Journal of Environmental Science and Technology

ISSN 1994-7887

Journal of Environmental Science and Technology 4 (5): 520-533, 2011
ISSN 1994-7887 / DOI: 10.3923/jest.2011.520.533

Comparative Study of the Removal of Cadmium from Aqueous Solution by using Low-cost Adsorbents

[1]A.B. Dekhil, [1,2]Y. Hannachi, [1]A. Ghorbel and [1]T. Boubaker
[1]Unité de Recherche: Chimie Théorique et Réactivité, Faculté des Sciences de Monastir, 5019 Monastir, Tunisie
[2]Department of Colloid Chemistry, Belgorod State Technological University, 308012 Belgorod, Russia

Corresponding Author: Y. Hannachi, Unité de Recherche: Chimie Théorique et Réactivité, Faculté des Sciences de Monastir, 5019 Monastir, Tunisie

ABSTRACT

The removal of Cd (II) from aqueous solution by different adsorbents was investigated. Grafted cellulosic fabrics with itaconic acid, green alga (*Caulerpa racemosa*), clarified sludge (a steel industry waste material), were used for the adsorption studies. The influence of pH, contact time, initial metal concentration, adsorbent nature and concentration on the selectivity and sensitivity of the removal process was investigated. The adsorption process was found to follow a first-order rate mechanism and rate constant was evaluated at 30°C. Langmuir and Freundlich adsorption isotherms fit well in the experimental data and their constants were evaluated. The thermodynamic studies showed that the adsorption was spontaneous and exothermic in nature. Results of the study showed that locally available materials such as green macroalga (*Caulerpa racemosa*), clarified sludge and grafted cellulosic fabrics can be used as efficient sorbents for cadmium ions removal, representing an effective and environmentally clean utilization of waste matter.

Key words: *Caulerpa racemosa*, grafted cellulosic fabrics, clarified sludge, langmuir isotherm, freundlich isotherm, gibbs free energy, first-order rate mechanism

INTRODUCTION

Industrial wastewater effluents, bearing heavy metals, pose a serious problem for the environment. Cadmium (Cd) which is widely used and extremely toxic in relatively low dosages, is one of the principle heavy metals responsible for causing kidney damage, renal disorder, bone fraction and destruction of red blood cells (Drash, 1993). Because of the toxicity and bioaccumulation, Cd (II) is considered as a priority pollutant by the U S Environmental Protection Agency. The permissible limit for Cd (II) as described by WHO is 0.01 mg dm^{-3}. The main anthropogenic pathway through which Cd (II) enters the water bodies is via wastes from industrial processes such as electroplating, plastic manufacturing, metallurgical processes and industries of pigments and Cd/Ni batteries (Cheremisinoff, 1995).

Therefore, cost-effective treatment technologies are needed to meet these requirements of recovery and/or removal of metal ions. During the last years, increasing attention has been focused on the separation, pre-concentration and/or determination of trace metal ions in the environment. This field of interest is becoming a real challenge due to the specificity, accuracy and sensitivity required by more and more stringent regulations (Van den Brandt *et al*., 2002; Papa *et al*., 2002).

Conventional technologies for the removal of heavy metal such as chemical precipitation, adsorption, electrolysis, ion exchange and reverse osmosis are often neither effective nor economical (Jakobsen *et al.*, 2004; Zheng *et al.*, 2008; Brown *et al.*, 2000; Osemeahon *et al.*, 2008; Kandah, 2004; Terdkiatburana *et al.*, 2008).

Among the physico-chemical treatment process adsorption is found to be highly effective, cheap and easy to adapt. Activated carbon in most cases has been used as an adsorbent for reclamation of municipal and industrial wastewater for almost last few decades (Ahn *et al.*, 2009; Kadirvelu and Namasivayam, 2003). But the high cost of activated carbon has inspired the investigators especially in developing countries like Tunisia to search for suitable low-cost adsorbents.

As a result, recent research has focused on the development of cost effective alternatives using various natural sources and industrial wastes (Babel and Kurniawan, 2003; Kumar *et al.*, 2009; Li *et al.*, 2007). Industrial wastes are potential low-cost adsorbents for metal removal since some of them displayed high ion exchange capability. Pretreatment of adsorbent is also commonly used to increase the adsorption capacity of these materials. Several researches have been made significant contributions in this area, utilizing a number of materials including fly ash (Wang and Wu, 2006; Visa *et al.*, 2010), sugar beat, rice bran, soybeans and cotton seed hulls (Mohammad *et al.*, 2003; Sud *et al.*, 2008; Dakiky *et al.*, 2002), low-grade phosphate (Kandah, 2004), reactive polymers (Coskum *et al.*, 2006), grafted cellulosic materials (Okieimen *et al.*, 2005), natural zeolite (Lee and Moon, 2001), etc. The objective of the study was to investigate comparative adsorption characteristics for removal of Cd (II) from aqueous solution by the use of low-cost abundantly available nonconventional adsorbents like grafted cellulosic fabrics with itaconic acid, green alga and clarified sludge. The effects of pH, contact time, adsorbent dosage level and initial metal concentration on the adsorption capacity were studied. During the work program, adsorption kinetics, isotherm models and thermodynamic parameters were also investigated.

MATERIALS AND METHODS

Adsorbents used: The clarified sludge was collected from sludge thickener of Basic Oxygen Furnace of Steel Industry, Steel Authority of Russia Limited, Belgorod. The surface area was determined by BET method and was found to be 78.55 $m^2 g^{-1}$. The chemical composition of clarified sludge is presented in Table 1.

The green macroalga (*Caulerpa racemosa*) was harvested from the coasts in Monastir, Tunisia. The sun-dried biomass was ground to particles of size fraction 180-1100 μm. The biomass was extensively washed with deionised water to remove extraneous materials as well as release common ions (e.g., Na^+ and Ca^{2+}) present in seawater. The washed biomass was dried at 80°C overnight and stored in a dry cabinet.

Cellulose fabrics were supplied from National society of cellulose and paper Alfa (SNCPA), Kasserine, Tunisia. Itaconic acid (IA) was purified by twice crystallizing from distilled water m.p. 166°C. Potassium persulfate was used as initiator. The fabric was soaked in a detergent solution for 60 min, followed by extensive washing with tap water until free from any detergent. The clean fabric was then washed with distilled water, squeezed and allowed to dry in an air oven at 60°C

Table 1: Chemical composition of clarified sludge

Constituent	Fe_2O_3	CaO	MgO	MnO	SiO_2	Na_2O	K_2O	Loss on ignition
Percent by weight (%)	48	23.4	2.5	0.2	12.6	0.7	0.5	12

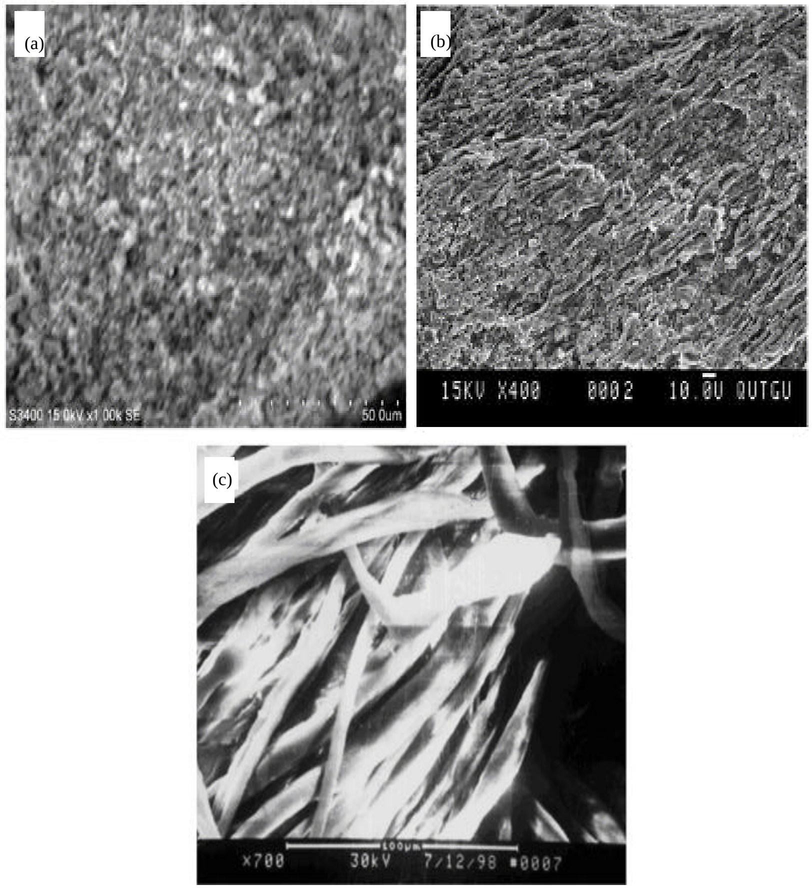

Fig. 1: SEM micrographs of (a) clarified sludge (1000x) (b) green macroalga (*Caulerpa racemosa*) (400x) and (c) grafted cellulosic fabrics (700x)

and finally stored in a vacuum desiccator ready for use. The procedure of grafting Itaconic acid onto cellulose using potassium persulfate as oxidizing initiator was reported in the literature (Sabaa and Mokhtar, 2002).

The above adsorbents were examined by scanning electron microscopy (JSM-T220 scanning microscope). The micrographs of the adsorbents obtained from SEM study are shown in Fig. 1a-c Which shows that the adsorbents had an irregular and porous surface texture. The study was conducted between May 2009 and December 2010.

Reagents and equipments: The chemical analysis of clarified sludge was carried out by standard methods (Vogel, 1989).

Batch adsorption studies: Using the necessary adsorbents in a 250 mL stoppered conical flask containing 100 mL of test solution batch adsorption studies were carried out at the desired pH value, contact time and adsorbent dosage level. Different initial concentration of Cd (II) solutions was prepared by proper dilution from stock 1000 mg L^{-1} Cd (II). pH of the solution monitored by adding 0.1 M HCl and 0.1 M NaOH solution as per required pH value. Necessary amount of adsorbent material was then added and contents in the flask were shaken for the desired contact time in an electrically thermostated reciprocating shaker at 110 strokes at ambient temperature, i.e. 30±2°C. The time required for reaching the equilibrium condition estimated by drawing samples at regular intervals of time till equilibrium was reached. The contents of the flask were filtered through filter paper and the filtrate was analyzed for Cd (II) concentration using Ati Unicam (Model 929) atomic absorption spectrophotometer

The percent removal of Cd (II) was calculated as follows:

$$\%\ \text{Removal of}\ \ \text{Cd(II)} = \frac{C_{initial} - C_{final}}{C_{initial}} \times 100 \tag{1}$$

where, $C_{initial}$ and C_{final} are the initial and final Cd (II) concentrations, respectively.

Adsorption experiments for the effect of pH were conducted by using a solution having 25 mg L^{-1} of Cd (II)concentration with an adsorbent dosage of 10 g L^{-1} and stirring the same for a contact time of 4 h. The effect of adsorbent dosage level on percent removal of metal was studied using Cd (II) concentration of 25 mg L^{-1} having pH adjusted to 5. Throughout the study, the contact time was varied from 15 to 300 min, the pH of the solution from 3 to 11, the initial cadmium concentration from 3 to 50 mg L^{-1} and the amount of adsorbent from 2.5 to 30 g L^{-1}.

Adsorption kinetics: The kinetic parameters for the adsorption process were studies on the batch adsorption of 25 mg L^{-1} of Cd (II) at pH 5. The contact time was varied from 15 to 300 min and the percent removal of Cd (II) was monitored during the study. The data was fitted to Lagergren equation:

$$\text{Log}\ (q_e - q) = \log q_e - \frac{K_{ad}}{2.303} \times t \tag{2}$$

where, q is the amount of Cd (II) (mg g^{-1} of adsorbent) removed at time t (min), q_e the amount of Cd (II) removed at equilibrium and K_{ad} is the rate constant of adsorption (min^{-1}) (Nyembe *et al.*, 2010; Moazed, 2008).

Adsorption isotherms: The adsorption isotherms for the Cd (II) removed were studied using initial concentration of Cd (II) between 10 and 100 mg L^{-1} at an adsorbent dosage level of 10 g L^{-1}.To find out the mechanistic parameters associated with cadmium adsorption, the results obtained by the adsorption experiments were analyzed by Langmuir and Freundlich models. According to Langmuir theory, it has been assumed that adsorption occurs at a specific homogenous site within adsorbent; each site is occupied only by an adsorbate molecule, all sites are equivalent and there are no interactions between adsorbate molecules. The linear form of Langmuir isotherm model can be represented by Eq. 3:

$$\frac{C_e}{q_e} = \frac{1}{q_{max} \times b} + \frac{C_e}{q_{max}} \tag{3}$$

where, C_e is the equilibrium concentration of adsorbate (mg L^{-1}), q_e the amount adsorbed at equilibrium (mg g^{-1} adsorbent) and q_{max} (mg g^{-1}) and b (L mg^{-1}) are the Langmuir constant related to the adsorption capacity and energy of adsorption, respectively (Koffi *et al.*, 2010).

Concerning the Freundlich equation, its empirical form is applicable to monolayer adsorption (Van der Waals adsorption) and multilayer adsorption (chemisorptions). In this model, lateral interaction between the adsorbed molecules and energetic surface heterogeneity are taken into account. The linear form of the Freundlich adsorption isotherm can be defined by the following equation:

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \quad (4)$$

where, q_e is the amount of adsorbate adsorbed per unit weight (mg g^{-1} of adsorbent), C_e the equilibrium concentration (mg L^{-1}) of the adsorbate and K_f is the Freundlich constant (Ahmed *et al.*, 2010; Zuhairi *et al.*, 2007).

Thermodynamic parameters: The thermodynamic equilibrium constant (K) for each system was obtained at 30±2°C by calculating the apparent equilibrium constant K'_C at different initial concentration of Cd (II) and extrapolating to zero.

$$K'_c = \frac{C_a}{C_e} \quad (5)$$

where, C_a is the concentration of Cd (II)on the adsorbent at equilibrium in mg L^{-1} and C_e is the equilibrium concentration of Cd (II) in solution in mg L^{-1}.

The Gibbs free energy (ΔG^0) for the adsorption process was obtained at 30±2°C using the formula:

$$\Delta G^0 = -RT\ln K_c \quad (6)$$

where, R is the ideal gas constant (8.314 J mol^{-1} K^{-1}) and T is the temperature in K.

RESULTS AND DISCUSSION

Effect of pH: Experiments concerning the effect of pH on the adsorption were carried out with the range of pH not influenced by the metal precipitation (as metal hydroxide).

The uptake of Cd (II) as a function of hydrogen ion concentration was examined over a pH range of 2-8 and shown in Fig. 2. Maximum Cd (II) removal was obtained in the pH range of 5-7. For brown macroalga with an initial concentration of 25 mg L^{-1} of Cd (II), maximum 96.8% removal was obtain at a pH value of 5. For clarified sludge, optimum pH for adsorption of Cd (II) as found to be 5. In case of grafted cellulosic fabrics also, maximum sorption of Cd (II) from aqueous solution occurred at a pH value around 5. Hence, pH 5 was considered to be the optimum pH for further studies. The effect of pH can be explained considering the surface charge on the adsorbent material. At low pH, due to high positive charge density due to protons on the surface sites, electrostatic repulsion will be high during uptake of metal ions resulting in lower removal efficiency.

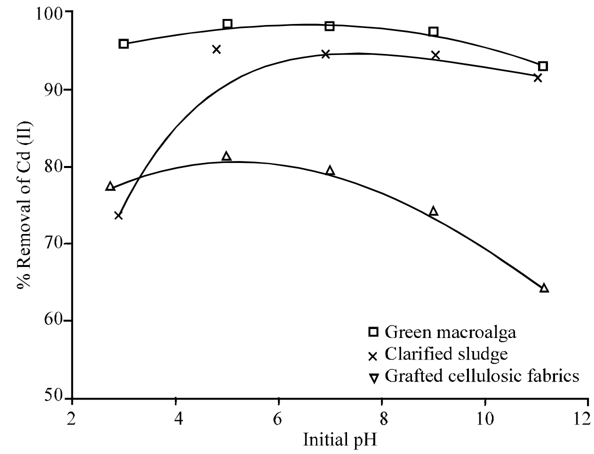

Fig. 2: Effect of pH on the adsorption of Cd (II) by selected adsorbents, initial Cd (II) concentration 25 ppm, adsorbent dosage 10 g L^{-1}, contact time 4 h and temperature 30°C

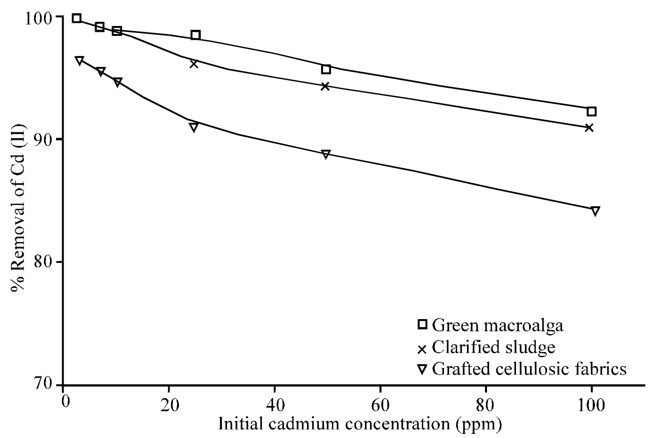

Fig. 3: Effect of initial concentration on the adsorption of Cd (II) by selected adsorbents: pH 5, adsorbent concentration 10 g L^{-1}, contact time 4 h and temperature 30°C

With increasing pH, electrostatic repulsion decreases due to reduction of positive charge density on the sorption sites thus resulting in an enhancement of metal adsorption. The above fact related to the effect of pH on adsorption also supported by several earlier workers (Kandah, 2004; Aklil *et al.*, 2004). At higher pH values OH ions compete for Cd (II) with the active sites on the surface of the adsorbents (Kalyani *et al.*, 2003).

Effect of initial Cd (II) concentration: The efficiency of Cd (II) removal is affected by the initial metal ion concentration, with decreasing removal percentages as concentration increases from 3 to 50 mg L^{-1} at constant pH of 5 (Fig. 3). Adsorbent dosage level maintained at 10 g L^{-1} for all the adsorbents considered for study. This effect can be explained as follows: at low metal ion/adsorbent ratios, metal ion adsorption involves higher energy sites. As the metal ion/adsorbent ratio increases, the higher energy sites are saturated and adsorption begins on lower energy sites, resulting in decreases in the adsorption efficiency (Zouboulis *et al.*, 2002).

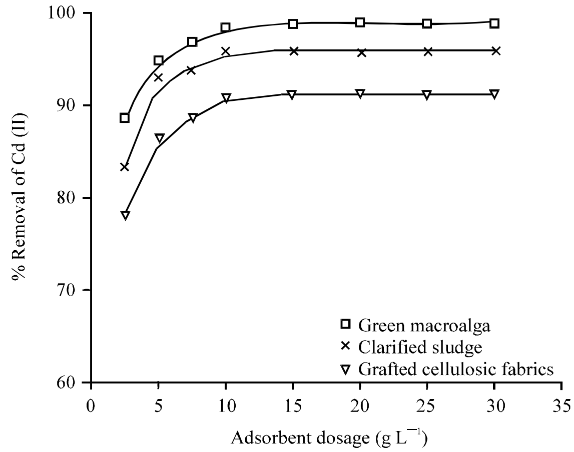

Fig. 4: Effect of adsorbent concentration on adsorption of Cd (II) by selected adsorbents: pH 5, initial Cd (II) concentration 25 ppm, contact time 4 h and temperature 30°C

Effect of adsorbent type and concentration: The effect of adsorbent type and its concentration is depicted in Fig. 4. The selected adsorbents were used at concentration ranging from 2.5 to 30 g L^{-1} in a batch adsorption technique.

In each case increase in adsorbent concentration resulted in an increase in percent removal of Cd (II). After certain adsorbent dosage the removal efficiency is not increased so significantly (less than 8%). At 5 g L^{-1} of adsorbent dosage level the removal of Cd (II) was found to be between 94.6% (green macroalga) and 82.3% (grafted cellulosic fabrics). At 10 g L^{-1} of green macroalga the removal of Cd (II) from solution was found to be 98.7%. In case of clarified sludge, Cd (II) removal efficiency of 95.8% was achieved at an adsorbent dosage level of 10 g L^{-1} and for grafted cellulosic fabrics under same condition the removal efficiency was 89.7%. It is evident that for all the adsorbents maximum removal efficiency was achieved at an adsorbent dosage level of 10 g L^{-1}. Therefore, the following experiments were carried out at adsorbent concentration of 10 g L^{-1}. The variation in sorption capacities between the various adsorbents could be related to the type and concentration of surface group responsible for adsorption of metal ions from solution (Dakiky *et al*., 2002). With increasing adsorbent dosage more surface area is available for adsorption due to increase in active sites on the adsorbent. It is known that algal cell walls are often porous and allow the free passage of molecules and ions in aqueous solutions (Davis *et al*., 2000). In addition, the constituents of the cell wall provide an array of ligands with a mosaic of functional groups capable of binding various metallic ions. This may explain the superior adsorption performance of green alga in comparison to other selected adsorbents.

Adsorption Cd (II) by clarified sludge may be attributed due to the combined effect of silica, metal oxides and carbon present in it as major constituents. In the case of grafted cellulosic fabrics the removal of cadmium ions can be explained in terms of the carboxylic groups on the grafts which provide additional binding sites for the metals ions. Besides, interpositioning of the grafts on the cellulosic substrate is associated with enhanced swelling in the metal ion solution and this should lead to increase in the levels of metal ion uptake .The availability of a particular functional group or binding site does not necessarily guarantee its accessibility as a sorption site for a metal ion, due to steric, conformational or other types of barriers (Dakiky *et al*., 2002).

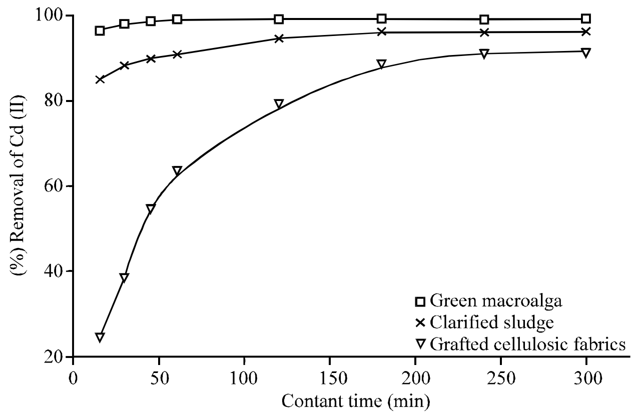

Fig. 5: Effect of contact time on the adsorption of Cd (II) by selected adsorbents: initial Cd (II) concentration 25 ppm, adsorbent dosage 10 g L^{-1}, pH 5 and temperature 30°C

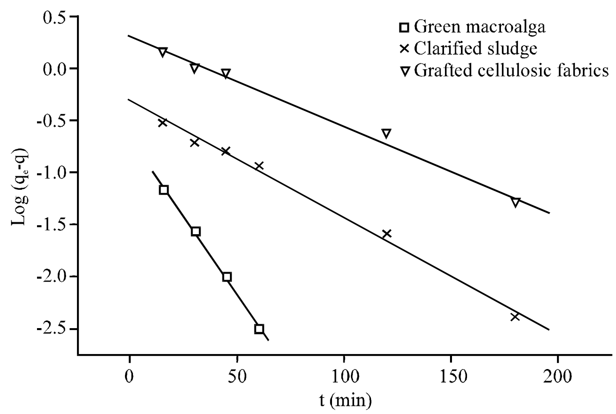

Fig. 6: Lagergren plot for the adsorption of Cd (II) by selected adsorbents: pH 5, initial concentration 25 mg L^{-1}, adsorbent dosage 10 g L^{-1} and temperature 30°C

Effect of contact time and adsorption rate kinetics mechanism: The study of adsorption kinetics describes the solute uptake rate and evidently these rate controls the residence time of adsorbate uptake at the solid-solution interface including the diffusion process. The mechanism of adsorption depends on the physical and chemical characteristics of the adsorbent as well as on the mass transfer process. The experimental runs measuring the effect of contact time on the batch adsorption of 25 mg L^{-1} Cd (II) at 30°C and at initial pH value 5 is shown in Fig. 5. It is obvious that increase in contact time from 0.5 to 2.0 h enhanced the percent removal of Cd (II) significantly (more than 10%). The initial rapid adsorption gives away a very slow approach to equilibrium. The nature of adsorbent and its available sorption sites affected the time needed to reach the equilibrium. For green macroalga this time is 1 h. In case of clarified sludge, time needed to reach the equilibrium is 3 h. For grafted cellulosic fabrics, a contact time of 4 h is needed for equilibrium to be established. All the other experiments on the physical properties of adsorption are conducted after 4 h of contact time.

The kinetics of Cd (II) adsorption was studies from the time versus % removal curves. The rate kinetics of Cd (II) adsorption on the green macroalga as well as on the other adsorbents observed to follow the first-order rate law derived by Lagergren Eq. 2. Figure 6 shows the Lagergren plot of log(qe-q) versus time (min) for all adsorbents.

Table 2: Lagergren rate constants for adsorption of Cd (II) on different adsorbents

Adsorbents	Lagergren rate constants, Kad (min^{-1})	r^2
Green macroalga	6.90×10^{-2}	0.9958
Clarified sludge	2.55×10^{-2}	0.9922
Grafted cellulosic fabrics	1.86×10^{-2}	0.9875

Table 3: Langmuir adsorption isotherm constants for Cd (II) on different adsorbents

Adsorbents	q_{max} (mg g^{-1})	b (L mg^{-1})	r^2
Green macroalga	15.53	0.299	0.9971
Clarified sludge	14.30	0.222	0.9955
Grafted cellulosic fabrics	13.69	0.102	0.9932

The linearity of these plots indicates that a first-order mechanism is indeed follow in this process. The rate constants (K_{ad}) for each system were calculated from the linear least square method and are given in Table 2 along with the correlation coefficient (r^2).

It is clear from these results that the correlation coefficient r^2 was highest for green macroalga (0.9958) followed by clarified sludge (0.9922) and grafted cellulosic fabrics (0.9875) .Therefore, it can be concluded that the kinetics of the Cd (II) adsorption on the different adsorbents was found to follow a first-order rate mechanism.

It is pertinent to mention that pH of the solution does not change significantly during the adsorption process.

The adsorption isotherms: The relation between the initial concentration of Cd (II) and its percentage removal from solution was studied for all adsorbents included in the study. The initial concentrations of Cd (II) studied were 10, 25, 40, 50, 80 and 100 mg L^{-1} at an adsorbent concentration of 10 g L^{-1}. The adsorption equilibrium data are conveniently represented by adsorption isotherms which correspond to the relationship between the mass of the solute adsorbed per unit mass of adsorbent q_e and the solute concentration for the solution at equilibrium C_e. The equilibrium data for Cd (II) adsorption on different adsorbents were fitted to Langmuir equation (Eq. 3), applied to equilibrium adsorption assuming mono-layer adsorption onto a surface with a finite number of identical sites, an equilibrium model able to identify chemical mechanism involved. Linear plots of C_e/q_e versus C_e (Fig. 7) were employed to determine the value of q_{max} (mg g^{-1}) and b (L mg^{-1}).

The data obtained with the correlation coefficients (r^2) was listed in Table 3. The Langmuir constants q_{max} and b are related to the adsorption capacity (amount of adsorbate adsorbed per unit mass of the adsorbent to complete monolayer coverage) and energy of adsorption, respectively.

The value of adsorption capacity q_{max} (maximum uptake) is highest (15.53 mg g^{-1}) for green macroalga. Grafted cellulosic fabrics shows the lowest value of adsorption capacity q_{max} (13.69 mg g^{-1}). However, the isotherm parameters, together with the correlation coefficients, of the Langmuir equation for the adsorption of Cd (II) on different adsorbents show that the Langmuir equation gives a good fit to the adsorption isotherm.

The essential characteristics of the Langmuir isotherm may be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L which is defined as:

$$R_L = \frac{1}{1 + bC_0} \tag{7}$$

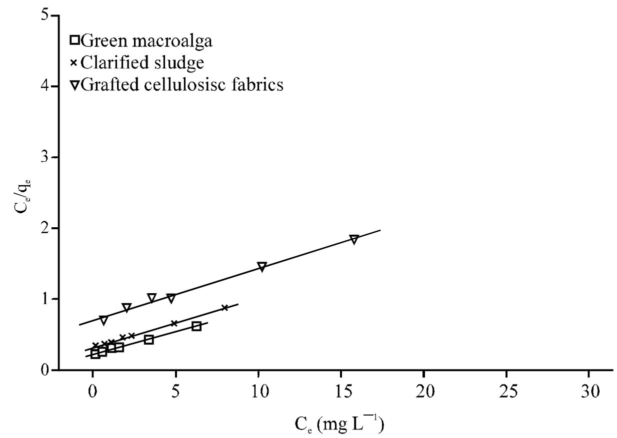

Fig. 7: Langmuir plot for the adsorption of Cd (II) by selected adsorbents: pH 5, adsorbent dosage 10 g L^{-1}, contact time 4 h and temperature 30°C

Table 4: Separation factor or equilibrium parameter R_L for adsorption of Cd (II) on different adsorbents

	Separation factor	Equilibrium parameter (R_L)
Adsorbents	Initial Cd (II) concentration (10 mg L^{-1})	Initial Cd (II) concentration (100 mg L^{-1})
Green macroalga	0.256	0.033
Clarified sludge	0.312	0.043
Grafted cellulosic fabrics	0.495	0.089

where, b is the Langmuir constant and C_0 is the initial concentration of Cd (II). The R_L value indicates the shape of the isotherm as follows:

R_L value	:	Type of isotherm
$R_L>1$	:	Unfavorable
$R_L = 1$	:	Linear
$0<R_L<1$	:	Favorable
$R_L = 0$	:	Irreversible

According to McKay R_L values between 0 and 1 indicate favorable adsorption. The R_L value for the adsorption of Cd (II) on different adsorbents at initial concentration of 10 mg L^{-1} (lowest concentration studied) and 100 mg L^{-1} (highest concentration studied) are listed in Table 4. The data obtained represent a favorable adsorption for all the adsorbents under study.

The Freundlich isotherm constants K_f and n are constants incorporating all factors affecting the adsorption process such as of adsorption capacity and intensity of adsorption. The constants K_f and n were calculated from Eq. 4 and Freundlich plots (Fig. 8).

The amount of absorbent required to reduce any initial concentration to predetermined final concentration can be calculated. The values for Freundlich constants and correlation coefficients (r^2) for the different adsorbents used during the study are also presented in Table 5.

The adsorption capacity K_f was highest for green macroalga (3.16), followed by clarified sludge (2.44) and grafted cellulosic fabrics (1.34). The values of n which reflect the intensity of adsorption,

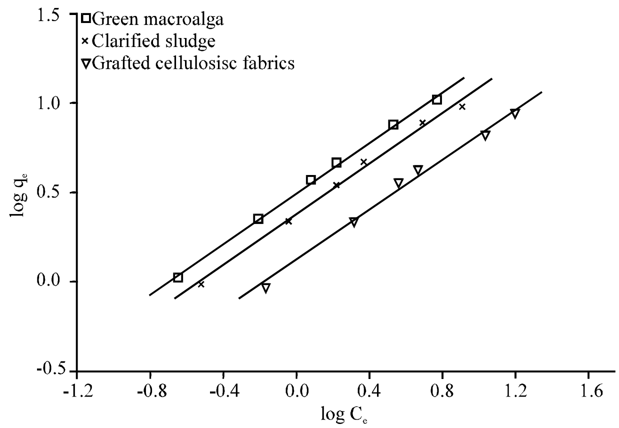

Fig. 8: Freundlich plot for the adsorption of Cd (II) by selected adsorbents: pH 5, adsorbent dosage 10 g L^{-1}, contact time 4 h and temperature 30°C

Table 5: Freundlich adsorption isotherm constants for Cd (II) on different adsorbents

Adsorbents	K_f	1/n	n	r^2
Green macroalga	3.16	0.705	1.418	0.9964
Clarified sludge	2.44	0.709	1.410	0.9945
Grafted cellulosic fabrics	1.34	0.701	1.426	0.9923

Table 6: Thermodynamic equilibrium constant (K) and Gibbs free energy (ΔG^0) at 30±2°C for adsorption of Cd (II) on different adsorbents

Adsorbents	Equilibrium constant (K)	Gibbs free energy- ΔG^0 (Kjmol^{-1})
Green macroalga	0.472×10^2	-9.713
Clarified sludge	0.351×10^2	-8.964
Grafted cellulosic fabrics	0.155×10^2	- 6.912

also presented the same trend. The n values (in range of 1.410-1.426) obtained for all the three adsorbents considered for study represent a beneficial adsorption. However, the r^2 values were found to be 0.9964 for the cadmium- green macroalga system, 0.9945 for the cadmium-clarified sludge and 0.9923 for the cadmium-grafted cellulosic fabrics. Therefore, it can be concluded that adsorption was also fitted well the Freundlich model.

Thermodynamics for adsorption: The process of Cd (II) adsorption can be summarized by the following reversible process which represents a heterogeneous equilibrium:

$$\text{Cd (II) in solution} \leftrightarrow \text{Cd (II) in adsorbent} \quad (8)$$

The thermodynamic equilibrium constant K obtained from calculating the apparent equilibrium constant K'_C at different initial concentrations of Cd (II) and extrapolating to zero. The Gibbs free energy for the adsorption process was obtained at 30°C using Eq. 6 (Table 6).

The Gibbs free energy indicates the degree of spontaneity of the adsorption process, where more negative values reflect a more energetically favorable adsorption process. The Gibbs free energy change values were obtained as -9.713, -8.964 and -6.912 kJ moL^{-1} which correspond, respectively to green macroalga, clarified sludge and grafted cellulosic fabrics. The negative ΔG^0 values indicated the feasibility of these adsorbents and spontaneity of the adsorption.

Table 7: Comparison of adsorption capacities of the adsorbents for the removal of Cd (II) with those of other adsorbents

Adsorbents	Adsorption capacities (mg g^{-1})	References
Calcite	18.52	Yavuz *et al.* (2007)
Olive cake	10.56	Doyurum *et al.* (2006)
Launea arborescens	11.50	Benhima *et al.* (2008)
Green macroalga	15.53	Present study
Clarified sludge	14.30	Present study
Grafted cellulosic fabrics	13.69	Present study

Comparison of Cd(II) removal with different adsorbents reported in study: The adsorption capacities of the adsorbents for the removal of Cd (II) have been compared with those of other adsorbents reported in literature and the values of adsorption capacities have been presented in Table 7. The values are reported in the form of monolayer adsorption capacity.

The experimental data of the present investigations are comparable with the reported values in some cases. The adsorption capacity varies and it depends on the characteristics of the individual adsorbent, the extent of surface/surface modification and the initial concentration of the adsorbate. However, the present experiments are conducted to find the technical applicability of the low-cost adsorbents to treat Cd (II).

CONCLUSIONS

This study showed that locally available materials such as green macroalga (*Caulerpa racemosa)*, clarified sludge and grafted cellulosic fabrics can be used as efficient sorbents for cadmium ions removal, representing an effective and environmentally clean utilization of waste matter.

The pH experiments revealed that the governing factors affecting the adsorption characteristics of all adsorbents are competition of the H^+ ions with Cd (II) ions at low pH values, maximum adsorption at pH 5 and at higher pH precipitation of cadmium hydroxyl species onto the adsorbents (pH 6-11). Increase in mass of adsorbent leads to increase in Cd (II) adsorption due to increase in number of adsorption sites. Maximum uptake of Cd (II) obtained at adsorbent dose of 10 g L^{-1} for all the adsorbents. The kinetics of the Cd (II) adsorption on the different adsorbents was found to follow a first-order rate mechanism.

Adsorption was fitted well both Langmuir and Freundlich models. The highest monolayer adsorption capacity was obtained 15.53 mg g^{-1} for green macroalga and lowest for grafted cellulosic fabrics 13.69 mg g^{-1} at optimum pH 5.0. Thermodynamic calculations showed that the Cd (II) adsorption was spontaneous in nature. The range of Gibbs free energy values ΔG^0 varies from -9.713 kJ moL^{-1} for green macroalga to -6.912 kJ moL^{-1} for grafted cellulosic fabrics. The best adsorbent for the Cd (II) removal is the green macroalga. The optimum conditions were pH 5, adsorbent dosage level 10 g L^{-1}, equilibrium contact time 1 h. More studies are needed to optimize the system from the regeneration point of view, to investigate the economic aspects and to confirm the applicability of this new sorbent under real conditions, such as in the industrial effluent treatment.

REFERENCES

Ahmed, Y.M., Abdullah-Al-Mamun, S.A. Muyibi , M.F.R. Al-Khatib, A.T. Jameel and M.A. Al-Saadi, 2010. Study of Pb adsorption by carbon nanofibers grown on powdered activated carbon. J. Applied Sci., 10: 1983-1986.

Ahn, C.K., Y.M. Kim, S.H. Woo and J.M. Park, 2009. Removal of cadmium using acid-treated activated carbon in the presence of nonionic and/or anionic surfactants. Hydrometallurgy, 99: 209-213.

Aklil, A., M. Mouflih and S. Sebti, 2004. Removal of heavy metal ions from water by using calcined phosphate as a new adsorbent. J. Hazard. Mater., 112: 183-190.

Babel, S. and T.A. Kurniawan, 2003. Low-cost adsorbents for heavy metals uptake from contaminated water: A review. J. Hazar. Mat., 97: 219-243.

Benhima, H., M. Chiban, F. Sinan, P. Seta and M. Persin, 2008. Removal of lead and cadmium ions from aqueous solution by adsorption onto micro-particles of dry plants. Colloid Surf. Biointerfaces, 61: 10-16.

Brown, P.A., S.A. Gill and S.J. Allen, 2000. Metal removal from wastewater using peat. Water Res., 34: 3907-3916.

Cheremisinoff, P.N., 1995. Handbook of Water and Wastewater Treatment Technology. M. Dekker Inc., New York, USA., ISBN-13: 9780824792770.

Coskum, R., C. Soykan and M. Sacak, 2006. Removal of some heavy metal ions from aqueous solution by adsorption using poly(ethylene terephthalate)-g-itaconic acid/acrylamide fiber. Reactive Functional Polymers, 66: 599-608.

Dakiky, M., M. Khamis, A. Manassra and M. Mereb, 2002. Selective adsorption of chromium (VI) in industrial wastewater using low-cost abundantly available adsorbents. Adv. Environ. Res., 6: 533-540.

Davis, T.A., B. Volesky and R.H.S.F. Vieira, 2000. Sargassum seaweed as biosorbent for heavy metals. Water Res., 34: 4270-4278.

Doyurum, S. and A. Celik, 2006. Pb(II) and Cd(II) removal from aqueous solutions by olive cake. J. Hazardous Mater B., 138: 22-28.

Drash, G.A., 1993. Increase of cadmium body burden for this century. Sci. Total Environ., 67: 75-89.

Jakobsen, M.R., J. Fritt-Rasmussen, S. Nielsen and L.M. Ottosen, 2004. Electrodialytic removal of cadmium from wastewater sludge. J. Hazard. Mater., 106: 127-132.

Kadirvelu, K. and C. Namasivayam, 2003. Activated carbon from coconut coirpith as metal adsorbent: Adsorption of Cd(II) from aqueous solution. Adv. Environ. Res., 7: 471-478.

Kalyani, S., A. Priya, P.S. Rao and A. Krishnaiah, 2003. Adsorption of nickel on fly ash in natural and acid treated forms. Indian J. Environ. Health, 45: 163-168.

Kandah, M.I., 2004. Zinc and cadmium adsorption on low-grade phosphate. Separation Purification Technol., 35: 61-70.

Koffi, L.C.K., K. Adouby, E.N. Wandan, B. Yao and K.P. Kotchi, 2010. Sorption and desorption of Pb(II) from aqueous solution using *Triplochiton scleroxylon* sawdust as sorbent. J. Applied Sci., 10: 1536-1544.

Kumar, J.I.N., C. Oommen and R.N. Kumar, 2009. Biosorption of heavy metals from aqueous solution by green marine macroalgae from Okha Port, Gulf of Kutch, India. Am. Euras. J. Agric. Environ. Sci., 6: 317-323.

Lee, D.H. and H. Moon, 2001. Adsorption equilibrium of heavy metals on natural zeolites. Korean J. Chem. Eng., 18: 247-256.

Li, F., P. Du, W. Chen and S. Zhang, 2007. Preparation of silica-supported porous sorbent for heavy metal ions removal in wastewater treatment by organic-inorganic hybridization combined with sucrose and polyethylene glycol imprinting. Anal. Chim. Acta, 585: 211-218.

Moazed, H., 2008. Ammonium ion removal from wastewater by a natural resin. J. Environ. Sci. Technol., 1: 11-18.

Mohammad, A., R.A.K. Rao, A. Shahana, A. Jameel and A. Rais, 2003. Adsorption studies on rice husk: Removal and recovery of Cd (II) from wastewater. Bioresour. Technol., 86: 147-149.

Nyembe, D.W., B.B. Mamba and A.F. Mulaba-Bafubiandi, 2010. Adsorption mechanisms of Co^{2+} and Cu^{2+} from aqueous solutions using natural clinoptilolite: Equilibrium and kinetic studies. J. Applied Sci., 10: 599-610.

Okieimen, F.E., C.E. Sogbaike and J.E. Ebhoaye, 2005. Removal of cadmium and copper ions from aqueous solution with cellulose graft copolymers. Separation Purification Technol., 44: 85-89.

Osemeahon, S.A., J.T. Barminas, B.A. Aliyu and I.I. Nkafamiya, 2008. Application of grafted membranes for sorption of Cd^{2+}, Fe^{2+} and Zn^{2+} ions in aqueous solution. Afr. J. Pure Applied Chem., 2: 32-36.

Papa, C.B., B. Coulomb, J.L. Boudenne, V. Cedra and F. Theraulaz, 2002. Spectrophotometric determination of aluminum in drinking waters by sequential injection analysis. Anal. Chem. Acta, 457: 311-320.

Sabaa, M.W. and S.M. Mokhtar, 2002. Chemically induced graft copolymerization of itaconic acid onto cellulose fibers. Polymer Testing, 21: 337-343.

Sud, D., G. Mahajan and M.P. Kaur, 2008. Agricultural waste material as potential adsorbent for sequestering heavy metal ions from aqueous solutions: A review. Bioresour. Technol., 99: 6017-6027.

Terdkiatburana, T., S. Wang and M.O. Tade, 2008. Competition and complexation of heavy metal ions and humic acid on zeolitic MCM-22 and actived carbon. Chem. Eng. J., 139: 437-444.

Van den Brandt, P., L. Voorrips, I. Hertz-Picciotto, D. Shuker and H. Boeing *et al.*, 2002. The contribution of epidemiology. Food Chem. Toxicol., 40: 387-424.

Visa, M., C. Bogatu and A. Duta, 2010. Simultaneous adsorption of dyes and heavy metals from multicomponent solutions using fly ash. Applied Surface Sci., 256: 5486-5491.

Vogel, A.I., 1989. A Textbook of Quantitative Chemical Analysis. 5th Edn., ELBS Publication, London, England.

Wang, S. and H. Wu, 2006. Environmental-begnign utilisation of fly ash as low-cost adsorbents. J. Hazard. Mater., 136: 482-501.

Yavuz, O., R.Guzel, F. Aydin, I. Tegin and R. Ziyadanogullari, 2007. Removal of cadmium and lead from aqueous solutions by calcite. Polish J. Environ. Stud., 3: 467-471.

Zheng, W., L. Xm, F. Wang, Q. Yang, P. Deng and G.M. Zeng, 2008. Adsorption removal of cadmium and copper from aqueous solution by areca a food waste. J. Hazardous Mater., 15: 490-495.

Zouboulis, A.I., N.K. Lazaridis and K.A. Matis, 2002. Removal of toxic metal ions from aqueous systems by biosorptive flotation. J. Chem. Technol. Biotechnol., 77: 958-964.

Zuhairi, A.A., B. Salamatinia and A.H. Kamaruddin, 2007. Removal of Zn and Cu from wastewater by sorption on oil palm tree-derived biomasses: A Preliminary study. J. Applied Sci., 7: 2020-2027.