

Removal of Cobalt (II) from Aqueous Solutions by Adsorption on Low cost activated carbon

R.PRABAKARAN[§] S.ARIVOLI^{*}

[§]Department of chemistry, Centre for Research and Development, PRIST University, Vallam, Thanjore (District), Tamilnadu, India.

[#]Mount Zion College of Engineering and Technology, Pudukkottai,

^{*} Department of chemistry, Thiru.Vi.Ka. Ka Government Arts College, Thiruvarur, India

Abstract

In this research work, activated carbon prepared locally from *Thespesia Populnea* bark (TPC) was examined for the removal of cobalt (II) from aqueous solution. The main parameters, like effect of adsorbent dosage, Co (II) concentrations, effect of contact time and effect of pH was studied in batch experiments. The experimental results were analyzed by using Langmuir, Freundlich, adsorption isotherm models. The kinetic data well described by the pseudo-first-order kinetic model. The various thermodynamic parameters such as ΔH° , ΔS° and ΔG° were also determined. The activated carbon produced from TPC was successfully employed for removal of cobalt (II) ion from aqueous solution and the technique appears industrially applicable and feasible.

Keywords: cobalt (II) ions, adsorption, kinetic, isotherm

Notations

C_i initial concentration of adsorbate (mol/L)

R Gas constant (8.1314)

T Temperature in Kelvin

ΔH° Enthalpy

ΔS° Entropy

ΔG° Free energy

Abbreviation

TPC -*Thespesia Populnea* Bark Carbon

Introduction

The safety our environment has been continuously rapid increase in urbanization, industrialization and human activities [1] Heavy metals are toxic pollutants released into the surface and ground water as a result of various activities such as industries, mining and agriculture [2]. The rapid pace of industrialization has led to severe problem of water pollution. Heavy metals can easily enter the food chain because of

their high solubility in water. These heavy metals may include copper, iron, zinc, cadmium, lead, cobalt etc. Thus taking into account the harmful effect of these heavy metals, that causes a number of health problems, diseases and disorders [3]

Cobalt (II) compounds are essential in many industries. Their applications in nuclear power plants, metallurgy, mining, pigments, paints and electronic are only few examples where the presence of cobalt in waste waters represents a major environmental problem [4, 5]. The treatment technologies more frequently cited for removal of heavy metals are carbon adsorption, wet oxidation, solvent extraction, precipitation, ultra filtration, reverse osmosis, ion-exchange, etc[6].

Among these options, adsorption is most preferred method and activated carbon is most effective adsorbent widely employed to treat wastewater containing different classes of metal ions/dyes, recognizing the economical drawback of commercial activated carbon. Activated carbon has been quite successful for removal of impurities from exhaust gas and waste water streams. The highly porous nature of the carbon provides a large surface area for contaminants to get deposited. The adsorption takes place because of the

attractive force between the molecules. In this study, the batch experiments were conducted in order to investigate the removal of cobalt (II) ions from aqueous solutions using locally prepared activated carbon from *Thespesia Populnea* bark (TPC).

Material and methods

Adsorbent preparation

Adsorbent (Activated Carbon Fig 1) has been produced by using air-dried *Thespesia Populnea* bark with conc. sulphuric acid in a weight ratio of 1:1. Then the product was heated in a furnace at 500°C for 12 hours and followed by washing with water until free from excess acid and dried at $150 \pm 5^\circ\text{C}$. The dried material was ground well to fine powder and sieved.



Fig (1) Activated Carbon

Batch equilibrium method:

The adsorption of cobalt (II) ion on TPC was studied by batch technique. The experiments were done at various temperature such as 30, 40, 50 and 60°C in batch process.

The experiments were carried out in different 100 ml iodine flasks. Prior to each experiment, a predetermined amount of adsorbent was added to each flask. The stirring was kept constant at 120 rpm. Each flask was filled with a known amount of sample before commencing stirring such as metal solutions with an initial concentration of 5 mg/L to 25 mg/L. The flask containing the sample was withdrawn from the shaker at the predetermined time interval, filtered and the residual of the metal ion concentration has been measured.

Results and discussion

Characteristics of the adsorbent

The physico chemical properties of the adsorbent are listed in Table 1.

Table 1-Characteristics of the Adsorbent

Sl. No	Properties	TPC
1	Particle size(mm)	0.041
2	Density (g/cc)	0.3243
3	Moisture content (%)	0.3255
4	Loss in ignition (%)	0.273
5	pH of aqueous solution	6.5

Effect of contact time and initial Cobalt (II) ion concentration

The effect of contact time on Cobalt (II) adsorption on TPC was investigated to study about the rate of removal of cobalt ion. Fig. 2 shows that the percentage removal of Cobalt (II) for various values of initial Co ion concentration ranging from 5 to 25mg/L. From Fig. 2, indicated that, the percentage of Cobalt (II) ions removed at 5, 10, 15, 20 and 25 mg/L levels from 25 to 61 respectively. As the concentration of metal ion increases, more and more surface sites are covered and hence at higher concentrations of metal ions the capacity of the adsorbent get exhausted due to non-availability of the surface sites [7].It is therefore evident that at low concentration ranges the percentage of adsorption is high because of the availability of more active sites on the surface of the adsorbent.

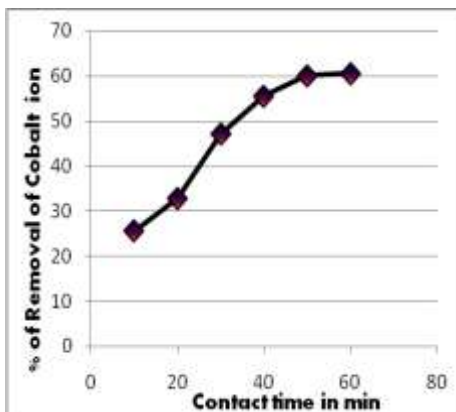


Fig. 2- Effect of Contact time on the adsorption of Cobalt (II) ion onto TPC

[Cobalt] = 50 mg/L: Adsorbent dose =
25mg/ 50ml: pH=6.5

Effect of adsorbent dose

The results for adsorptive removal of cobalt ions with respect to adsorbent dose are shown in Fig. 3. The adsorption of Cobalt ion on adsorbent was studied by varying the carbon concentration from 5 to 25 mg/50 ml while keeping the cobalt ion concentration as 50mg /L. From Fig. shows that the increase in adsorbent dosage from 5 to 25 mg/50 ml resulted in an increase from 73 to 86% in adsorption of cobalt ion. It is due to the availability of high binding sites for complexation of cobalt ions [8]. The equilibrium values were showed in Table.2.

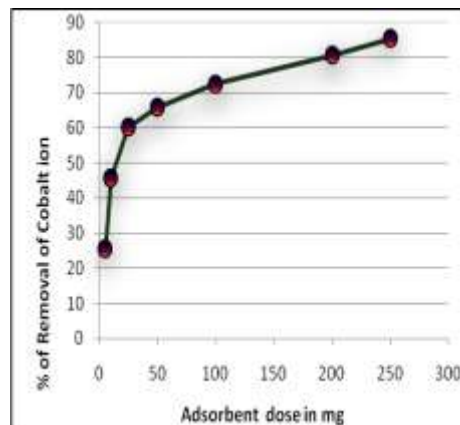


Fig. 3- Effect of Adsorbent dose on the adsorption of Cobalt ion onto TPC

[Cobalt] = 50mg/L: contact time = 60min:
pH=6.5

Adsorption isotherms

Adsorption isotherm study was done by four different temperatures which were are 30, 40, 50 and 60°C .Two most common isotherm models were used for describing the adsorption data, which were Langmuir and Freundlich isotherm. The Langmuir equation can be represented in the form of following equations.

$$C_{eq}/Q_{eq} = 1/Q_m b + C_{eq}/Q_m \quad (1)$$

Where C_{eq} is the equilibrium concentration of cobalt ion in solution (mg/L), Q_{eq} is the amount of cobalt ion adsorbed; Q_m and b is Langmuir constants related to adsorption efficiency and energy of adsorption, respectively.

Table 2 – Equilibrium parameters for the adsorption of Co (II) ions onto activated carbon

Cobalt ion (mg/L)	Temperature ° C											
	C _e (mg/L)				Q _e (mg/g)				Removal of Cobalt ion (%)			
	30	40	50	60	30	40	50	60	30	40	50	60
5	0.272	0.223	0.181	0.155	9.457	9.554	9.638	9.689	94.57	95.54	96.38	96.89
10	1.459	1.253	0.975	0.776	17.08	17.49	18.05	18.45	85.41	87.47	90.25	92.24
15	3.285	2.825	2.384	1.994	23.43	24.35	25.23	26.01	78.10	81.16	84.11	86.70
20	8.755	8.172	7.559	6.953	22.49	23.66	24.88	26.09	56.23	59.14	62.20	65.24
25	14.19	13.46	12.72	12.04	21.61	23.08	24.57	25.91	43.22	46.17	49.14	51.83

Table.3 Langmuir Isotherm, Freundlich Isotherm results and Dimensionless Separation factor for adsorption of Co(II) ion onto TPC

Cobalt ion, (mg/L)	Temp °C	Langmuir Isotherm			Freundlich Isotherm			Dimensionless Separation Factor(R _L)				
		Statistical parameters			Statistical parameters			[Cobalt ion]。 (mg/L)				
		r ²	Q _m	b	r ²	K _f	n	5	10	15	20	25
	30	0.9911	22.271	5.045	0.9231	3.181	4.618	0.038	0.019	0.013	0.008	0.006
	40	0.9912	23.752	4.480	0.9272	3.266	4.528	0.036	0.021	0.014	0.011	0.007
	50	0.9931	25.188	4.616	0.9331	3.368	4.512	0.041	0.021	0.014	0.010	0.007
	60	0.9913	26.525	4.773	0.9342	3.459	4.466	0.040	0.020	0.013	0.010	0.006

The linear plots of C_{eq}/Q_{eq} vs. C_{eq} suggest the applicability of the Langmuir isotherms Fig. 4. The values of Q_m and b were calculated from slope and intercepts of the plots are given in Table 3. From the results, it is indicated that the value of adsorption efficiency Q_m and adsorption energy b of the carbon increases on increasing the temperature. The values can conclude that the maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on adsorbent surface with constant energy and no diffusion of adsorbate in plane of the adsorbent surface. To confirm the favourability of the adsorption process, the separation factor (R_L) was determined and listed in Table 3. The values were established to be between 0 and 1 and confirm that the ongoing adsorption process is favorable [9]. The Freundlich isotherm is generally represented by the following equation.

$$\log Q_e = \log K_f + 1/n \log C_e \quad (2)$$

Where Q_e is the amount of cobalt ion adsorbed (mg/g), C_e is the equilibrium concentration of cobalt ion in solution

(mg/L), and K_f and n are constant integrates, the factors affecting the adsorption capacity and intensity of adsorption, respectively. Linear plots of $\log Q_e$ versus $\log C_e$ shows that the adsorption of cobalt ion obeys the Freundlich adsorption isotherm. In Fig.5, the Freundlich adsorption isotherm obtained by plotting C_e/q_e versus C_e for the adsorption of cobalt (II) on TPC at the different temperatures investigated, respectively. The K_f and n values are given in Table 3, which indicate that the increase of negative charges on the adsorbent surface makes electrostatic force like Vander Waal's between the carbon surface and cobalt ion.

The values clearly indicate the dominance in adsorption capacity. The intensity of adsorption is an indication of the bond energies between metal ion and adsorbent, and the possibility of slight chemisorptions rather than physisorption [10, 11]. However, the multilayer adsorption of cobalt ion through the percolation process may be possible. The values of n are less than one, indicating the physisorption is much more possible [12].

Table 4 – Equilibrium parameters for the adsorption of Cobalt ions onto TPC

Cobalt ion (mg/L)	Temperature ° C											
	C_e (mg/L)				Q_e (mg/g)				Removal of Cobalt ion (%)			
	30	40	50	60	30	40	50	60	30	40	50	60
5	0.272	0.223	0.181	0.155	9.457	9.554	9.638	9.689	94.57	95.54	96.38	96.89
10	1.459	1.253	0.975	0.776	17.08	17.49	18.05	18.45	85.41	87.47	90.25	92.24
15	3.285	2.825	2.384	1.994	23.43	24.35	25.23	26.01	78.10	81.16	84.11	86.70
20	8.755	8.172	7.559	6.953	22.49	23.66	24.88	26.09	56.23	59.14	62.20	65.24
25	14.19	13.46	12.72	12.04	21.61	23.08	24.57	25.91	43.22	46.17	49.14	51.83

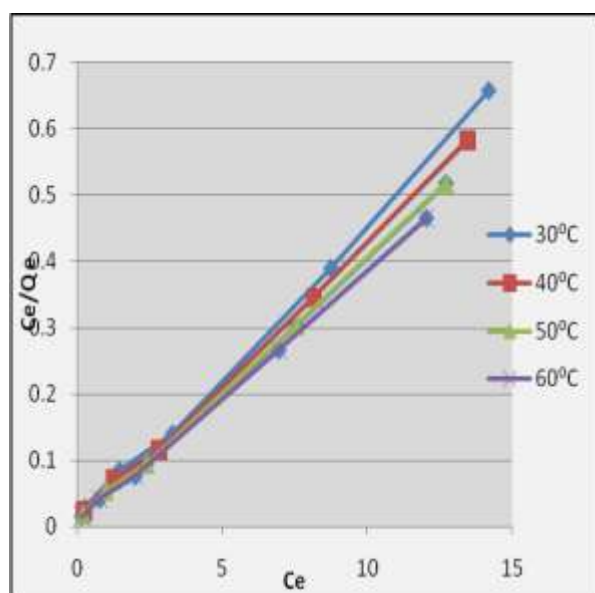


Fig. 4- Langmuir Isotherm for the adsorption of cobalt ion onto TPC

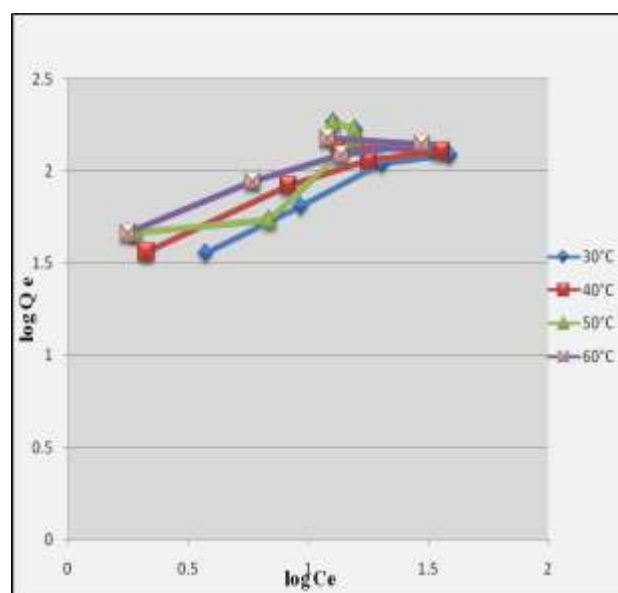


Fig 5- Freundlich Isotherm for the adsorption of cobalt ion onto TPC

Thermodynamic studies

The experiments were done at different temperatures of 30, 40, 50 and 60°. Variable thermodynamic parameters such as change in free energy (ΔG°) (kJ/mol), enthalpy (ΔH°) (kJ/mol) and entropy (ΔS°) (J/K mol) were determined by the following equations.

$$K_0 = C_{\text{solid}}/C_{\text{liquid}}$$

$$\Delta G^\circ = -RT \ln K_0$$

$$\log K_0 = \Delta S^\circ / (2.303R) - \Delta H^\circ / (2.303RT)$$

Where K_0 is the equilibrium constant, C_{solid} is the solid phase concentration at equilibrium (mg/L), C_{liquid} is the liquid phase concentration at equilibrium (mg/L), T is the temperature in Kelvin, and R is the gas constant. The ΔH° and ΔS° values obtained

from the slope and intercept of Van't Hoff plots are given in Table 4. The values of ΔH° is in the range of 1 to 93 kJ/mol indicates the favorability of physisorption. It is very clear that from the results that physisorption is much more possible for the adsorption for cobalt ion. The positive values of ΔH° indicate the endothermic nature of adsorption and it governs the possibility of physical adsorption[12,13]. The negative values of ΔG° are given in Table 4 indicate that the adsorption is greatly favorable for cobalt ion. The positive values of ΔS° in Table 4 shows the increased disorder and randomness at the solid solution interface of cobalt ion with TPC adsorbent. The results indicate that more efficient physisorption[11, 14 and 15].

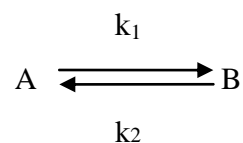
Table 5 – Equilibrium constant and thermodynamic parameters for the adsorption of Cobalt ion onto TPC

Cobalt ion (mg/L)	ΔH°	ΔS°	Temperature (°C)							
			K_0				ΔG°			
			30°	40°	50°	60°	30°	40°	50°	60°
5	16.474	78.149	17.41	21.44	26.59	31.17	-7198.2	-7976.9	-8810.0	-9522.8
10	20.147	80.919	5.855	6.984	9.259	11.89	-4452.2	-5057.9	-5976.8	-6854.9
15	16.890	66.219	3.566	4.309	5.291	6.521	-3203.2	-3801.2	-4474.3	-5191.2
20	10.620	37.015	1.284	1.447	1.645	1.876	-630.74	-962.16	-1337.5	-1742.6
25	9.7019	29.741	0.761	0.858	0.966	1.076	-687.22	-399.33	-92.817	-202.31

Adsorption kinetics

The kinetics of removal of Co (II) using TPC as an adsorbent, pseudo first order, has been tested with the experimental data. The sorption of cobalt ions on TPC may involve chemical sorption which can control the chemical reaction rate. The removal of cobalt ion from an aqueous solution obeys the reversible first order kinetics, when a single species considered on a heterogeneous surface. At equilibrium, the rate is the ratio of the concentration of adsorbate in adsorbent and concentration of adsorbate in aqueous solution given by K_0 . The results indicate that K_0 values decreases with increase in the concentration of the cobalt ion and increases with increase in temperature. The calculated values are listed

given in the Table 4. The heterogeneous equilibrium between the cobalt ion solution and the activated carbon are represented as



Where k_1 is the forward rate constant and k_2 is the backward rate constant. A indicate the cobalt ion remaining in the aqueous solution and B indicate that cobalt ion adsorbed on the surface of activated carbon. The rate constants calculated as earlier [10, 11 and 16]. The data are specified in Table 5, shows that the forward rate constant is much higher than the backward rate constant suggesting that the rate of adsorption is clearly dominant.

Table 6- Rate constants for the adsorption of metal ion ($10^3 k_{ad}, \text{min}^{-1}$) and the constants for forward ($10^3 k_1, \text{min}^{-1}$) and reverse ($10^3 k_2, \text{min}^{-1}$) process.

Temperature (°C)												
Cobalt ion mg/L	k_{ad}				k_1	k_2	k_1	k_2	k_1	k_2	k_1	k_2
	30	40	50	60	30		40		50		60	
5	0.057	0.061	0.065	0.070	0.054	0.003	0.058	0.002	0.063	0.002	0.068	0.002
10	0.032	0.035	0.040	0.046	0.027	0.004	0.030	0.004	0.036	0.003	0.042	0.003
15	0.025	0.027	0.030	0.033	0.019	0.005	0.021	0.005	0.025	0.004	0.028	0.004
20	0.019	0.020	0.022	0.023	0.010	0.008	0.011	0.008	0.013	0.008	0.015	0.008
25	0.016	0.017	0.019	0.020	0.007	0.009	0.008	0.009	0.009	0.009	0.010	0.009

A clear examination of the effect of cobalt ion concentrations on the rate constant K_{ad} (Table 5), the values help to describe the mechanism of metal ion adsorption taking place. In cases of strict surface adsorption a variation of rate should be proportional to the first power of concentration. However, when pore diffusion limits the adsorption process, the relationship between initial cobalt ion concentration and rate of reaction will not be linear. It shows that pore diffusion limits the overall rate of cobalt ion adsorption[12, 17].

Effect of pH

The solution of pH is an important parameter in the adsorption process of metal ions from aqueous solutions, which affect both the dissociation degree of functional groups from adsorbent surface and the

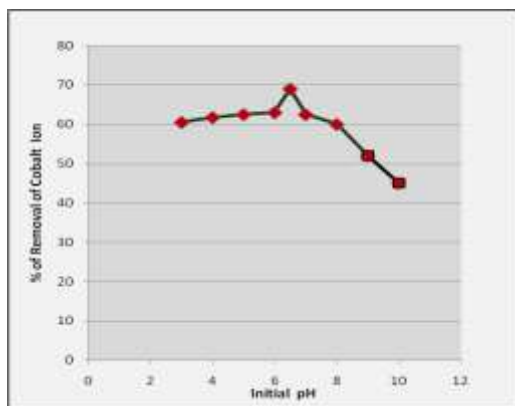


Fig. 6- Effect of pH on the adsorption of cobalt ion onto TPC

[Co]= 20mg/L: adsorbent dose = 25 mg /
50ml: contact time = 60min

speciation and solubility of metal ions[18]. The effect of pH on the removal of cobalt ion using TPC as an adsorbent was studied with initial pH range from 3-11. The relation between the initial pH of the solution and percentage removal of cobalt ion is depicted in Fig. 6. As can be seen from Figure observed that the percentage adsorption Cobalt ions increased appreciably (1-2 times) with increase of pH from 3 to 6.5 and consistent with results obtained by others.

Effect of the other ion

The effect of other ion like Cl^- on the adsorption process was studied at various concentrations. The effect of sodium chloride on the adsorption of cobalt ion on TPC is shown in Fig. 7. The low concentrate NaCl solutions have slight influence on the adsorption capacity.

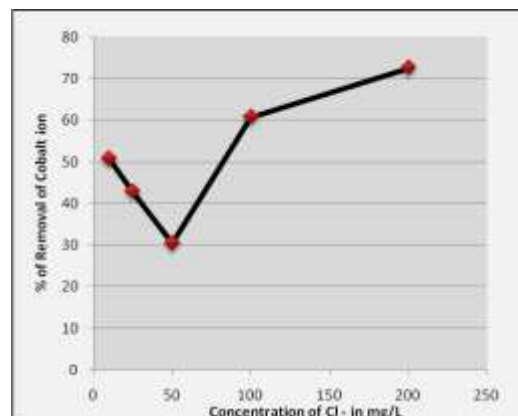


Fig. 7- Effect of other ions on the removal of Cobalt ion onto TPC

[Co] = 20mg/L: adsorbent dose = 25 mg /
50ml: contact time = 60ml

When the concentration of NaCl increases, the ionic strength is increased. At higher ionic strength, the adsorption of cobalt ion will be high due to the partial neutralization of the positive charge on the carbon surface and a consequent compression of the electrical double layer by the Cl^- anion. The chloride ion also enhances adsorption of cobalt ion by pairing their charges, and hence reducing the repulsion between the removal of cobalt ions on the surface. This initiates carbon to adsorb more positive cobalt ions [19, 20].

Desorption studies

Disposal of the exhausted adsorbent loaded with metal ions produce another environmental problem, as it is toxic material, which pollutes the environment. Therefore regeneration of the adsorbent material is of crucial importance in economic development. Desorption studies helps to illuminate the nature of the adsorption process and the recovery of metal ion from TPC. The reuse of regenerated activated carbon was found to be efficient. The effect of various reagents used for desorption studies indicate that hydrochloric acid is a better reagent for desorption, because more than 90% removal of adsorbed metal ion takes place. The reversibility of adsorbed metal ion in mineral acid or base is

in agreement with the pH dependent results obtained. Desorption of metal ion by mineral acids and alkaline medium indicates that the metal ion was adsorbed onto the activated carbon through by physisorption mechanism[20].

Conclusions

This research work proved that applicability of *Thespesia Populnea* bark were excellent low cost biosorbent for the removal of cobalt ions. The adsorption process was greatly based on solution of pH and effect of temperature. The kinetic study of Co (II) ion sorption on TPC was followed Pseudo- first-order kinetic model. The process of adsorption was tested by the Langmuir than Freundlich model. The thermodynamic parameters such as ΔH° , ΔS° and ΔG° clearly indicates the spontaneous and endothermic nature of the adsorption process.

Reference

- [1] J.Rivera – Utrilla, M.A. Ferro- Garcia, M.D. Mingorance and I.Bautista-Toledo, Adsorption of lead on activated carbons from olive stones. *J. Chem. Technol. Biotechnol.*, **1988**. 36: 47-52.
- [2]. S. Bounheng, N.; Kazunori, N. Munehiro, C. Nobou, N. Osamu, *Water Res.* **2006**, 40, 2295.

- [3]. WHO, Guidelines for Drinking Water Quality, *World Health Organization*, Geneva, **2006**.
- [4]. D.L. Baun and T.H.Christensen. Speciation of heavy metals in landfill leachate: a review. *Waste Manage. Res.* Vol. 22, **2004**, pp. 3–23.
- [5]. S. Babel and T.A.Krniavan. Low cost adsorbants for the heavy metals uptake from contaminated water: a review. *J. Hazard. Mater.* Vol. B 97, **2003**, pp. 219 – 243.
- [6]. T.A. Kurniawan Chan, G.Y.S., Lo, W.H., Babel, S. Physico-chemical treatment techniques for wastewater laden with heavy metals, *Chemical Engineering Journal*, **2006**, 118, pp 83-98.
- [7]. C. Namasivayam, N. Muniasamy, M. Gayathri, M. Rani K.Renganathan “Removal of Dyes from Aqueous solution by cellulosic waste orange peel”, *Biores. Technol.*, **1996**, 57, p.37.
- [8]. M. Mohapatra, T. Padhi, T. Dash, P Sing, S. Anand, and B.K.Mishra, “Cation sorption on nano structured high surface area γ -line ferrihydrite”, *J. Hazard.Mater.* **2009**, 148 (3)553-559.
- [9]. C.Namasivayam R.T Yamuna. “adsorption of direct dye red dye biogas residual slurry”, *environ. Pollut.* **1995**, 89p.1
- [10]. S. Arivoli, M. Viji Jam, and T. Rajachandrasekar, “Cobalt Adsorption on a Low Cost Carbon-Kinetic, Equilibrium and Mechanistic Studies”, *Mat Sci Res India*,3, **2006**, pp. 241-250.
- [11]. C. Namasivayam R. Jeyakumar, R.T.Yamuna, J. Jayanthi, dye removal from waste water by adsorption on waste Fe (III), Cr (III) hydroxide, *Waste Manage.* 14, **1994** 643 – 648.
- [12]. S. Arivoli, B. R. Venkatraman, T. Rajachandrasekar, and M. Hema, “Adsorption of Ferrous Ion from Aqueous Solution by Low Cost Activated Carbon Obtained from Natural Plant Material”, *Res J Chem Environ.*17, **2007**, pp. 70–78
- [13]. D. G. Krishna and G. Bhattacharyya, “Adsorption of Methylene Blue on Kaolinite”, *Appl Clay Sd*, 20, **2002**, p. 295.
- [14]. K.A. Krishnan, T.S. Anirudhan. Removal of Cadmium (II) from aqueous solutions by team- activated sulphurised Carbon Prepared from sugar Cane bagasse pith: Kinetics and equilibrium studies. *Water SA* 29(2), 147, **2003**.
- [15] S. Arivoli, K. Kalpana, R. Sudha, and T. Rajachandrasekar, “Comparative Study on the Adsorption Kinetics and Thermodynamics of Metal Ions onto Acid

Activated Low Cost Carbon”, *E J Chem*, 4, **2007**, pp. 238–254.

[16] W.J. Weber, Principle and Application of Water Chemistry, ed. S.D. Faust and J.V. Hunter. New York: Wiley, **1967**.

[17] Renmin Gong, Yingzhi Sun, Jian Chen, Huijun Liu, and Chao Yang, “Effect of Chemical Modification on Dye Adsorption Capacity of Peanut Hull”, *Dyes and Pigments*, 67, **2005**, p. 179.

[18]. Ma W. and Tobin J.M., Determination and modelling of effects of pH on peat biosorption of chromium, copper and cadmium. *Biochem. Eng. J.* Vol. 18, **2004**, pp. 33–40.

[19] B. Zhu, T. Fan, D. Zhang, Adsorption of copper ion from aqueous solutions by citric acid modified soybean straw. *Journal of hazardous materials* 153, **2008**, 300-308.

[20] M K. Sreedhar and T S .Anirudhan, *Indian J environ protect*, **1999**, 19, 8.