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Isothermal Removal PB (II) Metal Ion from Aqueous Solutions onto Local Eucalyptus Stem Based Activated Carbon

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ABSTRACT

Eucalyptus Stem was use to prepare activated carbon through chemical activation method with 0.5M NAOH and under temperature of 500 0C for 45min. Activated carbon is one of the most important industrial products due to its versatile applications. In this work, efficient activated carbon was produced and utilized for adsorption of lead (II) from simulated wastewater under varying operational parameters. The raw material (Eucalyptus) has been chemically modified by sodium hydroxide to improve its surface reactivity and enhance its adsorption capacity . The adsorbent was characterized by the FTIR analysis. The experimental data were analyzed by adsorption isotherms and kinetic models. Langmuir equation proved to be suitable to explain the adsorption process and the experimental results fit well with the pseudo- second- order model .The performance of the prepared Eucalyptus - based activated carbon suggests it can be used as low coast or cheap adsorbent for the treatment of water and removal of heavy metal ions from industrial effluents.

Keywords: Activated carbon, Biosorption, Eucalyptus, Isotherm, Wastewater treatment

1. INTRODUCTION

The contamination of water by heavy metal ions has increased over the last few decades due to industrial processes such as petroleum refinery process and the development of new technology in refining of petroleum. Heavy metals are continuously discharged into the aquatic surroundings from natural processes like volcanic activity and weathering of rocks. Additionally, industrial processes such as electro planting, metal finishing, metallurgical, chemical industrialization and mining industries have also contributed to an increase in the concentration of heavy metal in the water (1). Ions of heavy metals including: copper, lead, zinc, cadmium, nickel, mercury and chromium have significant impacts on the environment. They form very toxic ions and compounds forms; they are soluble in water and may be readily absorbed into living organisms (2). Also, toxic metals have adverse effect on the health of human, when they penetrated through the human organ and tissue as well as the entire systems. Lead in any concentrated can caused kidney damage and toxicity symptoms include impaired kidney function, poor reproductive capacity, hypertension, tumors, etc. (2) Furthermore, Metallic toxicant may find their way into the body, where they act through one or more of the following possible mechanisms. This include (a) Inhibition of enzymatic activities, (b) Attacks on cell membrane and receptor, or (c) Interference with metabolic cations. In the later case, heavy metals can increase the acidity of the blood which forces the body draw Ca from the bones to help restore blood pH. High concentration of Ca in the blood results in hardening of the artery walls and its progressive blockage of the arteries which leads to osteoporosis(3).

Nowadays many researchers are concentrate on the uptake of these metals in aqueous solutions using cheapest materials such as activated carbon, which is on the other hand, are prepared from a variety of local raw materials of vegetable origin, such as wood and peat. The by-products include soft lignocellulosics such as rice straw, soybean hull, sugarcane bagasse, peanut shell and harder materials such as pecan and walnut shells (4),(5). Some in place treatment technologies available for the removal of heavy metal ions from aqueous solutions are chemical precipitation, ion exchange, coagulation, and bioremediation and sorption/adsorption, Adsorption technique is excellent, easy and economic method for the removal of toxic pollutants from the aqueous solutions. Adsorption is a surface phen omenon which involves the attraction of adsorbate particles towards the surface of an adsorbent until equilibrium is attained between adsorbed particles and those freely distributed in the bulk gas or liquid(6).

Figure 1.1: Eucalyptus stems plant

Eucalyptus shown in (Figure 1.1) is a native plant of Kurdistan region and can be used to prepare charcoal with the potential to treat wastewater containing pollutants (5). A high surface area activated carbon with great potential for heavy metal removal can be obtained by chemical modification of charcoal with sodium hydroxide. This work is aimed at producing effective and low- cost activated carbon from eucalyptus biomass for wastewater treatment under various operational parameters.

In this work, the adsorption isotherm, Kinetic and thermodynamic of heavy metal ions onto eucalyptus based activated carbon were studied.

Adsorption isotherm is a functional expression that correlates the amount of solute adsorbed per unit weight of the adsorbent and the concentration of adsorb ate in bulk solution at a given temperature under equilibrium conditions. It is important to establish the most appropriate correlations for the batch equilibrium data using empirical or theoretical equations as it plays a functional role in predictive modeling procedures for analysis and design for adsorption systems.

2 MATERIALS AND METHODS

No	Chemicals	Company
1	Sodium hydroxide with purity 97%	Aldrich – Germany
2	Hydrochloric Acid with purity 37%	Riedal – deHean / Germany
3	Lead(II)nitrate with purity 99%	Merck
4	Pre- treated eucalyptus biomass	

2.1 Chemical Activation

2.1.1 Carbonization

The carbonization of the materials was done at 500oC for two 45 minutes and allowed to cool at room temperature according to the method of Ekpete. and Horsfal (10).

2.1.2 Preparation of Activated Carbon from Eucalyptus

A pre- washed and dried of eucalyptus stem was used as a starting material (see figure 3.1 a). The dried biomass was converted to charcoal in furnace at 500°C in the absence of oxygen over period of 2hr. After the sample cooled at room temperature, it was chemically treated in order achieve chemical activation. Briefly, 250 ml of NaOH (30% W/V) was added to 5.0 g of charcoal in beaker and heated at 60°C under constant stirring for 24 hrs. The treated charcoal was separated from the solution, cooled and washed with de- ionized water, The materials were washed again with hot distilled water and finally cold distilled water. Then, the material was heated at (80 °C) for 10 hrs to remove the moisture content. The obtained eucalyptus based activated carbon thus obtained was stored in desiccators for later use.

2.2 Preparation of standard solution

The stock solution of 1000mg/L of $Pb2+$ was prepared by dissolving by 1.3357g of $pbCl2$ in 1000 ml volumetric flask and fill up to the mark with distilled water. And then a certain volume 10 ml of oil has been added to above solution with efficient agitation.

2.3. Adsorption Properties

2.3.1. Dosage of Adsorbents

Different doses of the adsorbent were mixed with the metal ion and the mixture was agitated in a mechanical shaker. The percentage of different adsorption doses was determined by keeping all other factors constant.

2.3.2. Initial Concentration

In order to determine the rate of adsorption, different initial concentrations of metal ion ranging from 0.1-1gram were used. All other factors are kept constant.

2.3.3. Contact Time

The effect of period of contact linking the adsorbent and adsorbate on the removal of the metal ion in a single cycle was determined by keeping initial concentration, particle size, pH, dosage, and temperature constant.

2.3.5. Temperature

The adsorption experiments were carried out at constant temperatures, 30 ºC in a thermostated shaker machine. The constancy of the temperature was maintained with an accuracy of ± 0.5º C.

2.3.4. pH

Adsorption experiments were carried out at a range of pH 1-10.The acidic and alkaline pH of the medium has been maintained by adding the necessary amounts of hydrochloric acid and sodium hydroxide solutions.

2.3.6. Equilibrium Adsorption Isotherms

The adsorption data was evaluated using Freundlich model. The fitting parameter and calculated constants as well as graphical representation was obtained by linear regression analysis .The Freundlich model is represented by the following equation(12)
qe = Kf Ce1/n
qe = quantity adsorbed per gram of carbons in (mg/g), Kf = adsorption capacity, 1/n =adsorption intensity. The Pb2+concentration retained in the adsorbent phase was calculated according to equation(12)
qe= (Ci-Cf) V/W
Where Ci and Ce are the initial and equilibrium concentrations (mg/L) of Pb2+solution respectively; V is the volume (L); and W is the mass (g) of the adsorbent.

3. RESULT AND DISCUSSION

3.1 FT-IR characterization of eucalyptus activated carbon

One of the most important parameters that influence and determine the adsorption of metal ions from aqueous solutions by activated carbon are the carbon-oxygen functional groups present on the carbon surface FTIR spectroscopy is made for sample eucalyptus activated carbon, and those responsible for the adsorption of Pb2+. FTIR spectra for (a) eucalyptus biomass, (b) eucalyptus activated carbon (c) Pb2+ loaded eucalyptus activated carbon, are presented in (Figure 3.1). The spectrum of raw eucalyptus has a broad band at 3341.8 cm-1due to stretching vibration of the hydrogen bonded hydroxyl groups (- OH from carboxyls, phenols or alcohols) stretching vibration . The band at the 2923.5cm-1 is due to aliphatic C- H stretching either in aromatic methoxyl group or in methyl and methylene side chains). The adsorption band in the range 1595.6–1426.7 cm-1correspond t C- C stretch, the peak at the 1242.5cm-1indicate C - O group stretch , the long band at 1027.6 cm-1 refers to C- N group.

The weak band at the 1733.8 cm^{-1}refer to the H- C=O stretching vibration of olefins. The peak of around 1385 $cm^{-1}$is due to –C- H bending. The adsorption band in the range (1100- 1200 cm^{-1}) is related to stretching vibration of CO group in alcohol, ether, acid and/or ester. For the spectrum of eucalyptus activated carbon, a reduction in hydroxyl group and –C- H group was observed and increased stretching at 1568.7 cm^{-1}which refers to C=C group was also noticed. The two peaks at 1426.7$cm^{-1}$and 1242.5cm^{-1}were reduced. Additionally, the spectrum of eucalyptus activated carbon show new three small peak at the 877.92 cm^{-1}, 816.5 cm^{-1}(C- H), 751.27 cm^{-1}which may be due to lead chloride modification and dueto C- Cl stretch in alkyl halide. The spectrum of Pb^{2+}loaded- eucalyptus activated carbon in comparison with eucalyptus activated carbon, show decrease in the bands at 1576.4 cm^{-1} and 1158 cm^{-1}, and a new peak appeared at 1257.9cm^{-1}(C- O), this confirms the adsorption of Pb^{2+} onto eucalyptus activated carbon.

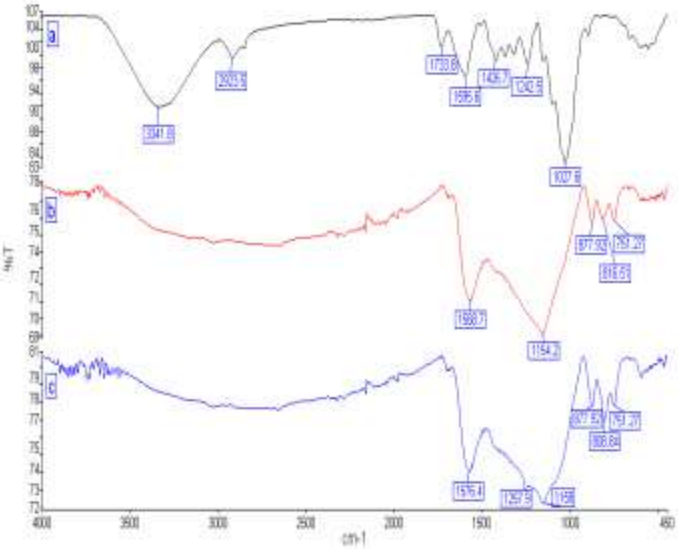

Figure 3.1.1: FT- IR analysis of (a) raw material (eucalyptus), (b) eucalyptus activated carbon (c) Pb2+loaded-eucalyptus activated carbon

In this study NaOH activation creates carbon surface rich in oxygen functional groups, The effectiveness of NaOH activation relative to either physical activation methods or activation by other chemical agents can be attributed to the ability of Na to form intercalation compounds with carbon easily. , formation of such functional group enhance the adsorption capacity(16) XRD analysis is made to identify the crystallographic structure of the samples (Figure3.2),The literature of carbon materials repeatedly refers to the crystallite and to the crystallite size, with its graphitic connotations, in analyses of structure within activated carbon based on XRD data. The XRD diagrams of activated carbon prepared from eucalyptus tree indicate the intense main peak shows the presence of highly organized crystalline structure of Carbon with crystalline structure Rhombohedral and carbon supplied with crystalline structure Orthorhombic were detected, this crystalline structure increase the adsorption of metals on to prepared activated carbon ,where the metals adsorbed on the upper layer of the crystalline structure of the carbon surface by means of physisorption .

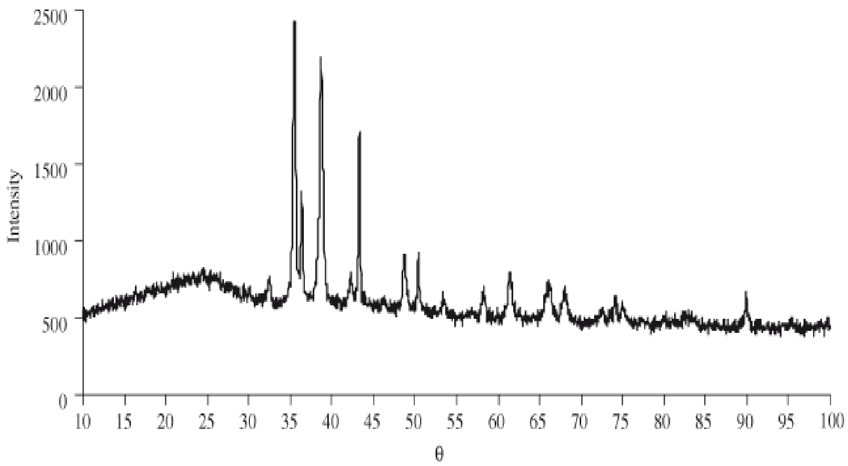

Figure 3.1.2: XRD pattern of eucalyptus core activated carbon

3.2 Effect of Adsorbent Dose, Contact Time and pH

The effect of the adsorbent dose was studied at temperature of (30oC) by varying the sorbent amounts from 0.2 to 1.2 g/L. For all these runs, initial concentration of Pb2+ were fixed as 1 mg/L. Figure3.2.1, the result shows that the adsorption of Pb2+ increases rapidly with increase in the amount of activated carbon prepared from eucalyptus tree due to greater availability of the surface area at higher concentration of the adsorbent. For sample the significant increase in uptake was observed when the dose was increased from 0.2 to 0.8 g/L. Any further addition of the adsorbent beyond this did not cause any significant change in the adsorption. This may be due to overlapping of adsorption sites as a result of overcrowding of adsorbent particles(14,15) , the contact time was in the 80min for the sample Table 1 . For the pH studies, the adsorption decreased as the pH increase, the optimum pH was attended at 6 Figure3.2.2. Activated carbon prepared from eucalyptus tree shows very strong adsorption and reduction properties.

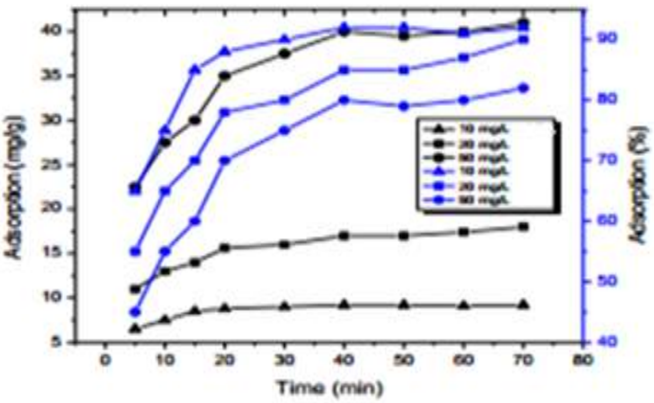

Figure3.2.2: Effect of contact time on adsorption of PB (II) (Temperature :30 0C, pH: 6.0, Adsorbent dose: 2g/l)

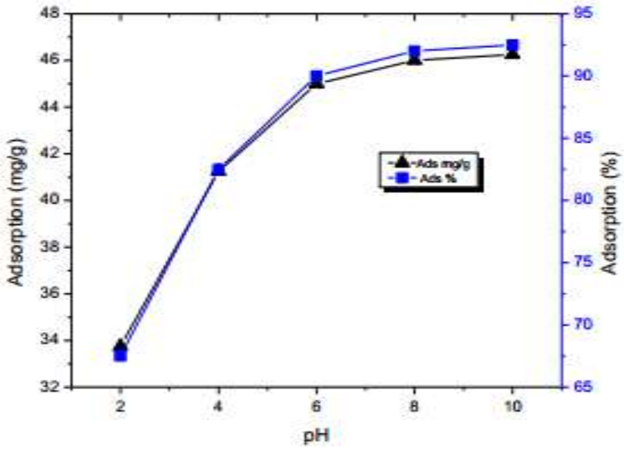

Figure 3.2.3: Effect of pH on adsorption of PD (II) (Temperature :30^{0}C, pH: 6.0, Adsorbent dose: 2g/l)

3.3 Adsorption Kinetics Models

Kinetic models such as the pseudo- first and pseudo- second were applied to investigate the kinetic mechanism of lead adsorption onto Eucalyptus activated carbon using the equations below. The integral form of pseudo- first - order is represented as:

$$\log(q_e - q) = \log q_e - \frac{K_{ad} t}{2.303}$$

Where q, q_e represent the amount of Pb(II) removed at time t (min) and equilibrium (mg/g) respectively , and Kad(min-1) is rate constant of the model.

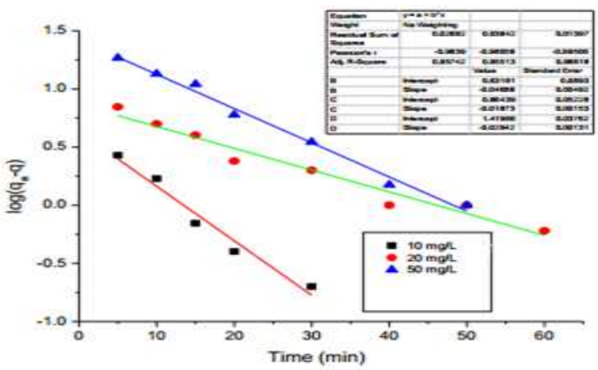

Figure 3.3.1: Pseudo- first - order model for Pb(II) removal

The integral form of pseudo- second- order equation is given as;

$$\frac{t}{q} = \frac{1}{K_2 q^2 e} + \frac{1}{q_e} t$$

Where K2 is the model rate constant, the experimental data were fitted into the two kinetic and obtained plots utilized to establish the various kinetic parameters. The suitability of the model was established based on the closeness of the correlation coefficient (R2) to unity.

The linear plots obtained showed the applicability of both kinetic equations. But the higher correlation coefficient (R2≈ 1.0) is an indication of the consistency of the experimental data to the pseudo- second- order equation compared with pseudo- first order equation (R2= 0.955–0.988). This can help us to conclude that the adsorption process may be chemisorption in nature

Table 3.1: kinetic parameters at different concentration

Kinetic models							
Pseudo-first-order					Pseudo-second-order		
Conc mg/L	qe exp. (mg/g)	K_1 (1/min)	q_e mg/g	R^2	K_2 (g/mg min)	q_e mg/g	R^2
50	41	0.068	26.3	0.988	248.60	44.21	0.999
20	18	0.043	7.31	0.955	85.70	18.9	0.998
10	9.2	0.11	4.3	0.957	18.60	9.5	0.998

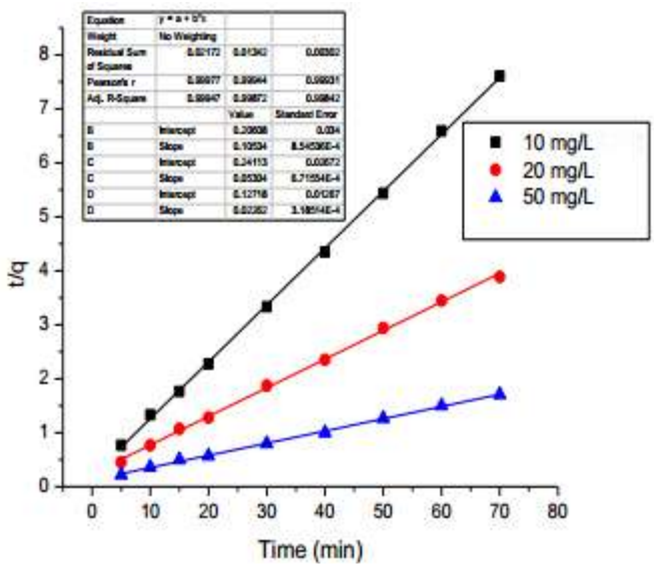

Figure 3.3.2: Pseudo- second- order model for PD (II) removal

3.4 Adsorption Isotherms

Two widely applied isotherm equations were applied to fit the experimental data obtained in this work. Freundlich and Langmuir equations were used and can be represented as follows:

$$\ln q_e = \ln K + \frac{1}{n} \ln C_e$$

$$\frac{1}{q_e} = \frac{1}{q_m K_f C_e} + \frac{1}{q_m}$$

The Pb(II) sorption by eucalyptus activated carbon obeyed the Langmuir isotherm as presented in (Table 3.2). The values of KL(0.618 L/mg)and qm (49.02 mg/g) were obtained from the model plot and tabulated below. The Freundlich constants k and 1/n were calculated to be 42.220 and 0.0778, respectively, indicating favorable adsorption by eucalyptus activated carbon

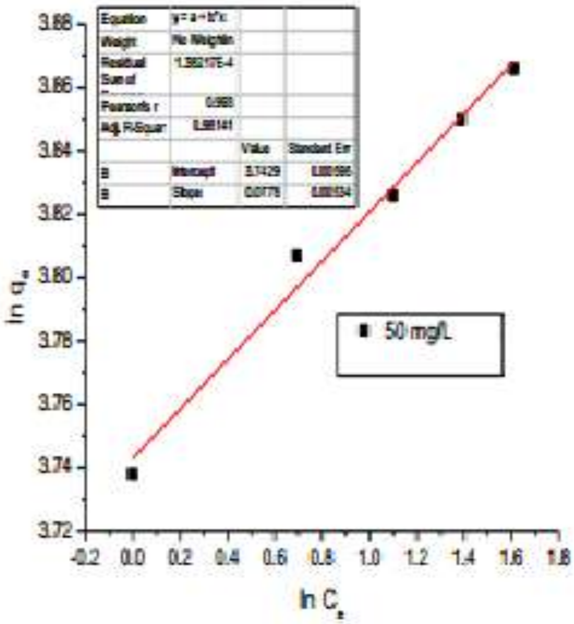

Figure 3.4.2: Langmuir adsorption isotherm

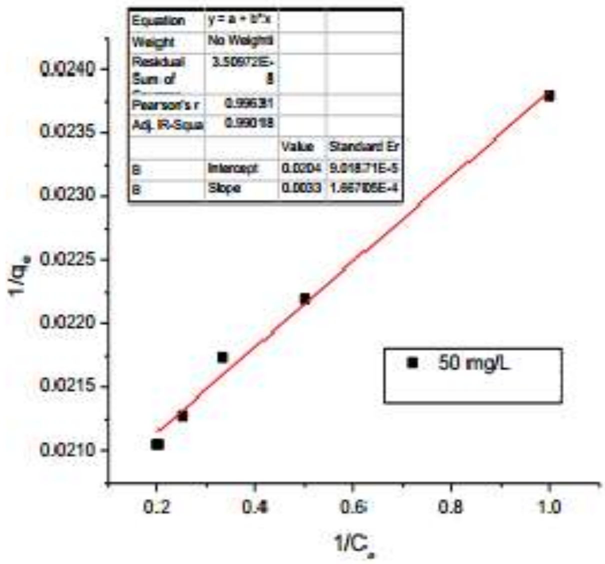

Figure 3.4.1: Freundlich adsorption isotherm

Table 3.2: Adsorption isotherm parameters at pH 6.0

Freundlich	Langmuir
k_f = 42.22 mg/g	q_m = 49.02 mg/g
1/n = 0.0778	K_L =0.618 L/mg
n = 12.85	R^2 =0.99018
R^2 =0.98141	

CONCLUSION

Activated carbon prepared from agricultural waste was done successfully .The various properties studied The present research work indicates the applicability of eucalyptus stem as an effective low cost adsorbent for the removal of lead ion from aqueous solution. The adsorption process was highly dependent on solution pH and adsorbent dose, also the results showed good adsorption capacity and intensity.

REFERENCES

[1]. Salih, S. J. "Batch Adsorption System of Hazardous Crystal Violet onto Treated Walnut Shell: Kinetic and Thermodynamic Studies." International Journal of Enhanced Research in Science Technology & Engineering, Vol. 4 pp: (55-66).

[2]. Olorundare, O. F., Krause, R. W., Okonkwo, J. O., & Mambapotential, B.B.(2012). Application of activated carbon from maize tassel for the removal of heavy metals in water. Physics and Chemistry of the earth, Parts A/B/C 104-110.

[3]. Ansari, R., & Mohammad- khah, A.(2009). Activated Charcoal: preparation, characterization and Applications: A review article. International journal of Chem Tech Research, Vol.1 , No.4, pp 859- 864.

[4]. Khan, A.A.(2012). Theory of adsorption Equilibria analysis based on general equilibrium constant expression. Turk J Chem, 219- 231.

[5]. Kamaa, O. G.(2011). Removal of reactive red 198 from aqueous solution by Potamogeton crispus. Chemical Engineering Journal, 579- 585.

[6]. Wang, L. W. (2008). Adsorption properties of Congo Red from aqueous solution on to surfactant- modified montmorillonite. Journal of Hazardous Materials, 173- 180.

[7]. Gregorio, C. P. M. (2008). Application of chitosan, a natural amino polysaccharide, for dye removal from aqueous solution by adsorption processes using batch studies: A review of recent literature. Progress in Polymer Science, 399- 447.

[8]. Doguc, J. Y. (2008). Dynamic analysis of sorption of Methylene Blue dye on granular and powdered activated carbon. Chemical Engineering Journal, 400-406.

[9]. Kinhikar, R. V. (2012). Removal of Nickel(II) from aqueous solution by adsorption with granular activated carbin(GAC). Research journal of chemical science. Vol. 2(6), PP 6- 11.

[10]. Mohamad- Nor, N., Lau, L. C., Lee, K. T., & Mohamad, A. (2013). Synthesis of activated carbon from lignocellulose biomass and Envi ronmental chemical Engineering, vol.1, Issue 4, pp 658- 666.

[11]. Hasar, H. (2003). Adsorption of nickel(II) from aqueous solution onto activated carbon prepared from almond husk. Journal of hazardous materials.vol.97, PP 49- 57.

[12]. Virginia ,H and Adrian ,B (2012).Lignocellolosic Precursors used in the synthesis of Activated carbon. Published By In Tech p.p 25-60.

[13]. Rajeshwari, Sivaraj and Rajendran, Venckatesh. (2010) Preparation and Characterization of Activated Carbons from Parthenium Biomass by Physical and Chemical Activation Techniques. E-Journal of Chemistry, 7(4), 1314-1319.

[14]. Viswanathan, B. Varadarajan,T.K Indra Neel,P.(2008) A process for the preparation of activated carbon from botanical sources, , Indian Pat. P.p 107-189.

[15]. Subhashree Pradhan (2011). Production and characterization of Activated Carbon produced from asuitable Industrial sludge (research project)p.p 12-33.

[16]. Chandrakant D. Shendkar, Rasika C. Torane, Kavita S. Mundhe, Ashish A. BhaveNirmala R. Deshpande. (2012). Characterization of Activated Carbon prepared from Achyranthes aspera Linn. by X-ray fluorescence spectroscopy (XRF).Journal of natural product and plant resourse. 2(2),p.p 295-297.

[17]. Roop, B. and Goyal, M. (2005) Activated Carbon Adsorption, CRC Press, Taylor & Francis Group, 6000 Broken Sound Parkway NW, Suite 300 Boca Raton, FL, USA 33487–2742.

[18]. Nurul′Ain. Bint. Jabit. (2007).The Production and Characterization of Activated Carbon Using Local Agricultural Waste through Chemical Activation Process, p.p 10-40.

[19]. Mopoung .S and Nogklai, W. (2008)Chemical and surface properties of longan seed activated charcoal. International Journal of Physical Sciences Vol. 3 (10), pp. 234-239.

[20]. Sax ,N, Irving .Dangerous properties of industrial material . Reinhold publishing crop. New York :cite in info@nortiamerica.com.

[21]. Senthil ,P and Kirthika ,K (2009).Equilibrium and Kinetic study of adsorption of Nickel from aqeous solution on to Bael tree leaf powder . Journal of Engineering Science and Technology.Vol. 4, No. 4 351 – 363.