
ADSORPTIVE REMOVAL OF IRON METAL USING PITHACELOBIUM DULCE BIOCHAR AS ADSORBENT

SUCHISMITA DASH

M.Tech Scholar

Chemical Engineering Dept.,
NIT RAIPUR, Chhattisgarh

Mr.V.K. SINGH

Assistant Professor

Chemical Engineering Dept.,
NIT RAIPUR, Chhattisgarh

ABSTRACT

In this study, adsorption of iron from its aqueous solution using activated biochar from Pithecellobium dulce wood as adsorbent was evaluated. The experiments were conducted to investigate the effects of pH, contact time, initial metal concentration and temperature on percentage removal of Fe(II) ions. The adsorbent was characterized using different techniques such as SEM, EDS, XRD and FTIR. The percentage removal of 92.85% was achieved at experimental conditions of pH 8, adsorbate concentration of 14mg/l and temperature of 323 K for an adsorbent dose of 0.08 g in 50 ml solution. The percentage removal was found to increase with an increase in temperature. The adsorption isotherms followed Langmuir isotherm model. The kinetics of the process was analyzed using pseudo first-order, pseudo-second order and intra particle diffusion models and found that pseudo second order model is best fitted.

Keywords - Adsorption, XRD, Kinetics, Isotherm

1.INTRODUCTION

Water pollution due to the disposal of heavy metals continues to be a great concern worldwide. Consequently, the treatment of polluted industrial wastewater remains a topic of global concern. Heavy metals pollution occurs in industrial wastewater such as that produced by metal plating facilities, mining operations, battery manufacturing processes, production of paints and pigments and the ceramic and glass industries. This wastewater commonly includes Cd, Pb, Cu, Zn, Ni, Mn and Fe. When this metal bearing waste water is released to the eco-system or the water bodies, they pose threat to living organisms, therefore it becomes important to develop technologies that result in effective removal of heavy metals from waste waters. Different alternatives for treating effluents are chemical precipitation, membrane process, ion exchange, liquid extraction and electrodialysis. However, some limitations in these processes can be high energy requirement, generation of toxic sludge or other waste products that require disposal or treatment, having low efficiency, labor-intensive operation and lack of selectivity of the process [1-3]. In contrast, adsorption technique is comparatively more effective and convenient due to factors like low cost, simple design, easy handling and sludge-free cleaning operations [1-9]. It works in an attractive way, especially when the adsorbent is inexpensive and easily available. In recent years, various natural adsorbents such as agricultural wastes including sunflower stalks, Eucalyptus bark, maize bran, coconut shell, waste tea, rice straw, tree leaves, peanut and walnut husks have been tried to achieve effective removal of various heavy metals [5,6,12,20]. Bailey et al. (1999) have presented an interesting review, which focuses on the potential of a wide variety of low cost sorbents for heavy metals. According to him, a low cost sorbent can be assumed if it requires less prior processing, is abundant in nature, or is either a by-product or waste material from another industry. These materials could be alternatives for expensive treatment processes.

Among many heavy metals iron is selected because it is the most released metal by industries. It is harmful if swallowed more than 3ppm and causes serious conjunctivitis, choroiditis, retinitis and siderosis [13]. Among various biomass adsorbents, ganga emli wood was preferred for this study because it is easily available in countries like India. The ganga emli wood was first converted into carbon through pyrolysis at high temperature and then that carbon was activated using phosphoric acid. Removal of iron from wastewater and different parameters affecting the adsorption process were studied.

The objective of this study was (i) preparation of activated Pithecellobium dulce carbon (PLDC) through chemical activation with H_3PO_4 using Pithecellobium dulce (ganga emli) wood as raw material (ii) characterization of PLDC using SEM, EDX, XRD and FTIR (iii) study of different parameters like pH, adsorbent dose, concentration, contact time and temperature on adsorption of Fe by PLDC (iv) study of

kinetic, and equilibrium isotherms to describe the rate and mechanism of adsorption for determining the factors controlling rate of adsorption.

2. MATERIALS

The ganga emli wood was collected from the NIT Raipur campus and chemicals were purchased from the local market at Raipur (Chhattisgarh). Hydrochloric acid (HCL) was supplied by M/s Loba Chemicals, Mumbai (Maharashtra) whereas NaOH (pellet), and H₃PO₄ (85% purity) were supplied by M/s Merck Specialties Private Limited, Mumbai (Maharashtra). The iron compound was ferrous sulphate (Fisher Scientific make), having chemical formula FeSO₄.7H₂O and molar mass 278.01 g/mol.

3. METHODS

3.1 Preparation of adsorbent

Preparation of adsorbent is divided into two stages: carbonization and activation process. Before the carbonization, the ganga emli wood was cleaned with Millipore ultrapure water to remove the adhering foreign matter from its surface. The wood was then dried in hot air oven for about 16 h followed by grinding and subsequent size separation through screening to obtain the particles in the size range -220 +350 mesh BSS. It was then carbonized at 480°C to get carbon. For activation, the carbon was mixed with 85% H₃PO₄ in 1:1(w/w) and put into muffle furnace at 400°C for 1hr. It was then cooled and washed, repeatedly, with Millipore ultrapure water till the the pH of the filtrate reaches 6-7. Finally, it was dried in hot air oven at 50°C for 24 h to get activated PLDC.

3.2 Preparation of Adsorbate

Metal solutions were prepared with analytical grade iron sulphate, distilled water was used for all dilution. Metal ion concentrations were measured with AAS (Atomic Adsorption Spectrophotometer). The instrument operating conditions (i.e., wavelength and slit width) were set according to the operating manual.

4. BATCH ADSORPTION EXPERIMENTS

The batch adsorption studies were carried out in an orbital shaker at 120 rpm. The effects of operating parameters such as solution pH, adsorbent dose, initial Fe(II) ion concentration, time and temperature on the adsorption process were studied. Experiments were carried out by taking 0.08 g adsorbent with 50 ml of metal solution in 100 ml Borocil conical flask which was shaken in an orbital shaker. The initial pH was adjusted by using 0.1 N NaOH and 0.1 N HCL solutions with the help of a pH meter. The suspensions were filtered and metal concentrations in the supernatant solutions were measured using AAS (Atomic Absorption Spectrophotometer). The removal of Fe(II) ions from the test solution by the adsorbent was calculated by the following equation:

$$\text{Percentage removal of Fe(II) ions} = \frac{C_i - C_f}{C_i} \times 100 \dots\dots\dots(1)$$

$$\text{Adsorption capacity} = \left(\frac{C_i - C_f}{m} \right) * V \dots\dots\dots(2)$$

Where, C_i = Initial Fe(II) ions concentration, mg/l

C_f = Final Fe(II) ions concentration, mg/l

V = Volume of solution, litre

m = Mass of adsorbent, g

5. BATCH KINETIC AND ISOTHERM STUDY

To determine the time (t) necessary for attaining the equilibrium, the kinetics of adsorption was studied. Reweighed amounts of the adsorbents were added to 50 ml aqueous solution containing 14mg/l of Fe(II) ions in a series of conical flasks. The flasks were then kept in a temperature controlled orbital shaker for stirring at 120±5 rpm. At the end of the shaking for a predetermined period (t), the flasks were withdrawn, solutions were filtered, and the filtrates were analyzed for the Fe(II) ions concentration. The experiments were conducted at three different temperature viz., 30, 40 and 50 °C.

For the analysis of adsorption isotherms, the experiments were carried out at pH 8 by adding fixed amount of adsorbent in 50 ml of iron solution. The initial concentration (C_0) was varied in the range of 14-24 mg/l. Adsorbent was separated from the solution after 1 hr, and the Fe(II) ions concentration in the filtrate was estimated.

Pseudo-first-order, pseudo-second-order and intraparticle diffusion were used for kinetic modeling whereas Langmuir, Freundlich and Temkin isotherms were used to describe the adsorption process.

6. CHARACTERIZATION OF PLDC

To analyze different functional groups corresponding to different bond stretching present at the surface of adsorbent, Fourier transform infrared spectroscopy was used. For dilution, the sample was mixed with KBr (sample to KBr ratio 1:25). A translucent disk was prepared by pressing the mixed sample in a KBr press, using model M-15 and the pellet, thus obtained, was analyzed between frequency ranges of 500 to 4000 cm^{-1} by averaging 16 scans for each spectrum. For morphology, pore distribution and compositional analysis the SEM and EDX were done by means of ZEISS EVO Series Scanning Electron Microscope Model EVO 18 instrument in a vacuum environment at 1.50KX magnification. The X-ray diffraction (XRD) pattern analysis was done by PAN analytical 3 kW X'pert Powder.

7. RESULTS AND DISCUSSION

7.1 XRD Analysis of PLDC

The X-ray diffraction (XRD) pattern of PLDC, carried at room temperature, is shown in Fig.1 (a). No sharp peak in the pattern indicates that the adsorbent PLDC is lacking inorganic material and having an amorphous structure.

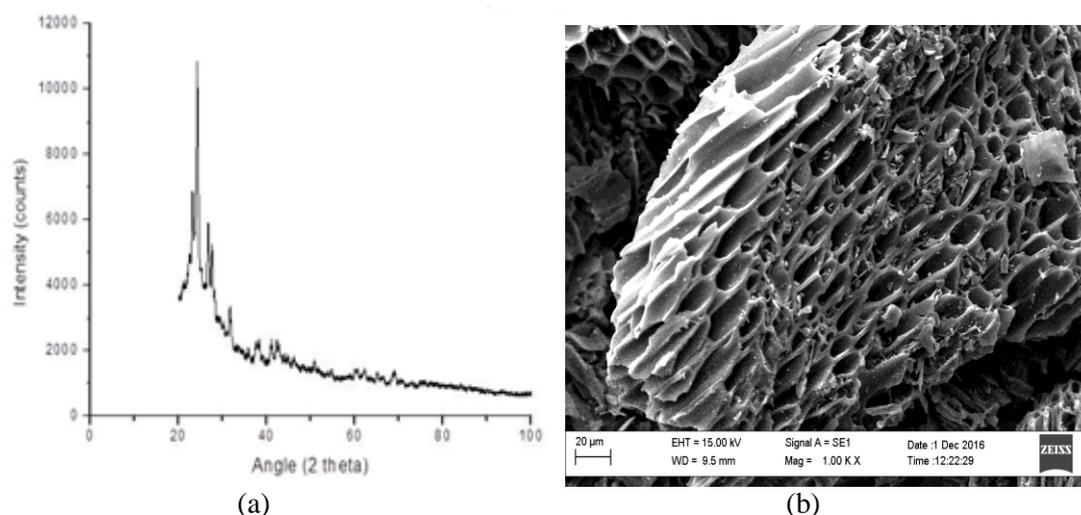


Figure 1: (a) XRD spectra of PLDC and (b) SEM image of PLDC before adsorption

7.2 Scanning Electron Micrographic Analysis (SEM)

The rough surface of PLDC with number of pores and cavities reveal good possibility of metal adsorption, Fig. 1 (b).

7.3 EDS Analysis of PLDC

The elemental composition of PLDC before adsorption was found as 60.81 % C, 32.11% O, 0.07 % Na, 6.78 % K, Mg 0.06% and 0.17 % S on weight basis.

7.4 FTIR Analysis

Fig. 2 shows the FTIR spectra of PLDC before adsorption. The peak at wavelength 3428.4 cm^{-1} corresponds to the presence of alcohols and phenols. The peaks at 1703.2 cm^{-1} wavelength is due to presence of primary amines. Peaks observed at 1595.0 correspond to aromatic and small peaks at 1167.73 cm^{-1} , and 1040.05 cm^{-1} are due to presence of alkyl halides and aliphatic amines respectively.

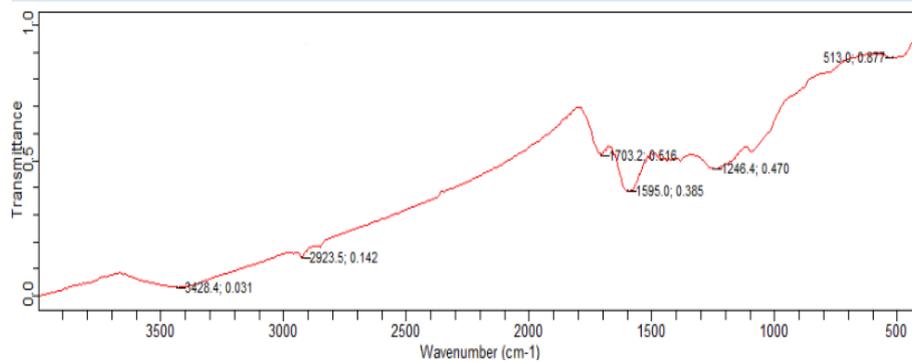


Figure 2: FTIR image of PLDC

7.5 Effect of pH

The pH of the metal solution played an important role in the adsorption of Fe(II) ions. With an increase in pH from 2 to 8, percentage adsorption increases. At lower pH values, the surface charge on the adsorbent is positive and because of this the H⁺ ions compete with metal ions for active sites in adsorbent [20,22]. Increase in pH result in the electrostatic repulsion between the cations and surface sites, there by the competing effect of the H⁺ ions decreases and the positively charged Fe(II) ions get adsorbed on the free binding sites, resulting an increase in the total metal uptake, as shown in figure-3(a).

7.6 Effect of Adsorbent Dose

The adsorbent dose was varied in the range of 0.01 to 0.1 g by fixing parameters like initial metal concentration, contact time, temperature and pH shown in Fig. 3 (b). It was found that the removal of Fe(II) ions increases upto certain limit and then remains almost constant[11,22]. This is because the number of available active sites increased by increasing the adsorbent dose from 0.02 g to 0.08 g, resulting in the higher removal of Fe(II) ions and it reaches the maximum removal of Fe(II) ions at an optimum dose of 0.08 g for the adsorbent PLDC.

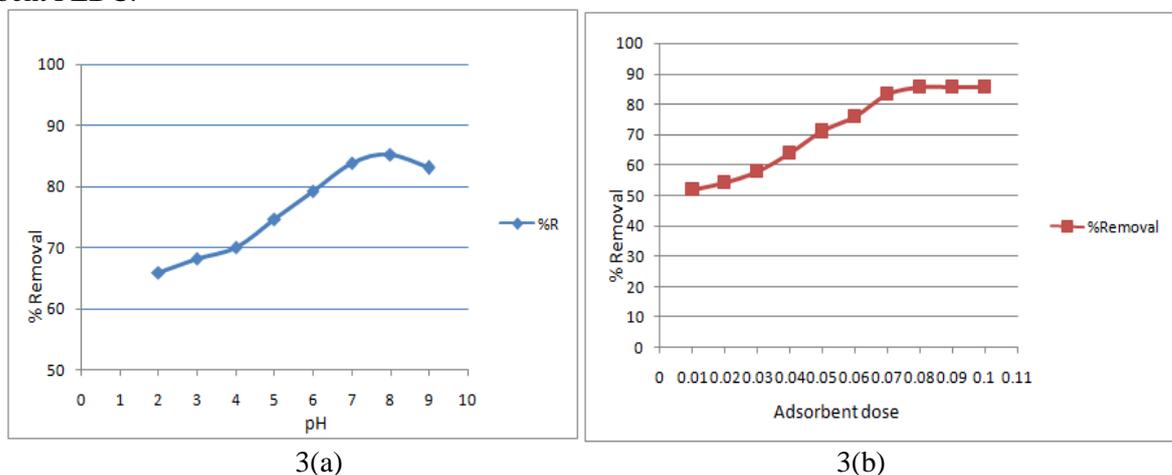


Figure 3: (a) and (b) shows the effect of pH and adsorbent dosage on percentage Fe(II) ions removal by PLDC

7.7 Effect of Initial Concentration

The effect of initial metal concentration was analysed by varying initial metal concentration from 14 to 24 mg/l as shown in figure 3(d). The decrease in the removal of Fe(II) ions may be due to the saturation of the available active sites because only the fixed quantity of adsorbent was used for all the initial Fe(II) ions concentrations[13,17,18].The fixed amount of adsorbent can be able to remove only the fixed amount of metal ions present in the solution.

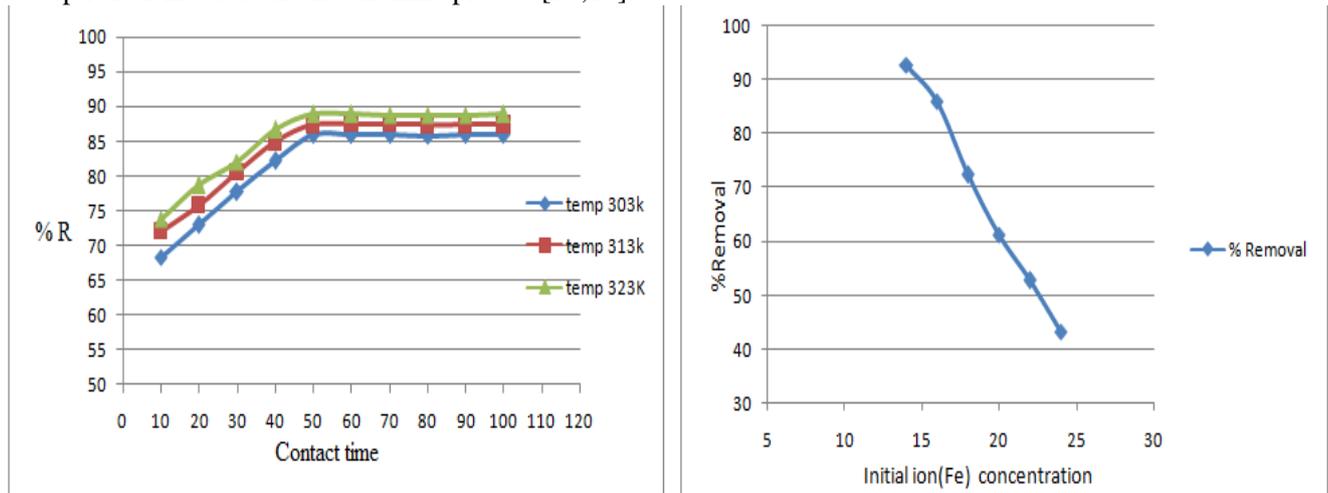
7.8 Effect of Contact Time

The effect of contact time on adsorption of Fe(II) ions at different temperature was determined while keeping adsorbent dosage, initial concentration and pH constant as shown in Fig. 3 (c). The fast adsorption at

the early stage may be due to the initial concentration gradient between the adsorbate in solution and the number of vacant sites available on the adsorbent surface. The attainment of equilibrium adsorption might have been due to reduction in the available active adsorption sites on the adsorbent with time resulting to limited mass transfer of the adsorbate molecules[20,21].

7.9 Effect of Temperature

The adsorption was carried out at three different temperatures i.e. 303, 313, and 323 K as shown in Fig. 3(c). The percentage removal of metal was found to increase with increasing temperature, revealing that the adsorption of metal is an endothermic process[14,16].



3(c)

3(d)

Figure: 3 (c) effect of time and 3(d) effect of initial metal ion concentration on percentage Fe(II) ions removal by PLDC

7.10 Equilibrium Adsorption Study

Adsorption isotherms is the relationship between the solid phase concentration (q_e) and liquid phase concentration (C_e) of the solute at constant temperature. Adsorption isotherm of Fe(II) ions at 303, 313 and 323 K are shown in figure 3(d). For the dynamic adsorptive separation of solute from solution, the following isotherms Langmuir, Freundlich, and Temkin were studied.

7.10.1 Langmuir Isotherm

Adsorption isotherm reveals the interaction between adsorbate and adsorbent. For the monolayer adsorption on surface containing equal activation energy and finite number of identical sites, Langmuir isotherm model play a vital role [21].

7.10.2 Freundlich Isotherm

This isotherm is used to describe the multilayer adsorption with non-uniform distribution of heat and affinities over heterogeneous surface [19].

7.10.3 Temkin Isotherm

The Temkin isotherm is used for adsorption of heterogeneous system. The assumption for applicability of Temkin isotherm is that the heat of adsorption decreases linearly with increasing adsorption quantity, and the adsorption binding energy is distributed uniformly [20]. Isotherm parameters for the removal of Fe(II) ions by PLDC are given in Table 2.

7.11 Adsorption Kinetics

Pseudo-first-order, pseudo-second-order, and intraparticle diffusion [21] models were used to investigate the adsorption process of Fe(II) ions onto PLDC and the value of kinetic parameters along with correlation coefficient for these kinetic models are listed in Table 1. The linear correlation coefficient for the pseudo-second-order kinetic model is closer to unity than the pseudo-first-order kinetic model. Therefore, the sorption reaction can be approximated more favorably by the pseudo-second-order kinetic model for PLDC adsorbent.

Table 1. Kinetic parameters for the removal of Fe(II) ions by PLDC

Kinetic models	Equations	Parameters	Temperature		
			303 K	313 K	323 K
Pseudo-first order	$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t$	q_e exp (mg/g)	3.55	3.62	3.76
		q_e cal (mg/g)	0.33	0.34	0.33
		K_1 (min ⁻¹)	0.02	0.03	0.04
		R^2	0.94	0.92	0.91
Pseudo-second order	$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t$	q_e exp (mg/g)	3.55	3.62	3.76
		q_e cal (mg/g)	3.49	3.61	3.71
		K_2 (g/mg min)	0.43	0.44	0.45
		R^2	0.99	0.99	0.99
Intraparticle diffusion	$q = K_{id} t^{1/2} + C$	K_{id} (mg/g min ^{1/2})	0.16	0.17	0.18
		C (mg/g)			
		R^2	3.16	3.28	3.36
			0.98	0.98	0.98

Table 2. Isotherm parameters for the removal of Fe(II) ions by PLDC

Isotherms	Equations	Parameters	Temperature		
			303 K	313 K	323 K
Langmuir	$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m}$	K_a (L/mg)	0.33	0.27	0.25
		q_m (mg/g)	13.17	13.28	14.02
		R^2	0.99	0.99	0.99
Freundlich	$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$	K_F [(mg/g)/(mg/L) ^{1/n}]	4.69	5.74	5.61
		n	2.35	2.46	2.69
		R^2	0.97	0.96	0.97
Temkin	$q_e = B_T \ln A_T + B_T \ln C_e$	K_T (L/mg)	5.08	6.59	7.28
		B_t	2.54	2.76	2.92
		R^2	0.95	0.94	0.95

8. CONCLUSION

The effects of different parameter like pH, adsorbent dosage, concentration, contact time and temperature on removal of Fe(II) ions were studied. The adsorption was found to increase with increase in temperature, adsorbent dose and contact time. SEM of adsorbent after adsorption indicates that macro-pores on the surface of PLDC were filled up by the metal molecules. Langmuir isotherm model was found to be best fit with high-correlation coefficient. The kinetic study data indicates that the adsorption of Fe(II) ions on adsorbent followed the second order kinetics. Maximum adsorption capacity was found to be 12.8 mg/g for PLDC at 323 K. Finally it can be concluded from the study that PLDC is a suitable adsorbent for adsorption of Fe(II) ions.

9. REFERENCES

- [1] Njikam, E., Schiewer, S. 2012. Optimization and kinetic modeling of cadmium desorption from citrus peels: a process for biosorbent regeneration, *J Hazardous Materials*, Vol 8, pp. 213-214.
- [2] Kumar, PS., Gayathri, R., Senthamarai, C., Priyadharshini, M., Fernando, PSA., Srinath, R. 2012. Kinetics, mechanism, isotherm and thermodynamic analysis of adsorption of cadmium ions by surface-modified *Strychnos potatorum* seeds, *Korean J Chem Eng*, Vol 29, pp. 52–60.
- [3] Sheela, T., Nayaka, Y.A., Viswanatha, R., Basavanna, S., Venkatesha, T.G. 2012. Kinetics and thermodynamics studies on the adsorption of Zn(II), Cd(II) and Hg(II) from aqueous solution using zinc oxide nanoparticles, *J Powder Tech*, Vol 217, pp.163–70.
- [4] Silva Claudineia, R., Gomes Taciana, F., Andrade Graziela, C. R. M., Monteiro Sergio, H., Dias Ana, C.R., Zagatto Elias, A. G., Tornisielo Valdemar, L. 2013. *J Agr Food Chem*, Vol 61, pp. 2358–2363.
- [5] Emmanuel, K. A., Rao, A.V. 2009. Comparative Study on Adsorption of Mn(II) from aqueous Solutions on Various Activated Carbons, *J of Chemistry*, Vol 6, pp.693-704.
- [6] Reddad, Z., Gerente, C., Andres, Y., Cloirec le P. 2002. Adsorption of several metal ions onto a low-cost biosorbent: Kinetic and equilibrium studies, *J Environ Sci Technol*, Vol 36, pp. 2067-2073.
- [7] Aksu, Z. 2001. Equilibrium and kinetic modelling of cadmium biosorptions in a batch system: Effect of temperature, *J Sep Purif Technol*, Vol 21, pp. 285-294.
- [8] Aannadurai, A., Juang, R. S., Lee, D. J. 2002. Adsorption of heavy metals from water using banana and orange peels, *J Water Sci Technol*, Vol 47, pp.185-190.
- [9] Gnanasambandam, R., Protor, A. 2008. Determination of pectin degree of esterification by diffuse reflectance Fourier Transform Infrared Spectroscopy, *J Food Chem*, Vol 68, pp.327-332.
- [10] Sar, A., Tuzen, M., Soylak, M. 2007. Biosorption of Pb(II) and Ni(II) from aqueous solution by lichen biomass, *J Biochem Eng*, Vol 37, pp. 151-158.
- [11] Ademiluyi, F. T., Nze, J.C. 2011. Multiple adsorption of heavy metal ions in aqueous solution using activated carbon from nigerian bamboo, *J Research in Engineering and Technology*, Vol 187, pp. 2321-7308.
- [12] Kyzas, G. Z., Bikiaris, D. N., Kostoglou, M., Lazaridis, N. K. 2013. Copper removal from aqueous systems with coffee wastes as low-cost materials, *J Environmental Management*, Vol 94, pp. 1915-1929.
- [13] Emeka Osakwe, Charles., Sanni, Isma'i., Sa'id, Suraji., Zubairu, Adamu. 2014. Adsorption of Heavy Metals from Wastewaters Using Adonosa digitata Fruit Shells and Theobroma cacao Pods as Adsorbents: A Comparative Study, *J Environmental Health Science & Engineering*, Vol.18, pp.212-245.
- [14] Rungrodnimitchai, S., Kotatha, D. 2015. Chemically modified ground tire rubber as fluoride ions adsorbents, *J Chemical Engineering*, Vol 282, pp. 161–169.
- [15] Choksia, P. M., Joshib, V.Y. 2007. Adsorption kinetic study for the removal of nickel (II) and aluminum (III) from an aqueous solution by natural adsorbents, *J Desalination*, Vol 208, pp. 216–231.
- [16] Emmanuel, K.A., Rao, A.V. 2008. Adsorption of Mn(II) from aqueous solutions using pithacelobium dulce carbon, *Rasayan J. Chem*, Vol 1, pp.840-852.
- [17] Emmanuela, K. A., Rao, A.V., Nagalakshmi, T.V., Reddy, M.G., Diwakarb, P. P., Sureshbabue, Ch. 2015. Factors influencing the removal of fluoride from aqueous solution by Pithacelobium dulce Carbon, *J Der Pharma Chemica*, Vol. 7(2), pp. 225-236.
- [18] Kamari, A., Yusoff, S. N. M., Abdullah, F., Putra, W. P. 2014. Biosorptive removal of Cu(II), Ni(II) and Pb(II) ions from aqueous solutions using coconut dregs residue: Adsorption and characterisation studies, *J Process Safety and Environmental Protection*, Vol 85, pp.1912-1919.
- [19] Hasar, H. 2008. Adsorption of nickel(II) from aqueous solution onto activated carbon prepared from almond husk, *J Hazardous Materials*, Vol B97, pp.49–57.
- [20] Patnukao, P., Kongsuwan, A., Pavasant, P. 2008. Batch studies of adsorption of copper and lead on activated carbon from *Eucalyptus camaldulensis* Dehn. Bark, *J Environmental Sciences*, Vol 20, pp. 1028–1034.