc ions [8] on bone char as an adsorbent. The uptake of cadmium and lead by baker's yeast [9] studied by Goksungur et al. (2005). Li Q., Wu, S.et al. (2004) compared sorption $Pb2^{+}$ and Cd^{2+} for agro-wastes of P. Chrysosporium [10]. Manju G.N.and Anirudhan (1997) reported the application, sorption of Chromium (VI) by coconut fiber piths charcoal [11]. Adsorption study of Al3+, Co2+ by Fluted Pumpkin [12] work done by Michael Horsfull Jnr et.al. (2005). The Mirtezky et. al. (2005) worked on Cd (II) Ni (II), Cu (II) by three macrophyte sorbent [13]. Research carried out Othman and Amin (2003) to study significance sorption behavior by rhizopus biomass for Cu^{2+}, Mn^{4+}, and $Zn2^{+}$[15]. The crab shell waste contains chatoyant was checked for sorption of Ni (II) by Pradan et.al. (2005) [18] Padmavathy et.al. (2003) investigated nickel (II) ions by deactivated protonated yeast [17]. Periasamy and Namasivaym (1995) prepared agro-waste activated carbons for nickel sorption [19]. Ricardo. C., et.al, (2004) showed sorption of rice milling by-products [23], can have good uptake for cadmium and lead. Sorption of Pb (II) on activated Bituminous Coal was reported by Singh D. and Rawat N.S. (1993) [24]. Mohamed Chaker Ncibi and et al. reported sorption of Cd^{2+}, $Pb^{2+,}$ NI^{2+}, and $Zn2^{+}$ by mangifera indica. Mohammad Ajmal and et al (1998), reported the Minamata [14] tragedy in Japan

DOI: 10.9790/2402-10210105

1953-1960 due to metallic mercury released from industries passed to human being largely by natural food chain by fish. While diseases like “Itai-Itai” occurred in the farmer who drank water containing cadmium reported by Benefield, Jadleins and Weand et al. (1982) [7]. Mercury is widely used in industry excessive mercury dangerous to humans, it will cause stomach upset and ulcer, mental disorder, liver, and brain damage [22] reported by Ramos, L, et al.(1999) .Hence, removal of Pb^{2+} from effluents is needed. The sorbent that is cheap, abundant obtained from other industries [6] was presently preferred for sorption process was reported by Bailey, S.E et al. (1999). The adsorption of Pb^{2+} on the sorbent S-IV has been investigated carrying out batch studies. The effects of variables via contact time, sorbent dose, pH and temperature has been studied. The data has been analyzed in the light of adsorption isotherm models. Kinetics modeling has been carried out to establish the order of reaction. An attempt has also been made to determine the mechanism of these model ions using the intraparticle diffusion model put forth by Weber and Morris. Thermodynamic parameter via KD,ΔG has also been calculated to determine the spontaneity of the process.

II. Materials and methods

2.1 Preparation of biosorbent: The sieved biomass of *Cicer arientinum* was taken in a beaker and soaked in AR conc. Nitric acid for 2 hours. The mass was then heated on a water bath till the brown fumes ceased. It was then washed thoroughly with distilled water till the brown black mass was acid free. It was then dried at 110 ^{0}C in the oven for 3 hours. The dried material was then passed through 0.63 mm mesh get particles of uniform size. The present work deals with the study of adsorption of heavy metals Pb^{2+} ions on chemically treated biomass of *Cicer arientinum S-IV*.

2.2 Experimental: Adsorption experiments were carried out for adsorption of lead using sorbents S-IV A standard solution of $Pb(NO_3)_2$ of strength 0.00202 gm Pb^{2+}/ml. was prepared (solution A). To the 50 ml of solution A exactly 50 ml of distilled water were added in a conical flask maintained at constant temperature in a thermostat. To this 500 mg of the appropriate sorbent S-IV 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 gm. 2.0 gm, 5.0 gm. Amount of lead in the filtrate was determined by titrating against standardized E.D.T.A. The effect of contact time, temperature, pH of solution, and material dose on removal of the Pb^{2+} ion was studied. (All Chemicals used Merck Chem.).

III. Result and Discussion

3.1 Characterization of biosorbents.The physical parameters like bulk density (g/cc), moisture content, volatile matter, and ash content are 0.42%, 4.5%, 5.1%, and 10.3%, respectively. The IR spectrum of the sieved biomass of C. arientinum shows absorption peaks at 3,340 cm−1 for broad -OH, 2,924 cm−1 for -NH, and 1,725 cm−1 for COOH.

3.2 Effect of parameters:

3.2.1 Effect of contact time: 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-IV is 27.0 %. The % adsorption of Pb^{2+} ion from its solution of concentration 200 mg/dm^3 was found to be 58.7 %

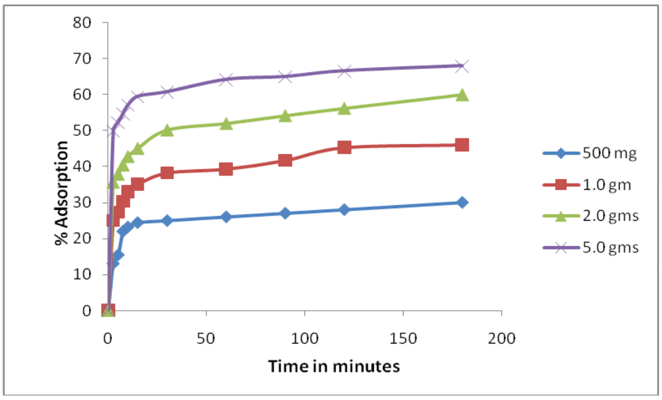

Fig. -1 Effect of time on % adsorption by S-IV Fig-2 Plot of adsorption capacity vs. time for Pb^{2+}

3.2.2 Effect of material dose: The uptake capacity of any adsorbing material increases with increase in the dose as more sites are available for adsorption on the sorbent. The trends in adsorption of Pb^{2+} on S-IV are increased with increasing the biomass dose. For S- IVthe x/m value falls from 49.2 mg/g to 9.89 mg/g. Increase in the material dose from 500 mg to 5 gm/100 ml shows increase in % 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.

3.2.3 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, 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. Adsorption continuous increase is seen in % adsorption with rise in pH. For pH 5, 6 and 7 the % adsorption is 50.5, 63.5 and 65.4 respectively. (**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 desorbs all metal bound to the biomass. As pH increases the concentration of protons decreases, allowing more metal to be adsorbed.

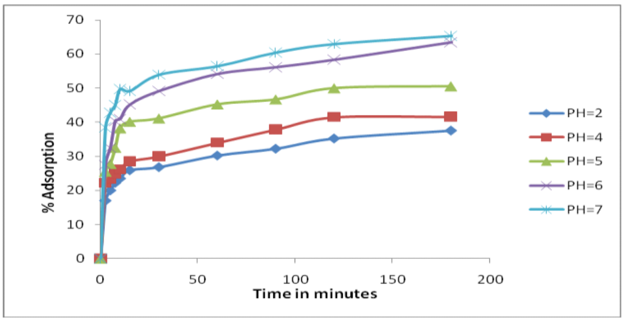

Fig-3 Effect of pH on % adsorption of Pb^2

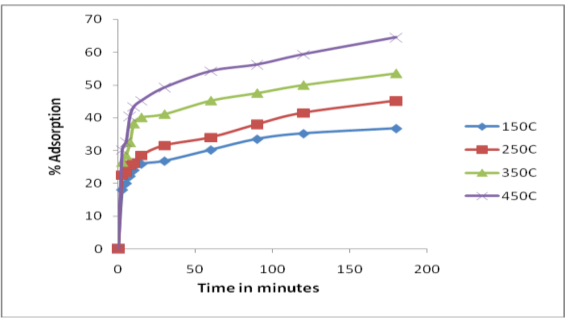

Fig-4 Effect of temperature on % adsorption of Pb^{2+}

3.2.4 Effect of temperature: The study of adsorption of Pb^{2+}under optimum conditions, revealed that with increase in temperature there is a substantial increase in % adsorption by S-IV also shows an increasing trend in adsorption with rise in temperature. S-IV show enhancement in adsorption from 37% at 15 °C to 65 % at 45°C. **Figure-4,** as the temperature is increased from 15 °C to 45°C. These results indicate that the process of adsorption of the metal ion on S-IV 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 literature[18]. 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 temperature for working with S-IV appears to be at 45°C**.**

3.2.5 Thermodynamic studies of adsorption of Pb^{2+} : The equilibrium constant KD for adsorption on S-IV were calculated from the experimental data. From the values of KD at different temperature it can be concluded that adsorption is an endothermic and temperature activated process. The ΔG values on S-IV, are $_+$ve at 15 °C, 25 °C, and 35 °C with the values decreasing with increasing temperature. At 45 °C ΔG = - 1013 j/mol . This indicates that the adsorption on S-IV is a highly energy activated process. The isosteric heat of adsorption for Pb^{2+} on S-IV was calculated using the formula.

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

The value of ΔH adsorption was found to lie between 8.16 kJ/mole. to 3.022 kJ/ mole over the temperature range studied. An increase in the value of KD from 0.5225 to 2.264(Table-1) with rise in temperature indicates that at higher temperature the mobility of the Pb^{2+} ions is enhanced resulting in the effective interaction between the sorbent and sorbate.

Table-1

3.2.6 Adsorption isotherms

To explain the adsorption of Pb^{2+} on treated *Cicer atientinum* stalks, the data obtained from the adsorption experiments was fitted in to Langmuir and Freundlich adsorption isotherm models. The applicability of the models was checked by plotting graphs of Ce/qe vs. Ce and log Ce vs. log x/m respectively. The plots of Ce/qe vs. Ce for adsorption on sorbent S-IV were straight lines however the values of Langmuir constant were negative indicating the no applicability of this model. The Freundlich equation gave plots with S-IV shows K=

45.8 and 1/n = 1.124, R^2= 0.933. 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 arientinum* appears to be governed not by any single mechanism but by different mechanisms such as ion–exchange, complexation etc.in addition to adsorption.

3.2.7 Kinetic studies:

Kinetics of adsorption of Pb^{2+} on S-IV was modeled by the pseudo first order equation proposed by Lagergren. The plots of log (qe-qt) vs. t yielded plots as shown in **figure—5**, using various sorbent doses. For the sorbent S-IV the plots of log (qe-qt) vs. t are expected to yield straight lines if adsorption follows pseudo first order reaction. The data was also fitted in the pseudo second order model proposed by Ho and McKay. The plots of t/qt vs. t yielded straight lines as shown in **Figure-6** with linearregression coefficient of 0.98 (Table-2) and second order rate constant K2 = 0.7129.(Table-2) It can thus be concluded that the adsorption of Pb^{2+} on S-IV obeys the second order kinetics.

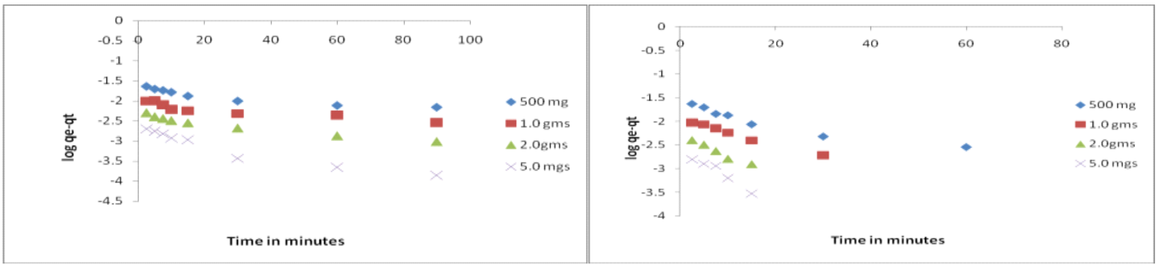

Fig. 5 Plot of (log qe-qt) vs. Time for adsorption of Pb^{2+} by S-IV

Fig.6 Plots of t/qt vs. Time for adsorption of Pb^{2+} Fig.7 plot of Q vs t $^{1/2}$

3.2.8 Webber –Morris intaparticle diffusion model: Adsorption kinetics is usually controlled by different mechanisms, the most limiting mechanism being the diffusion mechanism. The plots of Q vs. t ½ 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 .For all material doses studied the contribution of boundary layer diffusion is insignificant.

IV. Conclusions

The results of adsorption studies of Pb^{2+} on S-IV shows that Equilibrium time for adsorption of Pb^{2+} by S-IV is 120 minutes. A 5 gm dose of shows maximum adsorption is about 66%. Optimum pH for adsorption of lead, S-IV pH 7 is better. The % adsorption decreases from 66% (pH=7). ΔG values for adsorption on S-IV are positive for 15°C, 25°C, 35°C, while ΔG value at 45°C is negative. Increase in KD values is observed on S-IV from 15°C -45°C . The adsorption follows the Freundlich model with Kf values of 46.03 and 45.8 for S-IV, indicating good adsorption. However the possibility of other mechanisms such as ion exchange complexation cannot be ruled out particularly on S-IV, as the values of coefficient of determination is 0.933. Kinetic modeling indicates that the adsorption follows pseudo second order kinetics. K_2 values for S-IV is 0.7129, with R^2 0.98.

Acknowledgement

I Dr. A. A. Kale sincerely thankful to Principal, Dr.A.S. Burungale, S.M Joshi College Hadapsar Pune-28 for encouragement during the research work.

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