International Journal of Current Trends in Engineering & Technology
ISSN: 2395-3152
Volume: 03, Issue: 06 (November -December, 2017)

Neelgiri bark as an adsorbent: Evaluation of adsorptive characteristics for Pb (II) from aqueous solution

Nitish Gupta[1*] and K. K. Kushwah[2]

[1]Department of Applied Chemistry and chemical Technology , Shri G.S. Institute of Technology and Science, 23 Park Road Indore (452003) Madhya Pradesh, India

[2]Department of Applied Physics, Jabalpur Engineering College, Jabalpur, India

* Corresponding author. Tel. + 91 9926497917; fax: +91 731 2432540

E-mail address: ngupta@sgsits.ac.in; nitish.nidhi75@gmail.com

Abstract: - *Biosorption is one of the most useful techniques for environmental remediation especially for heavy metal pollution. Kinetics of the biosorption is of great significance to evaluate the performance of neelgiri bark powder and gain insight into the underlying mechanisms. Presently, the removal of Pb (II) from aqueous solutions using neelgiri bark powder is investigated. Adsorption study were performed in batch adsorption techniques to evaluate various parameters like the effects of pH, time of contact, dose of neelgiri bark, Pb(II) ion concentration and temperature of solution. The adsorption of Pb (II) increased with dose of adsorbent and reached maximum at 1.0g/ 100mL at pH 8. Kinetic models like pseudo first and second-order were used to correlate the adsorption data. Among the two kinetic models, the second-order rate expression fitted well with high correlation coefficient and their kinetic constants were computed. Two isotherm models, Freundlich and Langmuir isotherm were used to know adsorption mechanism and Langmuir correlated the data well inferring a monolayer adsorption at the binding sites on the surface of the adsorbent. It may be concluded that neelgiri bark can be used as an effective adsorbent for removing Pb (II) ions from aqueous solutions.*

Keywords: Neergiri bark; Adsorption kinetics; Langmuir and Freundlich isotherm; Pb (II) ions.

1. INTRODUCTION

Pollution of the environment by toxic heavy metals is a serious problem. It arises due to many anthropogenic activities like industries waste and sewage disposal and, a focus of attention of environmentalist worldwide. Among the heavy metals Lead is most toxic and frequently found in wastewater coming out from industries involved in processing of lead chemicals and allied products; lead acid storage batteries, ceramic and glass industries, lead smelting and electroplating industries, thus its removal is of utmost required . Lead causes harmful effect to both flora and fauna; like in humans lead is responsible for anemia, brain damage, mental deficiency, anorexia, vomiting and malaise in humans [1–5]. Permissible limit of 0.05 mg/L is recommended by WHO for lead in water [3]. Various conventional Methods used for the removal of lead from wastewater such as precipitation, evaporation, electroplating, ion exchange, reverse osmosis and membrane separation. However, these methods are either costlier or not Eco-friendly and dumping of resultant toxic metal sludge or insufficient for metal removal at low concentration (1 to 100 mg/L of dissolved metal) [1]. Adsorption is efficient and easy process of removal from dilute solutions. However, the use of commercially available activated carbon and zeolite [2] for this process is very expansive and not feasible at large scale operations. Thus the researchers were oriented towards lost cost and abundantly available adsorbents which are the wastes material such as rice husk [3], saw dust [4], palm shell activated carbon [5], banana stem [6], lowny grass [7], orange peel [8], tree fern [9], grape stalk [10], tea waste [11], neem bark [12], and peanut hulls [13] etc. The benefit of these natural substances are (a) the miscellany biological binding sites, (b) uniform and small particle size (c) less reactive toward the 1S and 2S periodic group metals as compared to ion-exchange resins. In the present study, Neelgiri bark powder is used as an adsorbent which is abundantly available. The aim of the study was to recite the removal of lead ions at relatively low concentration with process dependency on adsorption isotherm, kinetics and various adsorption batch parameters.

2. Materials & Methods

2.1 Reagents and Standard solution

Chemicals used in present study, were of analytical reagent grade and doubly distilled water was used in the entire experiments. The glassware was kept in 10% HNO_3 (v/v) acid for 24 h and then rinsed many times with doubly distilled water prior to use. Pb (II) ion (1g/L) stock solution was prepared by dissolving Pb $(NO_3)_2.H_2O$ (Merck India) in doubled distilled water and serial diluted to get solution of desired concentrations. The pH was adjusted using 0.1 M NaOH or 0.1 M HCl.

2.2 Adsorbent

The bark of Neelgiri was used as an adsorbent in the present study. Surface adhered impurities of the Neelgiri bark was washed with doubly distilled water and oven dried at 80^{0}C. Then was ground to get fine powder in a ball mill and the resulting powder were sieved to obtain particle size -80 + 200 mesh size. The bark powder contains hemicelluloses, α cellulose, and lignin, carbohydrate, fibers. The dried sample of bark was preserved in desiccators.

Table 1: Kinetic models and their parameters

Lagergren Pseudo I-order	**Pseudo II-order**
$\text{Log}\ (q_e - q_t) = \log q_e - (k_1/2.303)\ t$	$t/ q_t = (1/ K_2 q_e^2) + t/q_e$
Constant k_1 is calculated by plotting Log Log $(q_e - q_t)$ Vs. T	Constant k_2 is calculated by plotting t/ q_t Vs. T

2.3 Batch adsorption study

Batch adsorption experiments were carried out by reacting 1 gm of bark powder into Erlenmeyer flasks containing 100 mL of known concentration of lead ion solution. The flasks were agitated at 200 rpm for 2 h. at 25^0 C. After equilibrium had been established, then adsorbent solution mixture was separated by centrifugation (Matzer-OPTK**)** at 500 rpm for 05 min. The concentration of the metal in the remaining solution was analyzed by atomic adsorption spectrophotometer (Perkins Elmer- A analyst 100). The amount of metal adsorbed (mg/L) was calculated as follows:

$$Q = v\ (C_i - C_f)\ /\ m \qquad (1)$$

Where C_i & C_f (mg/L) are Pb (II) ion concentration at initial and final stages in the solution, respectively, v (L) is the solution volume & m (g) is the mass of Neelgiri bark powder.

2.4 Kinetic study

Kinetic of reaction indicate the mechanism of adsorption and subsequently investigation of the controlling mechanism of the biosorption as either mass transfer by diffusion or chemo-sorption and also used to optimize various parameters for designing industrial scale batch process [14].

2.4 Isotherm study

The adsorption isotherm depicts how metal ion interacts with adsorbents and thus is critical in optimizing the efficient use of adsorbents. In the present study two isotherms were applied which are reported in table 2.

Table 2: Isotherm models and their parameters

Freundlich adsorption isotherm model	**Langmuir adsorption isotherm model**
$\log q_e = \log K_F + 1/n \log Ce$	$1/q_e = 1/b.\Theta^0\ 1/C_e + 1/\ \Theta^0$
Where constant K_F is a adsorption capacity and constant n related to intensity of adsorption	Where constant b (*L/mg*) is a affinity of binding site and Θ^0 represents a particle limiting adsorption capacity

3. Result and Discussion

3.1 Effect of pH and Contact time

Effect of contact time ranging 15-60 min at different pH (2-10) on the adsorption of Pb (II) ions onto Neelgiri bark powder (Fig. 1) showed that the amount of adsorbed Pb(II) ions increases with pH and it declines after pH 8. The equilibrium contact time of about 50 *min* is required for the lower concentration (i.e. 10 *mg/l*) and almost 55 min for the concentration (50 &100 *mg/l*) and for 200 *mg/l* even higher time is required for maximum removal of Pb(II) ions. Furthermore, adsorption capacity increases from 0.91 to 14.6 *mg/g* as the concentration of Pb (II) ions increases from 10 to 200 mg/*L* at pH, 8. In addition, regarding the biosorption dynamic profile, it can be divided into some categories: (i) in first phase study increase (ii) second phase adsorption levels off (transition phase) (iii) last phase a plateau regime; other researchers [1, 16] also reported the same sorption profile. The binding of metal ions by surface functional groups was strongly pH dependent [17]. It increases as pH of the solution increases from pH 2 -8. These increasing trends can be interpreted in term of competitive approach of protons and metal ions for the same adsorbing sites thus lower adsorption at lower pH. However as pH increases surface of adsorbent become negative and favor the adsorption of Pb (II) ions thus higher percentage of removal at pH value 8. Above pH 8, a decrease in the adsorption of Pb (II) ions was observed. At higher pH the metal ions in aqueous solution may undergo polymerization salvation, precipitation of hydroxide species of metal and hydrolysis [17] at higher pH value making the true adsorption study difficult.

International Journal of Current Trends in Engineering & Technology
ISSN: 2395-3152
Volume: 03, Issue: 06 (November -December, 2017)

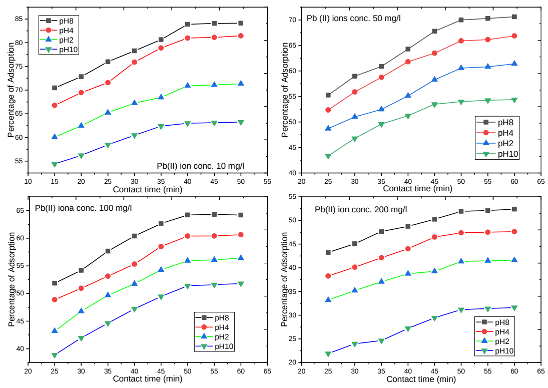

Fig. 1 Effect of pH and contact time on the percentage removal of Pb (II) ions onto Neelgiri bark.

3.2 Effect of biosorbent dosage, initial metal ion concentration, temperature and applicability of adsorbent for industrial effluents

Neelgiri bark dosage has a great influence on the removal of Pb (II) ions and determines the potential of Neelgiri bark through the various functional groups available to absorb Pb (II) ions at a given concentration. At equilibrium, Pb (II) ion adsorption increases with an increase in biomass dosage from 0.1 to 2 g while adsorption capacity decreases (Fig. 2 A). The decrease in the adsorption is due to the concentration gradient between the neelgiri bark powder and the Pb(II) ions ; however, loading capacity is decreased as dose of neelgiri bark is increased(Fig. 2 B). Percentage removal of the Pb (II) ions as a function of temperature is shown in Fig.2 (C). Temperature has a negative effect on the adsorption of Pb (II) ions adsorption and inferring the exothermic nature of adsorption. The adsorption percentage of Pb (II) ions was studied with 1 g neelgiri bark dose at temp. Range from 30 to 60^0C keeping other parameters fixed. This is due to the fact at higher temperature particles agglomeration and thermal energy induced desorption of Pb (II) ions decrease the adsorption. The applicability of neelgiri bark of the effluent samples which were collected from Khan River catchment area which is near to industrial area is shown in Fig. 2 D. 500 mL effluent sample was diluted to make 1 litre solution using double distill water and solution was kept for 24 h undisturbed and filtered through whatman filter paper no. 42. The initial Pb (II) concentration is decreased from 60 mg/L to 51.5 mg/L at the equilibrium agitation time respectively. Thus neelgiri bark showed adequate efficiency and showing applicability for purification of effluents after activation or some improvement in the adsorbent.

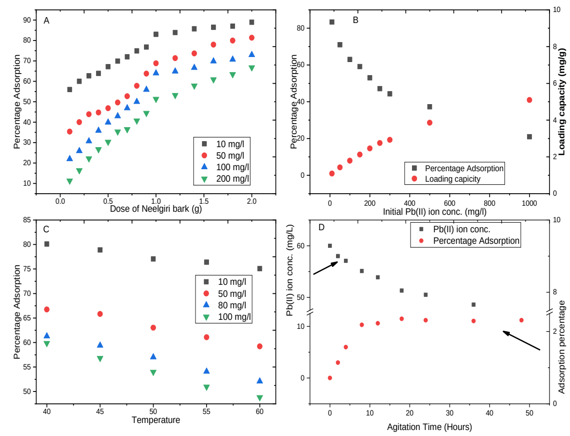

Fig. 2 (A) Effect of dose of adsorbent (B) initial metal ion conc. (c) Temperature (d) applicability of adsorbent for wastewater.

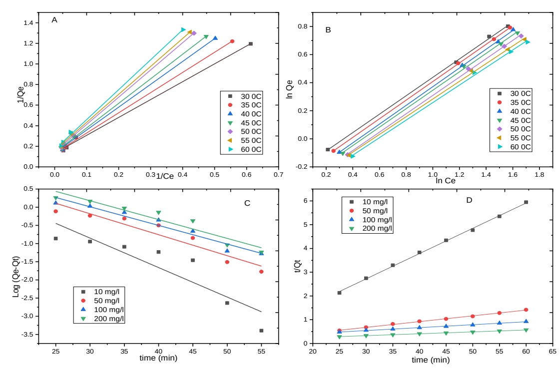

Fig. 3: (A) Langmuir isotherm graph (B) Freundlich isotherm graph (C) Pseudo first-order graph (D) pseudo second-order graph.

3.3 Isotherm and Kinetic studies

The values obtained using kinetic models, namely Pseudo first order and pseudo second order applied to know the variation of adsorbed Pb (II) ion with contact time. The resulting graph and kinetics parameters are presented in Fig. 3 (A), Fig. 3 (B) and Table 3 respectively. As seen, the correlation coefficient for pseudo second order model is higher than pseudo first order model thus the rate limiting step might be chemical biosorption [15]. Adsorption isotherms represent the equilibrium relationship between metal ions and unit weight of Neelgiri bark. In the present study two isotherm models were applied and showed in Fig. 3 C and D. The Freundlich isotherm constants k and n and Langmuir constants b and θ^0 are reported in table 4. The value of Freundlich constant n obtained between 1 and 10 which represents applicability of this model for adsorption of Pb (II) ions [3]. The Langmuir monolayer adsorption capacity is found to be 7.53 *mg/g*.

Table 3: Kinetic constant for the adsorption of Pb (II) ions onto Neelgiri bark

Pb(II) ions Conc. (*mg/l*)	Pseudo First-order			Pseudo Second-order		
	K_1	q_e	R^2	K_2	q_e	R^2
10	0.187	38.25	0.775	0.470	9.40	0.998
50	0.133	35.41	0.889	0.050	41.22	0.997
100	0.118	35.35	0.936	0.173	81.04	0.996
200	0.119	53.64	0.900	0.091	125.63	0.998

Table 4: Isotherm constant for the adsorption of Pb (II) ions onto Neelgiri bark

Temp. (^{0}C)	Langmuir isotherm			Freundlich Isotherm		
	θ^0	b	R^2	K	n	R^2
30 ^{0}C	7.51	0.230	0.996	1.525	1.526	0.999
35 ^{0}C	7.53	0.260	0.997	1.367	1.509	1.000
40 ^{0}C	7.35	0.302	0.997	1.221	1.501	1.000
45 ^{0}C	7.14	0.334	0.998	1.169	1.523	0.998
50 ^{0}C	6.78	0.309	0.998	1.065	1.530	0.999
55 ^{0}C	6.20	0.438	0.998	1.061	1.588	0.998
60 ^{0}C	5.94	0.490	0.998	1.005	1.602	0.998

4. Conclusions

In this paper, neelgiri bark powder was used for the removal of Pb (II) from aqueous solution. Pb (II) ions adsorption attained maxima at pH 8 and decreases as further increase in pH value. Langmuir isotherm show higher Correlation coefficient than Freundlich isotherms thus better fitted and monolayer sorption capacity was calculated 7.53 *mg/g.* Computation of experimental data indicates pseudo-second-order kinetics model is fitted well than pseudo first order model. Pb (II) ions adsorption decrease at higher temperature indicating exothermic behavior of process. It can be concluded that neelgiri bark can be used as a promising adsorbent for the removal of Pb (II) from the aqueous solutions.

References

[1]. M. M. M. Rahmati, P. Rabbani, A. Abdolali, and A. R Keshtkar, Kinetics and equilibrium studies on biosorption of cadmium, lead and nikel ions from aqueous solutions by intact and chemically modified brown algae. J. Hazard. Mater. 185 (2011). 401-407.

[2]. T. Li, H. Yang, Y. Zhap and R. Xu, Novel modified pectin for heavy metal adsorption. Chin. chem. leH. 18 (2007).

[3]. N. Gupta, S. S. Amritphale and N. Chandra, Removal of lead from hybrid precursor prepared by rice hull, J. Hazard. Mater. 163(2009) 1194-1198.

[4]. A. Shukla, Y. H. Zhang, P. Dubey, J. L. Margrave and S. S. Shukla, The role of saw dust in the removal of unwanted materials from water. J. Hazard. Mater. 95 (2002) 137-152.

[5]. Y. S. Ho, and A. E. Ofomaja, Kinetic and thermodynamics of lead ions sorption on palm kernel fiber from aqueous solution, Prac. Biochem. 40 (2005) 3455-3461.

[6]. B. F. Neoline, D. M. Manohar, and T. S. Anirudhan, Kinetic and equilibrium modeling of lead (II) sorption from water and waste water by polymerized banana stem in a batch reactor, Sep. & Purif. Technol. 45 (2005) 131-140.

[7]. D. Lu. , Q. Cao, X. Cao, and F. Luo, Removal of Pb (II) using the modified lawny grass: Mechanism kinetics equilibrium and thermodynamic studies. J. Hazard. Mater. 166 (2009) 239-247.

[8]. Z. Xuan, Y. Fang, X. Li, Y. Liu, and F. Luo, Study on the equilibrium, kinetics and isotherm of biosorption of lead ions onto pretreated chemically modified orange peel, Bio. Eng. J. 31 (2006) 160-164.

[9]. Y. S. Ho, W. T. Chiu, C. U. Hsu and C.T. Huang. Sorption of lead ions from aqueous solutions using tree fern as adsorbent, Hydrometallurgy 73 (2004) 55-61.

[10]. M. Martinez, N. Miralles, S. Hidalgo, N. Foil, I. Villaeseasa and J. Poch, Removal of lead (II) & Cadmium (II) from aqueous solutions using grape stalk waste. J. Hazard. Mater. 133 (2006) 203-2011.

[11]. B. E M. P. K. Amarasinghe and R. A. Willams, Tea Waste as a low cost adsorbent for the removal of Cu & Pb from wastewater. Chem. Eng. J. 132 (1-3) (2007) 299-309.

[12]. T. K. Maiya, A. K. Bhattacharya and S. K. Das, Adsorption of Pb (II) by saw dust and neem bark from aqueous solutions. J. Environ. Prog. 27 (3) 2008, 313-328.

[13]. P. Brown, I. A. JeFcoat, D. Parrish, S. Gil and E. Gaham., Evaluation of the adsorptive capacity of Peanut hull pellets for heavy metals in solution. Adv. Environ. Res. 4(1) (2000) 19-29.

[14]. V. J. Larsen and H.H. Schierup, The use of Barley straw for the removal of heavy metals from

wastewater, J. Environ. Qual. 10(2) (1981) 1203-1208.

[15]. Y. S. Ho, Review of second order models for adsorption systems. . J. Hazard. Mater. B136 (2006) 681-689.

[16]. M. C. Ncibi, B. Mahjoub, M. Seffen, F. Brouers, and S. Gaspard, Sorption dynamics investigation of Chromium (VI) onto Posidonia Oceanica ibers: Kinetic modeling using new generalized fractal equation, Biochem. Eng. J. 46 (2009) 141-146.

[17]. J. Acharya, J. N. Sahu, C. R. Mohanty and B. C. Meikal, Removal of lead (II) from waste water by activated carbon developed from Tamarind wood by zinc chloride activation. Chem. Eng. J. 149(2009) 249-262.