

Kinetics and adsorption studies of lead (II) onto activated carbon using low cost adsorbents

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Received: 21/11/2017, Accepted: 07/05/2018, Available online: 02/08/2018

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Abstract

The removal of Lead (II) from aqueous solutions using *Fagopyrum esculentum* Moench (Buckwheat) and *Bambusa vulgaris* (common bamboo) as adsorbents was investigated. The effects of various experimental parameters such as initial concentration, contact time and pH have been studied using batch adsorption technique. All the Adsorption isotherm models fitted well with the adsorption data. However, Freundlich isotherm displayed a better fitting model than the other two isotherm models due to high correlation coefficient (R^2). This indicates the applicability of multilayer coverage of the Pb (II) on the surface of adsorbent. The adsorption kinetics was studied using four simplified models and it was found to follow the pseudo-second-order kinetic model which confirmed the applicability of the model. The adsorption mechanism was found to be chemisorption and the rate-limiting step was mainly surface adsorption.

Keywords: Lead; Batch method; Adsorption; Multilayer

1. Introduction

Water pollution caused by heavy metals has posed a significant threat to the environment and public health because of their toxicity, accumulation in the food chain and persistence in nature (Bahadir *et al.*, 2007). Lead, an element which has been used for years, can be regarded as a longstanding environmental contaminant. All the chemicals/compounds containing lead are considered as cumulative poisons that usually affect the gastrointestinal track, nervous system and sometimes both (Nadeem *et al.*, 2005). According to the US Environmental Protection Agency (EPA) the permissible level for lead in drinking water is 0.05 mg L^{-1} (Bhattacharjee *et al.*, 2003) and that of Bureau of Indian Standards (BIS) is 0.01 mg L^{-1} (BIS, 1981). Therefore, a very low concentration of lead in water is very toxic (Bhattacharjee *et al.*, 2003). The chief source of lead in water is from the effluents of processing industries. Lead is also used in many commercial products like storage batteries and plastic water pipes. Therefore, the safe and effective disposal of lead in wastewater poses a challenge since lead does not degrade in environment like organic pollutants (Jalali *et al.*, 2002; Gupta *et al.*, 2011; Sekar *et al.*, 2004). At present, various methods like chemical

precipitation, electrochemical reduction, ion exchange, reverse osmosis, membrane separation, and adsorption have been developed to remove Pb^{2+} from wastewater (Conell *et al.*, 2008; Acharya *et al.*, 2009; Ricordel *et al.*, 2001; Saeed *et al.*, 2005; Doyurum *et al.*, 2006). Adsorption of activated carbon has been shown to be very effective for the removal of toxic metal ions from aqueous solutions. However, the high cost of activated carbon limits its use especially in developing countries. This has led for the search of activated carbons from cheap and renewable sources by various researchers over the years (Ferro *et al.*, 1990; Sohail and Qadeer, 1997; Netzer and Hughes, 1984). Therefore, for the present study we have chosen the precursor for synthesis of activated carbon which is from common bamboo and common buckwheat plant. It can be an alternative for the adsorption of heavy metals from aqueous solution since they are abundant in nature, inexpensive, require little processing and are effective materials. These waste materials have little or no economic value and often creates disposal problem.

2. Materials and methods

2.1 Synthesis of adsorbents

For the synthesis of adsorbents, the raw materials, i.e., stems and leaves of *Bambusa vulgaris* (BVC), *Fagopyrum esculentum* Moench (FEMC) plants, were collected and sun-dried for a few days. The dried materials were crushed manually into smaller pieces and were packed in clean stainless-steel containers and put in a Muffle furnace at $650 \pm 20 \text{ }^\circ\text{C}$ for 4 h in a uniform nitrogen flow wherein carbonization was done. The already carbonized materials were then grounded into fine powder with mortar and pestle and washed with distilled water to remove impurities and dried in hot air oven at $110 \text{ }^\circ\text{C}$. The dried carbons were then pulverized in the planetary Ball Mill at 600 rpm for around 10 min to obtain uniform size. Once the carbons were prepared, surface modification was done by the following process.

2.2. Surface modification of the synthesized adsorbents.

Fifteen grams of the prepared carbon was taken in a 500-ml beaker, and 0.1N HNO_3 solution was gradually added until the sample was fully submerged. The mixture was then thoroughly shaken for 3 h in a rotary shaker.

Thereafter, it was filtered using Whatman No. 42 filter paper. The carbon was washed with double-distilled water several times for removal of excess of acid to maintain the pH of the carbon between 6.9 and 7 and then dried in an oven at 110 °C. After complete drying, the dried activated carbons were stored in airtight containers for further study. Similar procedure is followed for surface modification of carbon with 0.1N H₃PO₄.

2.3. Preparation of lead (II) solution

Stock solution of Pb(II) was prepared (1000 mg/l) by dissolving required amount of Pb(NO₃)₂ in acidified double distilled water. The stock solution was diluted with distilled water to obtain desired concentration ranging from 5 to 45mg L⁻¹. All the chemicals used were of analytical reagent grade. The lead (II) ions is analysed by atomic absorption spectroscopy at 283.3 nm, using graphite furnace Analytikjena Vario-6. The calibration is carried out versus an aqueous standards curve.

2.4. Adsorption studies of lead on activated carbons by batch method

In order to understand the adsorption behavior of lead, various experimental parameters have been investigated using batch adsorption experiments. The effect of initial concentration is studied by varying lead concentrations between 5-45 mg L⁻¹. The effect of contact time was studied by varying the agitating time (range:2-240 minutes) at fixed optimum initial concentration of lead (20 mg L⁻¹) with optimum dose of adsorbents (0.25 g L⁻¹) and also the effect of pH was studied ranging from 2-5.5. The percentage removal of the lead and the amount of lead adsorbed were calculated by the following equations.

$$\text{Percentage removal} = 100 \frac{(C_i - C_f)}{C_i}$$

$$\text{Amount adsorbed } (q_e) = \frac{(C_i - C_f)V}{M}$$

where C_i and C_f are the initial and final equilibrium solution concentrations of the lead (mg/L), V is the volume of the solution (L) and M is the mass of the activated carbon (g). The data obtained have been analyzed for adsorption isotherms models and Intraparticle diffusion model.

3. Results and discussion

3.1. Effect of initial concentration:

Effect of initial varying concentration of Pb (II) ions showed that the percentage adsorption decreases with increase in initial concentration of the adsorbate. This decrease in Pb (II) ions uptake capacity with increase in initial metal concentration may be due to the formation of clusters of carbon particles resulting in decreased surface area (Montanher *et al.*, 2005; Chen and Wu, 2004). The variation of percent removal of lead with increasing Initial concentration is shown in Fig. 1. The data reveals that under identical experimental conditions, the order of adsorption capacity of the various adsorbents is as: BVC (HNO₃) > BVC (H₃PO₄) > FEMC (HNO₃) > FEMC (H₃PO₄).

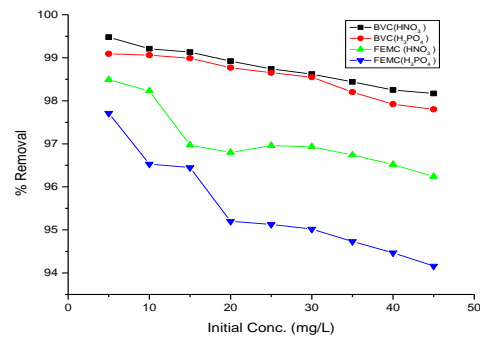


Figure 1. Variation of percent removal of lead with increasing initial concentration.

3.2. Adsorption isotherm

The relationship between the amount of a substance adsorbed per unit mass of adsorbent at constant temperature and its concentration in the equilibrium solution is called the adsorption isotherm (Feng *et al.*, 2004). Various adsorption isotherm models are employed in this study to describe the experimental adsorption isotherm (Langmuir, 1918; Freundlich and Helle, 1939; Temkin, 1940).

3.2.1. Langmuir adsorption model

The Langmuir adsorption model is the most common model used to quantify the amount of adsorbate adsorbed on an adsorbent as a function of partial pressure or concentration at a given temperature. It suggests the formation of monolayer adsorption and also the surface is energetically homogeneous (Feng *et al.*, 2004). The Langmuir equation which is valid for monolayer adsorption onto a surface is given below

$$q_e = \frac{Q_{max} K_L C_e}{1 + K_L C_e}$$

Where C_e is the equilibrium metal ion concentration (mg/l), q_e the amount of lead adsorbed at equilibrium (mg g⁻¹) and Q_{max} (mg g⁻¹) and K_L (L mg⁻¹) are Langmuir constants related to adsorption capacity and energy of adsorption, respectively.

The essential characteristics of the Langmuir equation can be expressed in terms of a dimensionless constant called separation factor (R_L, also called equilibrium parameter) which is defined by the following equation (Ozacar and Sengil, 2004; Mall *et al.*, 2006; Crini *et al.*, 2007).

$$R_L = \frac{1}{1 + K_L C_i}$$

where C_i (mg L⁻¹) is the initial adsorbate concentration and K_L (L mg⁻¹) is the Langmuir constant related to the energy of adsorption. The value of R_L indicates the shape of the isotherms to be either unfavorable (R_L > 1), linear (R_L = 1), favourable (0 < R_L < 1) or irreversible (R_L = 0), the results from Table 1 shows R_L < 1 in all the cases, this indicates a favorable isotherm for the adsorbents used in this study.

Table 2 compares the adsorption capacity of different types of adsorbents used for removal of Pb²⁺ ions. The most important parameter to compare is the Langmuir Q_{max} value since it is a measure of adsorption capacity of the

adsorbent. The value of Q_{max} in this study is larger than those in most of previous works. This suggests that Pb²⁺ ions could be easily adsorbed on the synthesized adsorbents.

Table 1. Adsorption isotherm parameters for Pb²⁺ adsorption on synthesized adsorbents.

Freundlich Isotherm	R²	Log K	1/n	n
BVC (HNO ₃)	0.999	0.931	0.601	1.654
BVC (H ₃ PO ₄)	0.991	0.484	0.625	1.596
FEMC(HNO ₃)	0.998	0.623	0.696	1.443
FEMC(H ₃ PO ₄)	0.993	0.362	0.653	1.517
Langmuir Isotherm	R²	Q_{max}	K_L	R_L
BVC (HNO ₃)	0.996	57.714	0.942	0.179
BVC (H ₃ PO ₄)	0.933	30.196	0.585	0.254
FEMC(HNO ₃)	0.978	56.497	0.797	0.202
FEMC(H ₃ PO ₄)	0.879	14.088	0.135	0.605
Temkin Isotherm	R²	B_T	Bl_n(A)	A_T
BVC (HNO ₃)	0.962	0.417	2.423	360.836
BVC (H ₃ PO ₄)	0.984	0.364	1.772	131.863
FEMC(HNO ₃)	0.934	0.329	1.464	92.224
FEMC(H ₃ PO ₄)	0.945	0.353	1.392	50.912

3.2.2 Freundlich adsorption model

Freundlich isotherm is an empirical equation describing the heterogeneous adsorption and assumes that different sites with several adsorption energies are involved (Sekar *et al.*, 2004; Crini *et al.*, 2007). The linear form of the Freundlich equation is shown below.

$$\log q_e = \log k + \frac{1}{n} \log C_e$$

Where C_e is the equilibrium metal ion concentration (mg L⁻¹), q_e the amount of lead adsorbed at equilibrium

(mg g⁻¹), K and 1/n are the Freundlich constants incorporating all the factors effecting adsorption capacity, an indication of favorability of metal adsorption onto adsorbent (Freundlich and Helle, 1939). The slope 1/n gives adsorption capacity and intercept log K gives adsorption intensity from the straight portion of the linear plot obtained by plotting log q_e versus log C_e gave a straight line with slope of 1/n, Freundlich constants K_F and n were also calculated and are listed in Table 1.

Table 2. A comparison of the adsorption capacity of the synthesized adsorbents with the literature data.

Adsorbent	Activating agent	Q_{max} (mg g⁻¹)	References
Rice husk	Tartaric acid	120.48	Wong <i>et al.</i> , (2003)
Sawdust (Pinus sylvestris)	Formaldehyde in Sulfuric acid	9.78	Taty-Costodes <i>et al.</i> , (2003)
Peanut husk	Sulfuric acid	29.14	Li <i>et al.</i> , (2006)
Banana stem	Formaldehyde	91.74	Noeline <i>et al.</i> , (2005)
Spent grain	Sodium hydroxide	35.5	Low <i>et al.</i> , (2000)
Alfalfa biomass	Sodium hydroxide	89.2	Tiemann <i>et al.</i> , (2002)
Sugarcane bagasse	Sodium bicarbonate	196	Junior <i>et al.</i> , (2006)
Bagasse fly ash	Hydrogen peroxide	2.50	Gupta and Ali (2004)
Nipah palm shoot biomass	Mercaptoacetic acid	52.86	Wankasi <i>et al.</i> , (2006)
Bamboo (BVC)	Nitric acid	57.71	This work
Bamboo (BVC)	Phosphoric acid	30.19	This work
Common Buckwheat (FEMC)	Nitric acid	56.49	This work
Common Buckwheat (FEMC)	Phosphoric acid	14.08	This work

3.2.3 Temkin isotherm model

The Temkin isotherm assumes that the heat of adsorption of all the molecules in a layer decreases linearly due to adsorbent-adsorbate interactions and that adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy (Areco *et al.*, 2010). The isotherm assumes that the fall in the heat of adsorption is linear rather than logarithmic as stated in Freundlich

expression (Teles *et al.*, 1993). Unlike the Langmuir and Freundlich equation, the Temkin isotherm takes into account the interactions between adsorbents and metal ions to be adsorbed and is based on the assumption that the free energy of sorption is a function of the surface coverage (Deng and Ting, 2005). The Temkin isotherm is applied in the following form

$$q_e = \frac{RT}{b_T} \ln(A_T C_e)$$

The linear form of Temkin equation is

$$q_e = \frac{RT}{b_T} \ln A_T + \frac{RT}{b_T} \ln C_e$$

$$q_e = \beta \ln \alpha + \beta \ln C_e$$

Where, $\beta = \frac{RT}{b_T}$; $\alpha = A_T$

T is the absolute temperature in Kelvin, R is the universal gas constant, 8.314 J/mol K, b_T is the Temkin constant related to heat of sorption (J mg^{-1}) and A_T the equilibrium binding constant corresponding to the maximum binding energy (L g^{-1}). The Temkin constants A_T and b_T together with R^2 values are shown in Table 1.

The equilibrium data analyzed from the three-isotherm model as indicated in Table 1 shows that Freundlich isotherms fitted more precisely due to high correlation coefficient value (R^2) than Langmuir and Temkin isotherm, this may be attributed to the heterogeneous distribution of the active sites and multilayer adsorption on the synthesized adsorbents (Gong *et al.*, 2011; Liu and Wang, 2013).

3.3. Effect of contact time

The removal efficiency and adsorption capacity of the adsorbents increase sharply in the initial stage and then gradually remain steady with the increase of agitation time (Fig. 2). The initial fast adsorption may be attributed to large uncovered surface area of adsorbents. With further increase in the agitation time, the availability of the uncovered surface area gradually diminishes. The uptake was slower at the final phase due to the internal surface adsorption attaining plateau region at equilibrium (Aroua *et al.*, 2008; Lo, 1999). The equilibrium was attained after shaking for 120 minutes. After equilibrium was attained, the percentage of sorption did not change with further increase in time. The decrease in the extent of removal of lead after 120 minutes of contact time in some cases may be due to the desorption process (Itodo *et al.*, 2009).

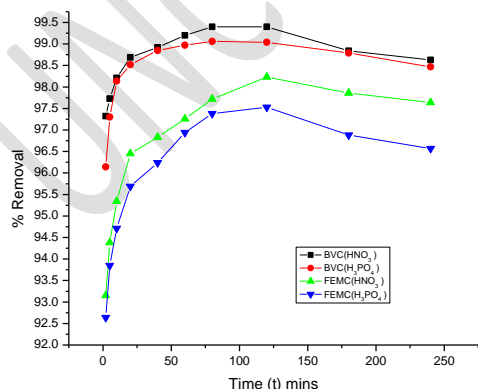


Figure 2. Effect of Contact time on percent removal of lead

3.4. Adsorption kinetics

One of the most important factors in designing an adsorption system is predicting the rate at which adsorption takes place, referred as the 'kinetics of sorption'. Three simplified kinetic models were adopted to examine the mechanism of the adsorption process.

3.4.1 Pseudo first-order model

Langergren and Svenska used rate equation to describe the adsorption of adsorbate from the liquid phase (Langergren & Svenska, 1898); the linear form of pseudo first order rate expression is given as

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t$$

where q_e and q_t (mg g^{-1}) are the adsorption capacities of Lead(II) ions at equilibrium and at time t (minutes), respectively, and k_1 is the rate constant of pseudo first-order kinetics. The correlation coefficient (R^2) and pseudo first order constant (k_1) for both adsorbents summarized in Table 3. The values of R^2 vary between 0.749-0.856. The calculated values from the first-order kinetic model show that the experimental results did not fit this model. The determination co-efficient is very low for the given materials. Moreover, large differences between experimental and calculated values of the equilibrium sorption capacities are observed (Table 3).

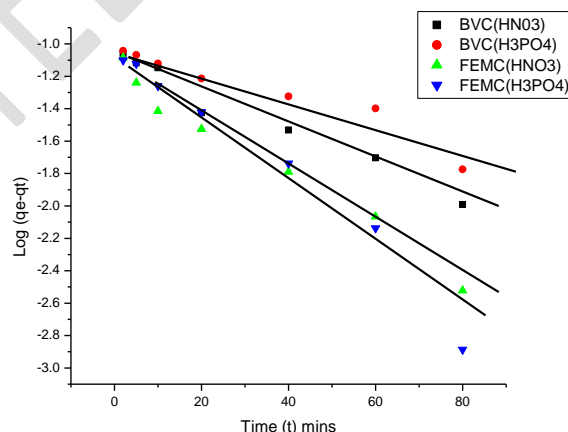


Figure 3. Pseudo-first order kinetic model fit for Pb(II) Ions adsorption on the adsorbents

3.4.2 Pseudo-second order model

The pseudo second-order rate expression, which has been applied for analyzing chemisorptions kinetics from liquid solutions (Ho, 2006; Shrihari and Madhan, 2005), is linearly expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$

Where k_2 is the rate constant for pseudo second-order adsorption ($\text{g mg}^{-1} \text{min}^{-1}$) and $k_2 q_e^2$ ($\text{mg g}^{-1} \text{min}^{-1}$) is the initial adsorption rate. The linear plot of t/q_t versus t , as shown in Fig. 4, shows a high linearity which yielded R^2 values that were greater than 0.999 for all adsorbents. Moreover, the calculated (cal) value of q_e (Table 3) from the

second-order kinetics was almost similar to the experimental (exp) values for all the adsorbents. Hence, it

can be concluded that the adsorption for both adsorbents was predominated by pseudo-second order kinetic model.

Table 3. Comparison of different kinetic models

ADSORBENT	BVC(HNO ₃)	BVC(H ₃ PO ₄)	FEMC(HNO ₃)	FEMC(H ₃ PO ₄)	
	q_e(exp) (mg g⁻¹)	58.453	40.341	30.257	24.234
Pseudo-first-order	q_e(cal) (mg g⁻¹)	45.231	23.544	12.782	9.562
	k₁ (1/min)	0.834	0.812	0.767	0.695
	R²	0.856	0.845	0.775	0.749
Pseudo-second-order	q_e(cal) (mg g⁻¹)	56.870	37.345	27.678	22.986
	k₂ (1/min)	0.826	0.897	0.833	0.762
	R²	1	1	0.999	0.999
Intraparticle diffusion model	k_{id} (mg/ g⁻¹/ min^{1/2})	0.012	0.009	0.029	0.026
	C	0.974	0.979	0.942	0.938
	R²	0.691	0.641	0.847	0.787

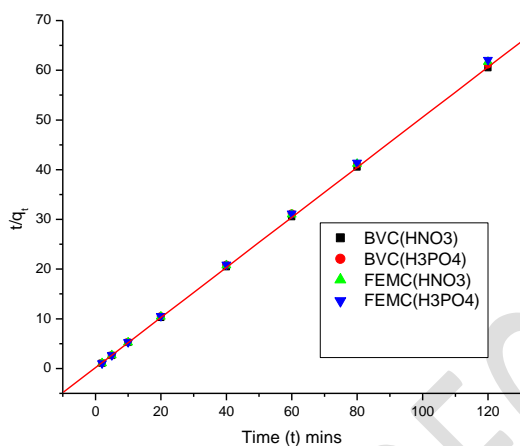


Figure 4. Pseudo-second order kinetic model fit for Pb(II) ions adsorption on the adsorbents

3.4.3. Intraparticle diffusion model

Intraparticle diffusion is a transport process involving the movement of species from the bulk of the solution to the solid phase. In a well stirred batch adsorption system, the intra-particle diffusion model has been used to describe the adsorption process occurring on a porous adsorbent (Webber and Morris, 1962; Ozacar and Sengil, 2005). According to Weber and Morris (1962), if the rate limiting step is intra-particle diffusion, a plot of solute adsorbed against the square root of the contact time should yield a straight line passing through the origin (Grente *et al.*, 2007). Also, the rate constant for intra-particle diffusion is obtained from the slope of the curve. Weber and Morris, (1962) theorized that the rate of intra-particle diffusion varies proportionally with the half power of time and is expressed as:

$$q_t = K_{id}(t^{1/2})C$$

where,

q_t = adsorbate uptake at time t , (mg g⁻¹)

K_{id} = the rate constant of intra-particle transport, (mg g⁻¹t^{1/2}), which can be evaluated from the slope of the linear plot of q_t versus $t^{1/2}$.

The values of intercept, c are related to the boundary layer thickness, i.e., the larger the value of the intercept, the greater is the boundary layer effect (Shrihari and Madhan, 2005; Webber and Morris, 1962). Fig. 5. shows the multilinearity in intra-particle diffusion plots for Pb(II) adsorption with different adsorbents. This indicates that intra-particle diffusion was not the only involved for Pb(II) adsorption, but there were some other processes involve in the rate controlling step. This suggests that adsorption occurred in three phases the initial steeper section represents surface or film diffusion; the second linear section represents a gradual adsorption stage where intra-particle diffusion is rate-limiting and the third section is final equilibrium stage. Thus, there were three processes controlling the adsorption rate.

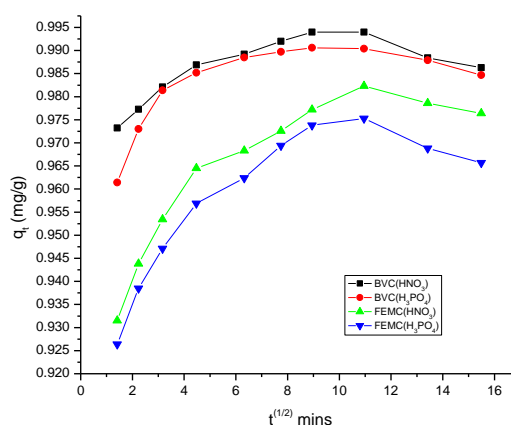


Figure 5. Intraparticle diffusion plots for the removal of lead by adsorption on various adsorbents

3.5. Effect of pH

pH is one of the key parameters which controls the adsorption efficiency by influencing the surface charges (Kannan and Rengasamy, 2005). It is an important

environmental factor influencing not only site dissociation, but also the solution chemistry of the heavy metals: hydrolysis, complexation by organic and inorganic ligands, redox reactions and precipitation. It strongly influences the speciation and adsorption availability of heavy metals (Esposito *et al.*, 2002).

The effects of initial pH on lead solution were investigated by varying the pH from 2 to 5.5 and using initial lead concentration of 20 mg L⁻¹ in 100 ml of lead solution with 1 g of adsorbent. The Lead adsorption usually increases as the pH is increased attaining optimum capacity at pH: 5.5 (Shukla *et al.*, 2002; Jalali *et al.*, 2002). Above pH 5.5, Pb(II) starts precipitating as Pb(OH)₂ and hence studies above this range are not conducted (Patnukao *et al.*, 2008).

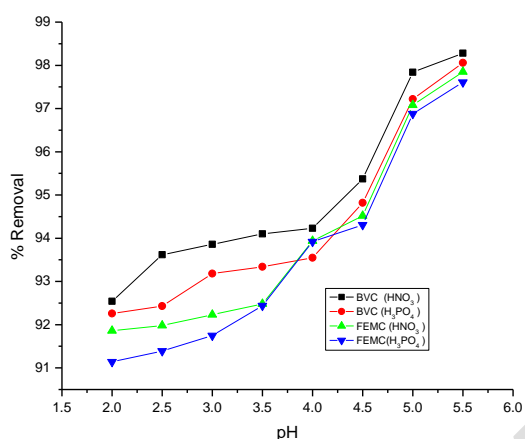


Figure 6. Effect of pH on percent removal of Lead.

4. Conclusions

Adsorption studies of lead on activated carbons was studied by batch method where effect of initial concentration, contact time and pH were the parameters considered for determining the adsorption efficiency of the synthesized carbon samples. The results of the percentage removal of lead increased with the increase of contact time and pH. On the contrary, the percentage of removal decreased with the increase in initial concentration of the standard lead solution. The equilibrium data was analyzed using Langmuir, Freundlich and Temkin adsorption isotherms. Freundlich isotherm displayed a better fitting model than the other two models with a higher correlation coefficient of 0.999 to 0.991 indicating a multilayer adsorption. Four adsorption kinetic models were studied, the pseudo second-order kinetic model accurately described the adsorption kinetics. The results show intraparticle diffusion was not the only rate limiting factor in adsorption of Pb(II) ions. The adsorption mechanism was found to be chemisorption and the rate-limiting step was mainly surface adsorption. Results from this study shows that both the adsorbents are very effective in the removal of Lead (II) ions. However, surface modification using HNO₃ gave a better result as compared to H₃PO₄. This suggests that surface modification using HNO₃ leads to the formation of more well-defined pores of different shapes and size attributing to its high surface area which trap more metal ions within the adsorbent. The novelty about these

bio-adsorbents is that the raw materials used are readily available almost throughout the year, inexpensive and user-friendly.

Acknowledgements

The authors acknowledge the staff of SAIF, NEHU Shillong for providing necessary laboratory facilities for analyzing lead samples.

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