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Research Article

ADSORPTION OF HEXAVALENT CHROMIUM BY ACTIVATED CARBON *MERREMIA EMARGINATA* (ACME) FROM SYNTHETIC AQUEOUS SOLUTIONS

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ABSTRACT

In this study, preparation of adsorbent from *Merremia emarginata* stem and its application for adsorption of chromium (VI) from aqueous solution was studied. The batch adsorption experiments were carried out to study the effect of contact time, adsorbent dose, effect of pH and effect of other ionic concentration on the removal of chromium (VI) by activated carbon. The equilibrium adsorption data were analyzed by Freundlich and Langmuir isotherm models. The thermodynamic parameters such as change in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were determined. Kinetic modeling of the process of removal was carried out and the process of removal was found to follow a pseudo second order model, Elovich model and Intraparticle diffusion model the value of rate constant for adsorption process was calculated. This study indicated that activated carbon *Merremia emarginata*, which is inexpensive, has efficiency to remove chromium (VI) from aqueous solution.

Keywords: Activated Carbon *Merremia emarginata*, (ACME), Chromium (VI) ion, Adsorption isotherm,Thermodynamic parameters, Kinetics, Equilibrium models.

1. INTRODUCTION

Heavy metal ions have become an ecotoxicological hazard of prime concern and increasing significance, because of their accumulation in living organisms. Chromium (VI) is considered to be a bioavailable element due to its good solubility in water, strong oxidation properties and permeability through cell membranes. Unfortunately, chromium (VI) compounds cause toxic, mutagenic and carcinogenic effects on individual organisms [1, 2]. Chromium (VI) is one of the most toxic and its effects are carcinogenic, mutagenic, and teratogenic to humans and animals. The removal of these toxic metals from aqueous solution has a significant responsiveness over the past decades to reduction their impact on the environment [3, 4]. Several physical and chemical methods have been technologically advanced for the removal of toxic metals from aqueous solution. It is more and more often observed that their permissible concentration in surface waters is exceeded several times, which is why it is extremely important to search for effective and economical methods of removing them. Adsorption is one of the more effective, reusability of material, low-cost, ease of process, short time and eco-friendly approach. Activated carbon is the most widely used adsorbent and can be prepared from biomass [5-8]. In this research, activated carbon prepared from *Merremia emarginata* stem, modified with Con. H_2SO_4. Batch method static conditions, adsorption isotherms, thermodynamic parameters and adsorption kinetics were determined.

2. EXPERIMENTAL

The chemicals used in these experimental activities were all of analytical grade. The standard stock solution of chromium (1000 mg/L) was prepared by dissolving calculated amount of 99.9% analytical-grade $K_2Cr_2O_7$ in 1000 mL of distilled water. All the required solutions are made ready with analytical-grade reagents and double-distilled water. All experimental solutions were prepared by diluting the stock solution to the required concentration.

2.1. Preparation of adsorbent

The present work, a locally available plant, known by the local community as *Merremia emarginata*, was used as an adsorbent andthis natural biomaterial is abundantly available at local area of Poompuhar. The stem of *Merremia emarginata* was washed with distilled water up to remove the dirt and dust successively dried in a hot air oven at 110°C. Afterward, carbonization of the stem was carried out by adding w/v ratio Con. H_2SO_4 to get the primary carbon. The primary carbon was activated by thermal under mandatory conditions.

2.2. Batch experiments

The method of batch experiments [9,10] were conducted to study the influence of important parameters like contact time, adsorbent dose, initial pH and ionic strength on the removal of Cr (VI) ion onto activated carbon *Merremia emarginata*. For Adsorption Isotherms, Cr (VI) ion solution of different concentrations (10-50 mg/L) and at different temperatures (30-60°C) with known pH and known amount of adsorbent (0.025 g/L) were agitated at 120 rpm until the equilibrium was reached then the solution was kept to settle down and the residual concentration of Cr (VI) ion were analyzed by UV-Visible spectrophotometer at 540 nm. The amount of adsorption at time t, q_t (mg/g), can be determined using the following formula,

$$q_t = V \times \frac{(C_0 - C_t)}{w} \qquad (1)$$

Where, $q_{(t)}$ is the mass of adsorbed Cr (VI)ion per unit mass of adsorbent (mg g^{-1}), V is the volume of the treated solution (ml), w is the mass of adsorbent (g), (C_0) and (C_t) are the initial and actual concentration (g dm^{-3}) of Cr (VI)ion at time, respectively. The percentage of removal can be calculated as following mathematical formula,

$$\% \text{ Removal} = \left(\frac{C_0 - C_t}{C_0}\right) \times 100 \qquad (2)$$

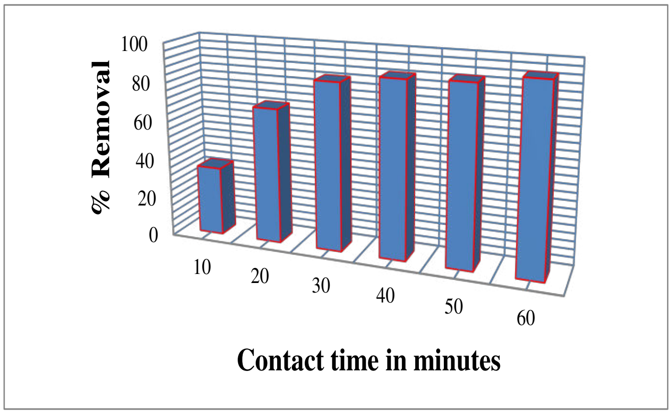
3. RESULT AND DISCUSSION

3.1. Effect of contact time

The effect of contact time [11, 12] on removal of Cr (VI) on to ACME adsorbent and to determine the optimum contact time between the adsorbate and adsorbent, the experiment was carried out at room temperature and altered the contact time like 10, 20, 30, 40, 50 and 60 min. using 25 mg adsorbent dose and by optimal pH of the solution. These results were shown in fig. 1 and the equilibrium data are given in table 1. The fig. shows that the removal of Cr (VI) was initially rapid at that time maximum of the adsorption was complete with in 30 min., equilibrium was achieved with in 50 min. therefore all subsequent experiments were selected for 60 min.

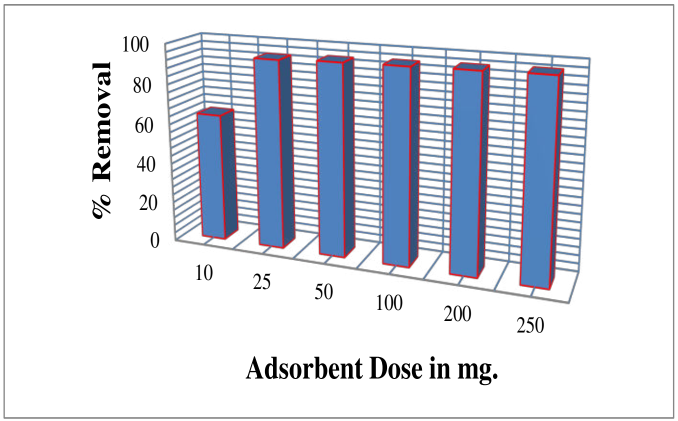
3.2. Effect of adsorbent dosage

The effect of ACME dose was studied by varying amount of adsorbent like10, 25, 50, 100, 200 and 250 mg the adsorbent dose [13] for 10 mg/L of Cr (VI) ion solution. The percentage of adsorption increased with increases in the ACME dose, which is attributed to increased carbon surface area and the availability of more adsorption sites. The results obtained from this study are shown in fig. 2, it reveals that 25 mg of adsorbent dose enough to each experiments.



[Cr (VI) ion,]=10mg/L; Temperature 30°C; Adsorbent dose=0.025g /50mL.

Fig. 1: Effect of Contact Time on the Removal of Cr (VI) ion



[Cr (VI) ion]=10mg/L; Temperature 30°C; Contact Time 60 min.

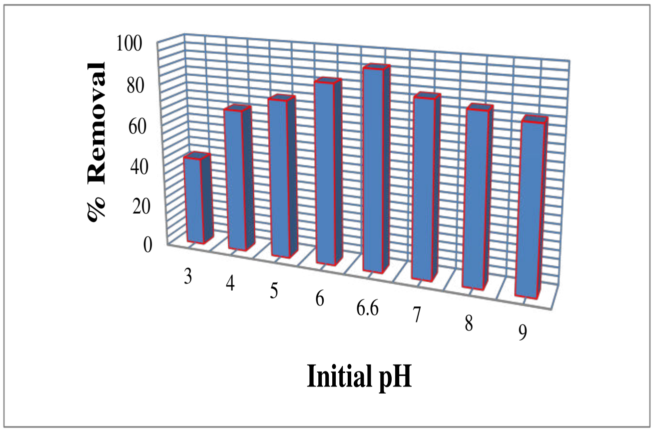
Fig. 2: Effect of Adsorbent dose on the Removal of Cr (VI) ion

Table 1: Equilibrium parameters for the adsorption of Cr (VI) ion onto ACME

C_0	Ce (Mg / L)				q_e (Mg / L)				Removal %			
	30°C	40°C	50°C	60°C	30°C	40°C	50°C	60°C	30°C	40°C	50°C	60°C
10	0.994	0.806	0.538	0.511	18.011	18.388	18.924	18.979	90.056	91.938	94.619	94.893
20	3.494	2.689	2.430	1.882	33.013	34.623	35.140	36.236	82.531	86.556	87.850	90.590
30	6.146	5.860	5.106	4.731	47.707	48.280	49.787	50.538	79.512	80.467	82.979	84.230
40	9.429	8.623	8.179	7.672	61.142	62.755	63.642	64.656	76.428	78.443	79.552	80.820
50	17.146	16.178	15.880	15.634	65.708	67.645	68.240	68.732	65.708	67.645	68.240	68.732

3.3. Effect of pH

Effect of solution pH [14] was studied in the pH range of 3-9 for removal of Cr (VI) ion from aqueous solution and keep on other parameters are constant. The percentage removal maximum at pH 6.8 that is pH_{zpc} (Zero point charge) shown in figure 3. The pH_{zpc} of any adsorbent is a very important characteristic at which the surface has net electrical neutrality there is nocompetitive effect. The neutral surface of adsorbent occur support for the maximum removal of Cr (VI)ion from aqueous solution, as the result pH of solution was optimized as pH 6.8.

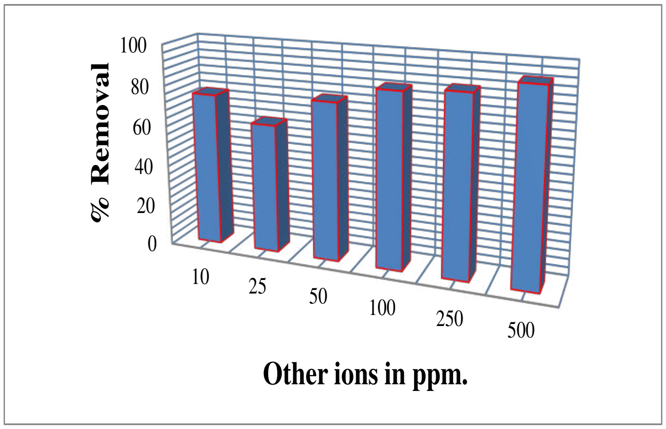


[Cr (VI) ion]=10mg/L; Temperature 30°C; Adsorbent dose= 0.025g/50mL.

Fig. 3: Effect of Initial pH on the Removal of Cr (VI) ion

3.4. Effect of ionic strength

The effect of ionic strength [15] was determined using different concentrations of chlorine solution such as 10, 25, 50, 100, 250 and 500 mg/L, and these results are shown in fig. 4. Chlorine concentrations range from 10 to 25 mg when the removal capacity decreases reveals an increase in competitive absorption. Here after increases the ionic strength of solution as well as removal capacity for that reason an electric double layer is formed on the adsorbent.



[Cr (VI) ion]=10mg/L; Contact time=60 min.; Adsorbent dose= 0.025g/50mL.

Fig. 4: Effect of ionic strength on the removal of Cr (VI) ion

3.5. Adsorption isotherm Models

The adsorption isotherm study was reveals that adsorption mechanism, the Freundlich model [16] which is an indicative of surface heterogeneity of the adsorbent is described by the following equation,

$$\log q_e = \log K_f + \frac{1}{n_f}\log C_e \quad (3)$$

Where, K_f and $1/n_f$ are Freundlich constants related with adsorption capacity and adsorption intensity respectively. The Freundlich plots drawn between log q_e and log C_e for the adsorption of Cr (VI)ion were shown figure 5, as a result listed in table 2.

The Langmuir adsorption isotherm [17] equation which is valid for monolayer adsorption on to a surface is given below,

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad (4)$$

Where, q_e (mgg^{-1}) is the amount adsorbed at the equilibrium concentration C_e (mol L^{-1}), q_m (mgg^{-1}) is the Langmuir constant representing the maximum monolayer adsorption capacity and K_L (L mol^{-1}) is the Langmuir constant related to energy of adsorption. The plots drawn between C_e/q_e and C_e, shown in figure 6, the feasibility of isotherm by the essential characteristics of the Langmuir isotherm can be expressed in terms of dimensionless constant separation factor R_L for the following equation.

$$R_L = \frac{1}{1 + K_L C_0} \qquad (5)$$

Where, C_o (mg/L) is the initial concentration of Cr (VI) ion and K_L (L/mg) is Langmuir isotherm constant. The parameter R_L indicates the nature of shape of the isotherm accordingly.

$R_L > 1$	-Unfavorable adsorption
$0 < R_L < 1$	-Favorable adsorption
$R_L = 0$	-Irreversible adsorption
$R_L = 1$	-Linear adsorption

The R_L values in the middle of 0 to 1 indicate favorable adsorption for all initial concentration (C_o) and temperatures studied. The calculated R_L values are given in table 3.

3.6. Thermodynamic treatment of the adsorption process

Thermodynamic [18] parameters studied the following equations,

$$\Delta G^0 = -RT\ln K_0 \qquad (6)$$

$$\ln K_o = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \qquad (7)$$

Where, ΔG^0 is the free energy of adsorption (kJ/mol), T is the temperature in (K), R is the universal gas constant (8.314 J mol/K), ΔH° is the standard heat change of sorption (kJ/mol) and ΔS° is standard entropy change (kJ/mol). The resultant data shown in table 4, negative ΔG° values were confirming the spontaneous nature of adsorption Cr (VI) ion onto ACME. The lesser values of ΔG° suggest that adsorption is physical adsorption process. The positive value of ΔH° further confirms the endothermic nature of adsorption process. The positive values of ΔS° showed increased randomness of the solid solution interface during the adsorption of Cr (VI) ion onto ACME.

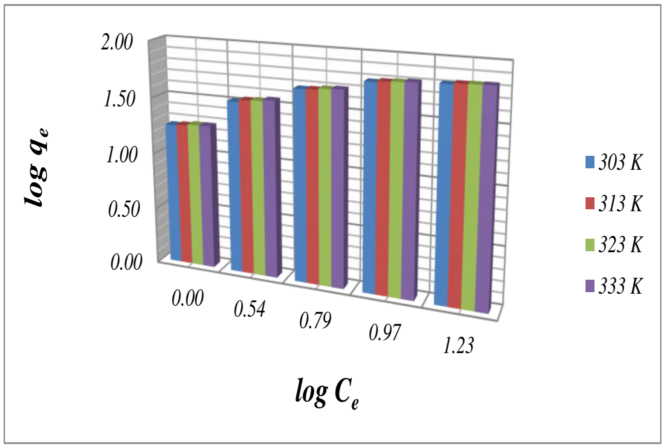


Fig. 5: Freundlich adsorption isotherm for the removal of Cr (VI) ion

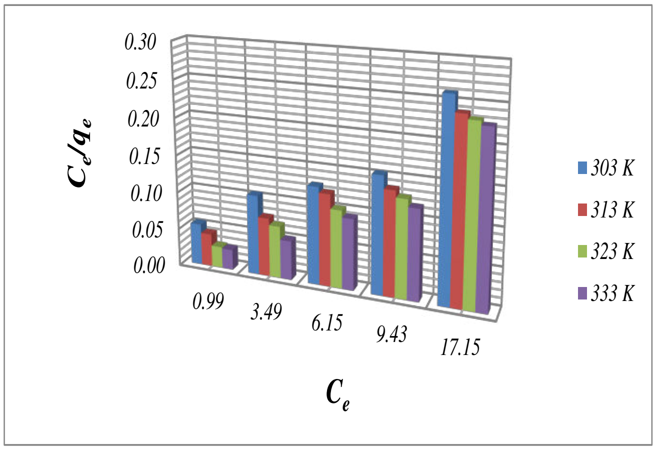


Fig. 6: Langmuir adsorption isotherm for the removal of Cr (VI) ion

Table 2: Freundlich and Langmuir isotherm parameter for the adsorption of Cr (VI) ion onto ACME

Model	Constant	Temperature (°C)			
		30	40	50	60
Freundlich	K_f (mg/g) (L/mg)$^{1/n}$	18.583	21.300	24.898	26.532
	n_f	2.068	2.204	2.497	2.558
	R^2	0.974	0.977	0.980	0.969
Langmuir	q_m (mg/g)	82.696	81.546	78.463	77.365
	K_L (L/mg)	0.237	0.306	0.420	0.516
	R^2	0.985	0.990	0.990	0.995

3.7. Kinetic models

Pseudo-second-order equations [19] can be used assuming that the measured concentrations are equal to surface concentrations. The linearized form of pseudo second order equation becomes.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right) t \quad (8)$$

Where, q_t (mgg^{-1}) is the amount of adsorbed Cr (VI)ionon the adsorbent at time t, q_e the equilibrium sorption uptake and k_2, is the rate constant of pseudo-second-order adsorption (min^{-1}). The plots drawn between $t/q_t$and t gives a straight line says second order kinetic model is applicable then q_e and k_2 are determined from the slope and intercept of the plots respectively. The high regression value indicate the adsorption reaction exist a pseudo-second-order and these values shown table 5.

The Elovich model equation is generally expressed as,

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \quad (8)$$

Where α is the initial adsorption rate (mg g^{-1} min^{-1}) and β is desorption constant (g/mg) during any one experiment. If Cr (VI) ion adsorption fits with the Elovich model, a plots drawn between q_t and ln(t) yields a linear relationship with a slope of (1/β) and an intercept of (1/β)ln(αβ). The Elovich model parameters α, β, and correlation coefficient (R^2) are summarized in table 5. This model indicates that the initial adsorption (α) increases with temperature similar to that of initial adsorption rate (h) in pseudo-second–order kinetics models.

Kinetic data was further analyzed using the intra-particle diffusion model based on the following equation.

$$\log R = \log K_{id} + \alpha \log t \quad (9)$$

Where, k_{id} is the intra-particle diffusion rate constant and it's related to the thickness of the boundary layer. According to above equation a plots drawn between log R and log t gives a straight line that's says the adsorption mechanism follows the intra-particle diffusion process in addition to the evidence of correlation co-efficient values are close to unity.

Table 3: Dimensionless seperation factor (R_L) for the adsorption of Cr (VI) ion onto ACME

(C_0)	Dimensionless separation factor(R_L)			
	30°C	40°C	50°C	60°C
10	0.2967	0.2465	0.1924	0.1623
20	0.1742	0.1406	0.1065	0.0883
30	0.1233	0.0983	0.0736	0.0607
40	0.0954	0.0756	0.0562	0.0462
50	0.0778	0.0614	0.0455	0.0373

Table 4: Thermodynamic parameter for the adsorption of Cr (VI) ion onto ACME

(C_0)	ΔG°				ΔH°	ΔS°
	30°C	40°C	50°C	60°C		
10	-5550.905	-6333.656	-7698.825	-8090.241	21.796	90.296
20	-3911.632	-4846.194	-5312.528	-6269.767	18.891	75.396
30	-3416.174	-3684.168	-4254.081	-4638.467	9.425	42.213
40	-2963.232	-3361.318	-3648.219	-3982.104	7.170	33.519
50	-1638.164	-1919.154	-2053.867	-2180.548	3.717	17.815

Table 5: Kinetic parameters for adsorption of Cr (VI) ion onto ACME

C_0	Temp°C	Pseudo second order				Elovich model			Intraparticle diffusion		
		q_e	k_2	R^2	h	α	β	R^2	K_{id}	α	R^2
10	**30**	19.8804	6.69E-03	0.9942	2.6446	2.7E+01	3.61E-01	0.9592	43.1899	0.1750	0.9729
	40	19.7794	9.12E-03	0.9965	3.5675	1.2E+02	4.45E-01	0.9592	52.1091	0.1350	0.9700
	50	19.7595	1.54E-02	0.9986	6.0213	6.7E+03	6.67E-01	0.9592	66.3170	0.0844	0.9661
	60	19.7640	1.64E-02	0.9988	6.4198	1.3E+04	7.03E-01	0.9592	6.2444	0.0796	0.9658
20	**30**	36.2654	3.86E-03	0.9945	5.0708	6.3E+01	2.05E-01	0.9549	40.9415	0.1668	0.9684
	40	38.0200	3.51E-03	0.9916	5.0699	6.1E+01	1.95E-01	0.9288	42.3489	0.1683	0.9470

	50	38.3935	4.01E-03	0.9960	5.9058	9.7E+01	2.05E-01	0.9601	45.8455	0.1556	0.9705
	60	38.9169	4.52E-03	0.9952	6.8519	2.2E+02	2.26E-01	0.9431	5.5152	0.1356	0.9567
30	**30**	51.4858	2.92E-03	0.9887	7.7374	2.0E+02	1.65E-01	0.8570	42.9132	0.1421	0.8781
	40	52.2172	3.70E-03	0.9974	10.0973	3.6E+02	1.71E-01	0.9402	46.7354	0.1323	0.9462
	50	54.4127	3.12E-03	0.9978	9.2507	1.7E+02	1.47E-01	0.9677	44.6012	0.1516	0.9733
	60	53.9586	4.56E-03	0.9999	13.2828	6.4E+02	1.73E-01	0.9889	5.5192	0.1246	0.9848
40	**30**	66.0197	3.35E-03	0.9996	14.5961	3.4E+02	1.27E-01	0.9734	43.5745	0.1414	0.9692
	40	67.6271	3.14E-03	1.0000	14.3791	3.5E+02	1.24E-01	0.9905	44.4777	0.1411	0.9855
	50	68.3123	3.37E-03	1.0000	15.7109	4.7E+02	1.27E-01	0.9820	46.3373	0.1351	0.9761
	60	69.3416	3.37E-03	0.9999	16.2085	5.4E+02	1.27E-01	0.9835	5.3504	0.1326	0.9783
50	**30**	68.4645	5.31E-03	0.9997	24.8776	4.2E+04	2.00E-01	0.9990	47.2657	0.0805	0.9996
	40	70.8405	4.24E-03	0.9991	21.2999	1.3E+04	1.76E-01	0.9834	46.6208	0.0895	0.9878
	50	70.6735	5.41E-03	0.9991	27.0035	4.0E+05	2.29E-01	0.9426	51.4173	0.0671	0.9481
	60	71.6314	5.16E-03	0.9998	26.4890	4.7E+04	1.92E-01	0.9980	5.4479	0.0802	0.9982

4. CONCLUSION

This study recommended that Activated Carbon *Merremia emarginata* can be used as an alternative adsorbent for removal of heavy metal ions from industrial wastewater due to its efficacy of chromium ion adsorption from synthetic aqueous solution. The isotherm equilibrium data fitted well with Langmuir isotherm model and maximum monolayer adsorption capacity (q_m) was found to be 82.696 mg/L. Thermodynamic parameters are the negative values of ΔG° indicated the spontaneity of Cr (VI) ion adsorption process and the positive values of ΔH° and ΔS° showed the endothermic nature and increasing randomness of the adsorption. The adsorption data was fitted well by pseudo-second order, Elovich model, and intra-particle diffusion models that are indicating chemical reaction is involved in the adsorption process. The adsorption process was found to be controlled by three steps of diffusion mechanisms. This study is evidence that activated carbon *Merremia emerginata* (ACME) was fair and business assistant adsorbent Cr (VI) ion from aqueous solution.

Conflict of Interest

None declared

5. REFERENCES

1. Arivoli S, Venkatraman BR, Rajachandrasekar T, Hema M. *Res J Chem Environ.,* 2007;**17:**70-78.
2. Arivoli S, Kalpana K, Sudha R, Rajachandrasekar T. *E J Chem.,*2007; **4:**238-254.
3. Sari A, Tuzen M. *J Hazard Mater*, 2008; **160:**349-355.
4. Gonza′ lez Bermu′ dez Y, Rodrı′guez Rico IL, Guibal E, Calero de Hoces M, Martı′n- Lara MA′. *Chem Eng J.,* 2012; **183:**68-76.
5. Gupta VK, Rastogi A. *J Hazard Mater.,* 2009; **163:**396-402.
6. Yeh KL, Chang JS. *Bioresour Technol.,* 2012; **105:**120-127.
7. Zheng H, Gao Z, Yin F, Ji X, Huang H. *Bioresour Technol.,* 2012; **117:**1-6.
8. Bulgariu D, Bulgariu L. *Bioresour Technol.,* 2012; **103:**489-493.
9. Park D, Yun YS, Park JM. *Ind Eng Chem Res.,* 2006; **45:**2405-2407.
10. Pistorius AM, DeGrip WJ, Egorova-Zachernyuk TA. *Biotechnol Bioeng.,* 2009; **103:**123-129.
11. Yang L, Chen JP. *Bioresour Technol.,* 2008; **99:**297-307.
12. Chen S, Yue Q, Gao B, Xu X. *J Colloid Interface Sci.,* 2010; **349:**256-264.
13. Bankar AV, Kumar AR, Zinjarde SS. *J Hazard Mater,* 2009; **170:**487-494.
14. Han X, Wong YS, Wong MH, Tam NF. *J Hazard Mater*, 2008; **158:**615-620.
15. Arivoli S, Hema M, Parthasarathy S, Manju N. *J. Chem. Pharm. Res.,*2010; **2(5):**626-641.
16. Arivoli S, Viji Jain M, Rajachandrasekar T. *Mat. Sci. Res. India,* 2006; **3:**241-250.
17. Arivoli S, Hema M. *Indian Journal of Chemical Technology*, 2009; **16(1):**38-45.
18. Arivoli S, Vijayakumaran V, Ramuthai S. *E-Journal of Chemistry,* 2009; **6(S1):**S347-S357.
19. Arivoli S, Hema M. *Intern J Phys Sci.,* 2007; **2:**10-17.