Available online www.jocpr.com

Journal of Chemical and Pharmaceutical Research, 2014, 6(6):799-808

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

The removal of chromium from aqueous solution by using green micro algae

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ABSTRACT

Adsorption is a unique process for the removal of pollutants from water and wastewater since the process is cost effective, easily adoptable and environmentally compatible. The micro algae are a promising way to produce a useful adsorbent for Chromium (VI) removal from aqueous solution. The specific surface area of the activated carbon was determined and its properties studied by scanning electron microscopy (SEM). Adsorptive removal of Chromium (VI) from aqueous solution on micro algae has been studied under varying conditions of agitation time, metal ion concentration, adsorbent dose and pH to assess the kinetic and equilibrium parameters. Adsorption equilibrium was obtained in 120 min for 20 to 120 mg/L of Chromium (VI) concentrations. The Langmuir, Freundlich, Temkin, Redlich-Peterson, Khan equilibrium isotherm models were found to provide an excellent fitting of the adsorption data. In equilibrium isotherm, the r2 values obtained were in the range of 0.2 to 1 (0.999 to 0.857) for Chromium (VI) concentration of 20 to 120mg/L, which indicates favorable adsorption of Chromium (VI) onto marine algae carbon. The adsorption capacity of Chromium (VI) 99.75%. The percent removal maximum in pH3. This adsorbent was found to be effective and economically attractive.

Key words: Green micro algae, Chromium, Langmuir, Freundlich, Temkin, Redlich, Khan isotherms.

INTRODUCTION

Heavy metal is important role of water pollution. The heavy metals are continuously released into the aquatic eco system from natural process such as volcanic activity and weathering of rocks. The effluents from mining, ore processing, metal processing, metal polishing, cleaning, paint manufacturing and battery manufacturing industries and acid rain contribute for the increasing metal loads in the water bodies [13]. The heavy metal contamination of the water system is responsible for serious diseases and death. Chromium is one of the few metallic elements found in the earth's crust. Large number of important alloys contains chromium as the principle element. Environmental pollution due to chromium arises from industrial and agricultural operations. Chromium has broad industrial applications, such as alloy industries, paper and pulp; basic steel works foundries and petroleum refining industries. Chromium is a trace element that is drinking water essential for most animals, including humans of that iron metabolism and maintenance of blood vessels. Eye irritation has been reported by factory workers exposed to chromium dust [1&2]. It is also increasingly used in metal plating, tanneries, and oil well drilling Exposure to Cr (VI) causes cancer in digestive tract and lungs [12] and may cause epigastric pain, nausea, vomiting, severe diarrhea and hemorrhage [7]. It can cause serious disorders and disease when accumulated at high levels and it can be ultimately lethal. There is suggestive evidence that Cr (VI) causes increased risk of bone prostate cancer, lymphomas, Hodgkins, leukemia, stomach, genital, renal, and bladder cancer, reflecting the ability of Cr (VI) to penetrate all tissues in the body [15].

The hexavalent form of chromium is considered to be a group "A" human carcinogen because of its mutagenic and carcinogenic properties [8].Hence it is essential to remove Chromium from industrial wastewater before discharging in to natural water sources to meet National Regulatory Standards as well as to protect public health. In recent times, Heavy metals in general and Chromium in particular has received a great deal of attention because of their toxicity. Though the most predominant forms of chromium are Cr (VI) and Cr (III), Cr (VI) is more toxic.

Conventional treatment methods for heavy metals containing waste water, chemical precipitation, Ferrite treatment system, sulphate precipitation, solvent extraction, evaporation, xanthate process etc[16,17&19], but due to operational demerits and the treatment cost is high .The need for cost effective and economic removal of toxic heavy metals from waste water resulted in a research for non-conventional materials and methods. Several low cost adsorbents include sawdust, orange peel, almond husk, parthenium etc.,[3-6].

The objective of the present study is to be prepare and characterize quality evaluate the efficiency of using green micro algae as an adsorbent for the removal of Chromium. The adsorption study was carried out systematically involving various parameters such as pH, agitation and adsorption dose.

EXPERIMENTAL SECTION

Biomass cultivation and preparation

Adsorbent Material

The green micro algae collected from in around Coimbatore Lake. Cultured on hostel waste water. After 10-day cultivation, cells were harvested by centrifugation (3500 rpm for 3 min), washed twice with distilled water, dried at 80°C until constant weight, and stored in a fridge.

Preparation of Cr(VI) stock solutions

Potassium dichromate were obtained in analytical grade (Merck Co.) and used without further purification synthetic 1000ppm stock solution prepared. 283 mg of K2Cr2O7 was added in the 100ml of distilled water in 1000ml volumetric flask. It was dissolved by shaking and the volume was made up to the mark.Chromium concentration of this solution was 1000 mg/l.The concentration of Cr (VI) was determined spectrophotometrically at 540 *nm* by complexing with diphenyl carbazide[21].

Adsorption dynamic experiments

Batch equilibration method

The adsorption experiments were carried out in a batch process at 30, 40, 50 and 60 °C temperatures. The known weight of adsorbent material was added to 50 mL of the chromomium solutions with an initial concentration of 20 mg/L to 120 mg/L. The contents were shaken thoroughly using a mechanical shaker rotating with a speed of 120 rpm. The solution was then filtered at preset time intervals and the residual chromium concentration was measured by using Double beam UV-VIS spectrophotometer (Thermo).

Effect of variable parameters:

Dosage of adsorbents

The various doses (20, 40, 60, 80, 100 and 120mg) of the adsorbents are mixed with the chromium solutions and the mixture was agitated in a mechanical shaker. The adsorption capacities for different doses were determined at definite time intervals by keeping all other factors constant.

Initial concentration of Chromium

In order to determine the rate of adsorption, experiments were conducted with different initial concentrations of dyes ranging from 20 to 120 mg/L. All other factors have kept constant.

Contact time

The effect of period of contact on the removal of the chromium on adsorbent in a single cycle was determined by keeping particle size, initial concentration, dosage, pH and concentration of other ions constant.

pH

Adsorption experiments were carried out at pH 2, 3, 4, 5, 6, and 7. The acidic and alkaline pH of the media was maintained by adding the required amounts of dilute hydrochloric acid and sodium hydroxide solutions. The parameters like particle size of the adsorbents, dye concentration, dosage of the adsorbent and concentration of other ions have kept constant while carrying out the experiments. The pH of the samples was determined using a portable pH meter, Eutech .

The concentration of heavy metal ions remaining in solution was measured by UV –Visible spectrophotometer (Evaluation-201). The effect of several parameters, such as pH, concentrations, contact time and adsorbent dose on the adsorption was studied. The pH of the adsorptive solutions was adjusted using sulfuric acid, sodium hydroxide and buffer solutions when required adsorption of metal ions on the walls of glass flasks determined by running the blank experiments was found negligible.

The results of these studies were used to obtain the optimum conditions for maximum heavy metal removal from aqueous solution. The percent heavy metal removal was calculated using Eq.

Metal ion removal (%) = $\frac{Co - Ce}{Co} X100$

Where *C*o: initial metal ion concentration of test solution, mg/l;
*C*e: final equilibrium concentration of test solution, mg/l.

RESULTS AND DISCUSSION

Effect of contact time and concentration

The experimental results of adsorptions of at various concentrations (20,40,60, 80,100 and 120 mg/L) with contact time, the equilibrium data were reveals that, percent adsorption decreased with increase in initial metal concentration, but the actual amount of dye adsorbed per unit mass of carbon increased with increase in metal concentration. It means that the adsorption is highly dependent on initial concentration of metal. It is because of that at lower concentration, the ratio of the initial number of metals to the available surface area is low subsequently the fractional adsorption becomes independent of initial concentration. However, at high concentration the available sites of adsorption becomes fewer and hence the percentage removal of metal is dependent upon initial concentrations. Equilibrium have established at 120 minutes for all concentrations. Figure 1 reveals that the curves are single, smooth, and continuous, leading to saturation, suggesting the possible monolayer coverage of the metals on the carbon surface.

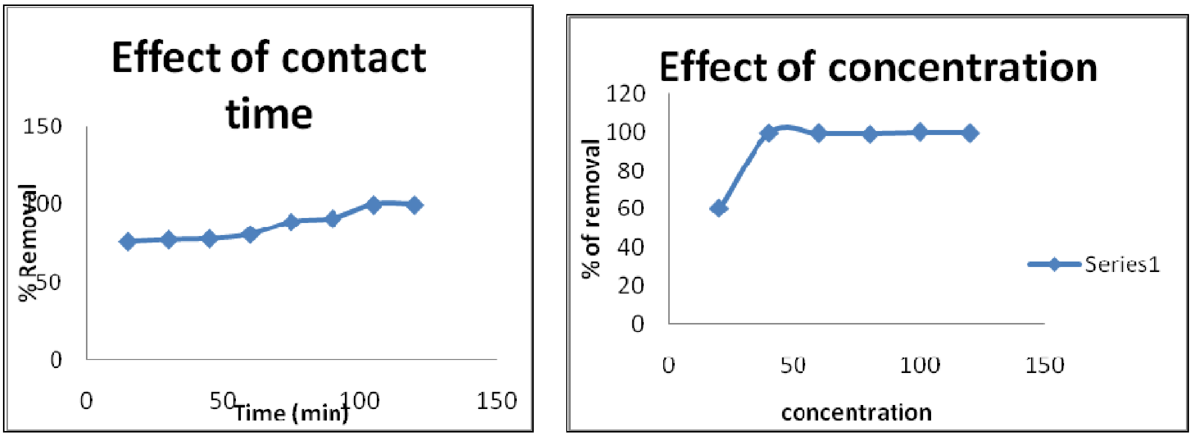

Figure -1 Effect of time and concentration

Effect of adsorbent dose

The results for adsorptive removal of Chromium (VI) dye with respect to adsorbent dose are shown in fig 2 over the range of 20 – 120 mg. The percentage removal of metal is seen to increase with adsorbent dose from fig 2. It is observed that there is a sharp increase in percentage removal with adsorbent dose for chlorella vulagris .It is apparent that the percentage removal of metal increases rapidly with increase in the dose of the adsorbents due to the greater availability of the exchangeable sites or surface area. Moreover, the percentage of metal adsorption on adsorbent is determined by the adsorption capacity of the adsorbents.

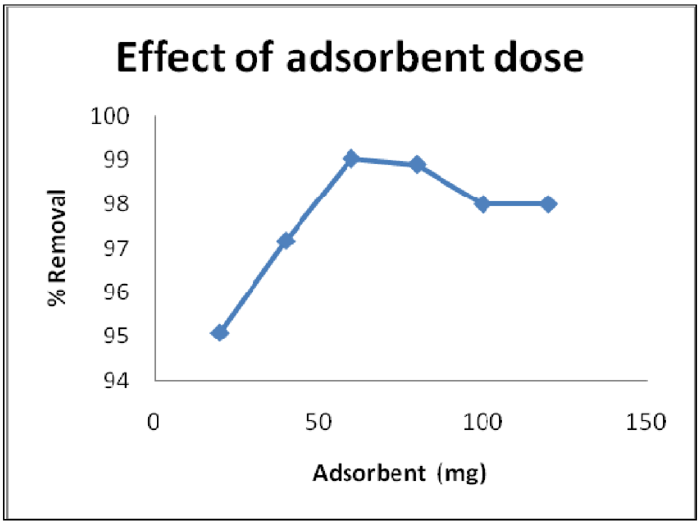

Figure- 2 Effect of adsorbent dose

Effect of pH

The pH is one of the most important parameter controlling uptake of metal from waste water and aqueous solutions. Figure 4 shows the effect of pH on metal removal efficiencies of chlorella vulagris. The effect of pH on adsorption of metal on chlorella vulagris was studied at room temperature by varying the pH of solution from 2- 8. The results are shown in fig 4. It can be observed that the removal of metal by Chlorella vulagris was maximum at pH 3, other pH shows minmum adsorption.

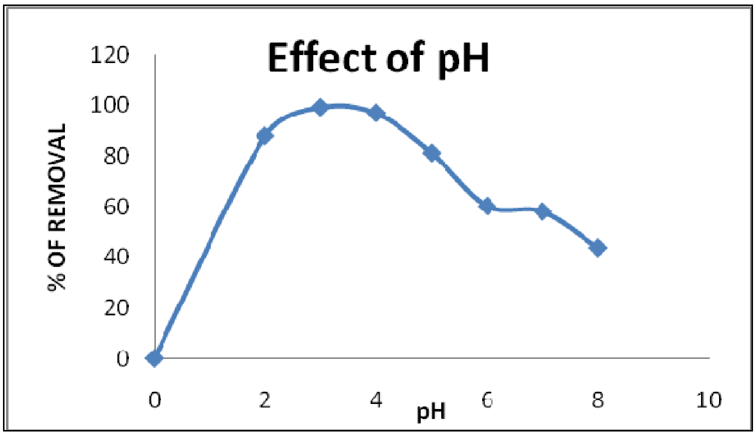

Figure-3 Effect of pH

Adsorption kinetics

Kinetic studies are necessary to optimize different operation condition for the sorption of dyes. The kinetics of Chromium onto Chlorella vulgaris was analyzed using pseudo-first order, second order and Intraparticle diffusion kinetic models.

The kinetic behavior as four rate equations reported in the literature namely, pseudo first order model, pseudo – second order model, and the intraparticle diffusion model are shown below.

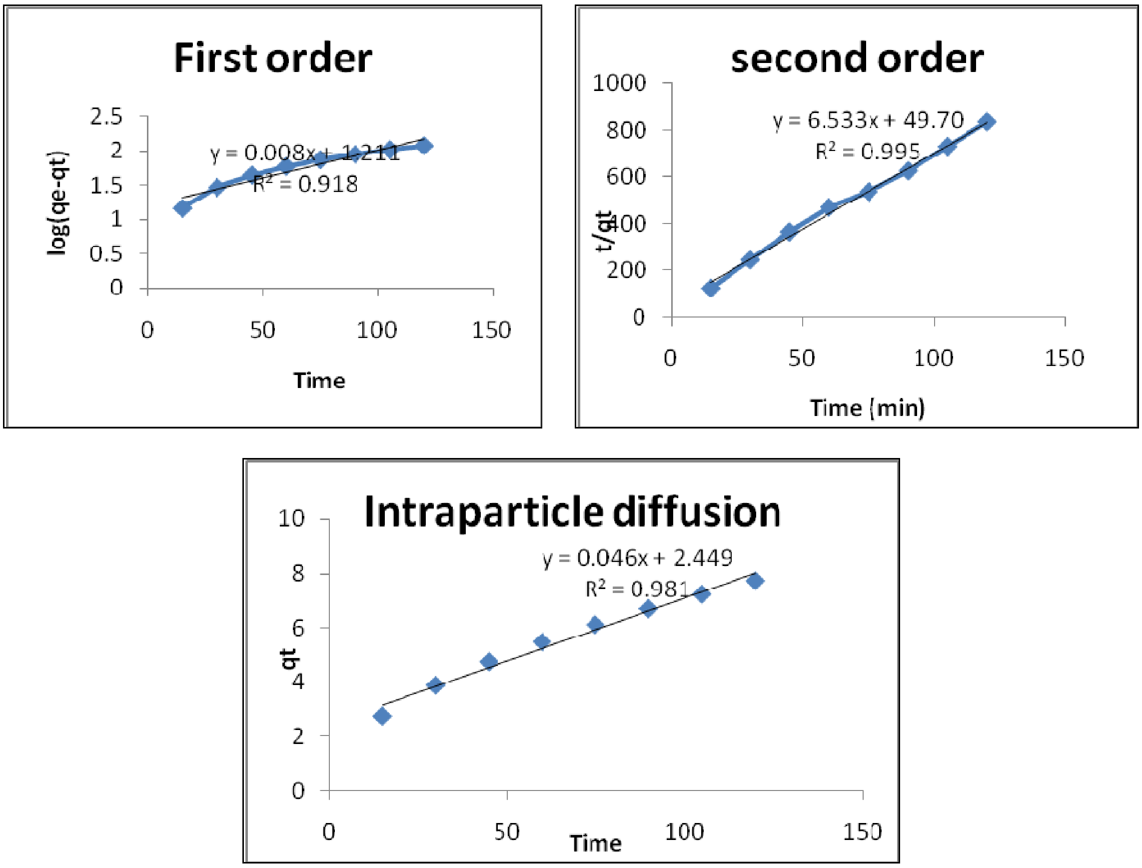

Figure 4 Pseudo – first and second order model, Interaparticle diffusion model

Adsorption isotherms

Adsorption isotherms parameters obtained from the different models provide important information on the surface properties of the adsorbent and its affinity to the adsorbate. Several isotherm equations have been developed and employed for such analysis and the important isotherms, Langmuir, Freundlich, Temkin, Redlich-Peterson and khan isotherms are applied in this study.

Langmuir isotherm

Langmuir adsorption isotherm is based on the assumption that, “Adsorption is a type of chemical combination in which adsorbate is adsorbed on the adsorbent surface and the adsorbed layer is unimolecular”. Langmuir equation [14],

$$q_e = \frac{Q_o k_L C_e}{1 + k_L . C_e}$$

where, qe is equal to the quantity of dye adsorbed in mg/g of the adsorbent,
Q0 is the maximum quantity of dye adsorbed in mg/gram of the adsorbent,

k_L and Ce is the constant of Langmuir adsorption and the dye concentration at equilibrium in mg/l respectively.

Langmuir adsorption parameters are determined by transforming the equation, which is in linear form. The Linear plot of Ce/qe Vs Ce showed that the adsorption followed Langmuir isotherm model (Figure 3). The values of monolayer capacity Q_0 and Langmuir constant k_L had been evaluated from the intercept and slope of these plots by using graphical techniques. The effect of isotherm shape has been taken into consideration with a view to predict whether the studied adsorption system is favorable or unfavorable. The essential features of the Langmuir isotherm may be expressed in terms of equilibrium parameter RL, which is a dimension less constant referred to as separation factor or equilibrium parameter RL=)1(10bC Where C0 is the initial concentration and k_L is the constant related to the energy of adsorption (Langmuir constant) table 1. The values of RL indicate the nature of the isotherm, if the conditions are (RL>1, RL=1, 0<RL<1 and RL= 0) are unfavorable, linear, favorable and irreversible respectively. The value of RL was less than one which showed that the adsorption process was favorable.

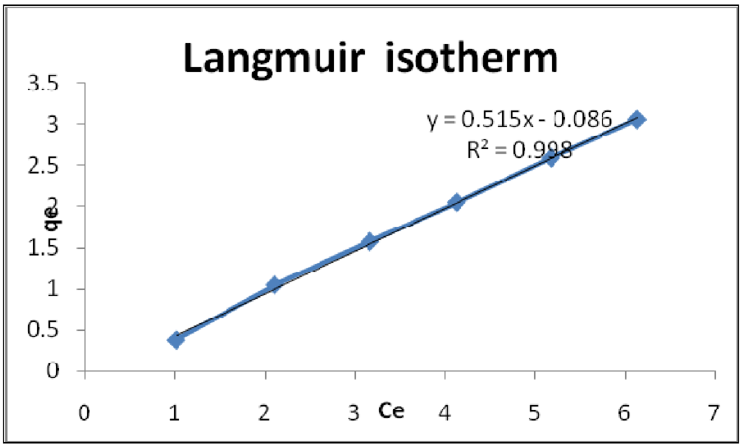

Figure-5 Langmuir isotherm

Freundlich Isotherm

Freundlich isotherm model was chosen to estimate the adsorption intensity of the adsorbate on the adsorbent surface. Linear form of Freundlich model [9] was expressed by

$$q_e = k_f . Ce^{1/n}$$

Where, qe is dye concentration in solid at equilibrium (mg/g),
Ce is dye concentration in solution at equilibrium (mg/L),
Kf is the Freundlich isotherm constant related to adsorption capacity (L/mg) and n is the Freundlich isotherm constant related to adsorption intensity.

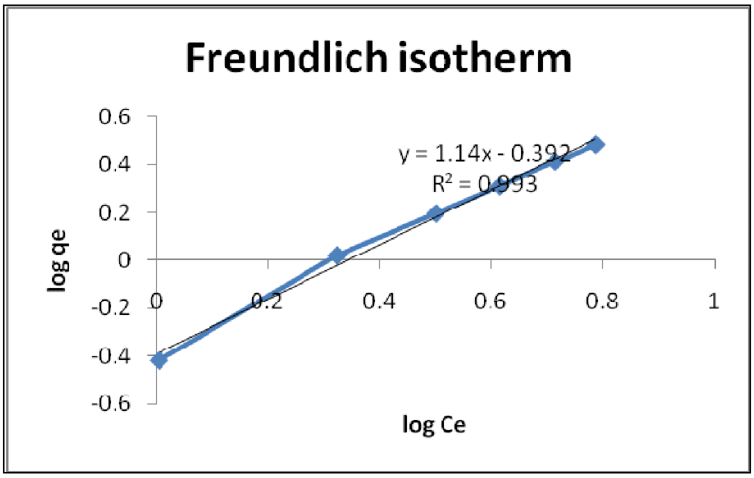

Figure-6 Freundlich isotherm

The linear plot of log q_e versus log C_e and the values of n and k_f calculated from the slope and intercept are given in table 1.The value of n was greater than one indicating the favorable adsorption of Cr Removal.

Temkin isotherm

The derivation of the Temkin isotherm assumes that the fall in heat of adsorption of all the molecules in the layer would decrease linearly with coverage due to sorbate/sorbent interactions. The Temkin isotherm is expresses by the following equation[10]:

$$q_e = \frac{RT}{b_t} \ln a_t . C_e$$

Where b_t is the Temkin constant related to heat of sorption (J/mol); a_t the Temkin isotherm constant(L/g);R, the gas contant(8.314 J/mol.K); and T, the absolute temperature(K)

In this work, the Temkin constant (b_t and a_t) are found to within a range 1.44 and 0.86 3 J/mol , the results indicate that the Temkin isotherm represents the adsorption process on Cr onto algae R^2 value is 0.950 better adsorption process.

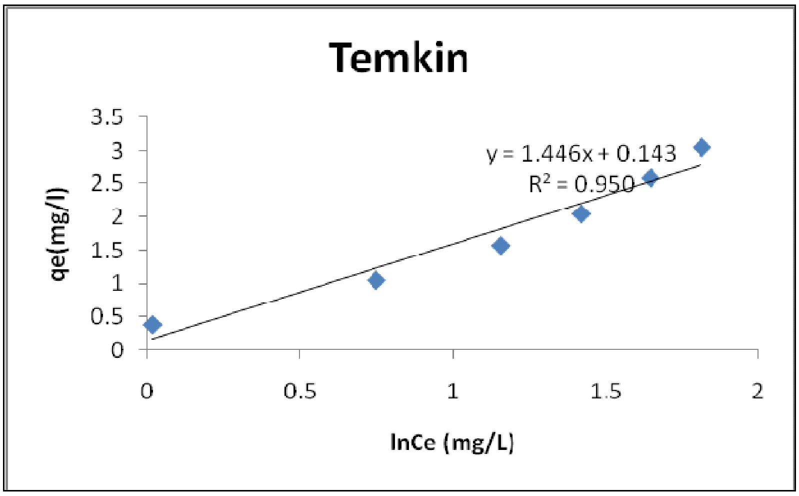

Figure-7 Temkin isotherm

Redlich –Peterson isotherm

The three parameter isotherm firstly proposed by Redlich and Peterson are modified to incorporate the features of both the Langmuir and Freundlich eqauations[10]. It can be described as follows

$$q_e = \frac{k_{RP} . C_e}{1 + P_e . C_e{}^g}$$

Where k_{RP} is the Redlich-Peterson isotherm constant (dm^3/g); p_e , the Redlich-Peterson isotherm model constant(dm^3/mg); and g , the Redlich-Peterson exponent .

The exponent (g) lies between 0 and 1. There are two limiting behaviors the Langmuir form for g=1, and the Henry’s law and at high adsorbate concentrations, its behavior approaches that of the Freundlich isotherm [18].

For the present application, the Redlich-Peterson isotherm constants for adsorption of k_{RP} , p_e and R^2 value 1.515 dm^3/g, 0.086 dm^3/mg and 0.999 respectively .

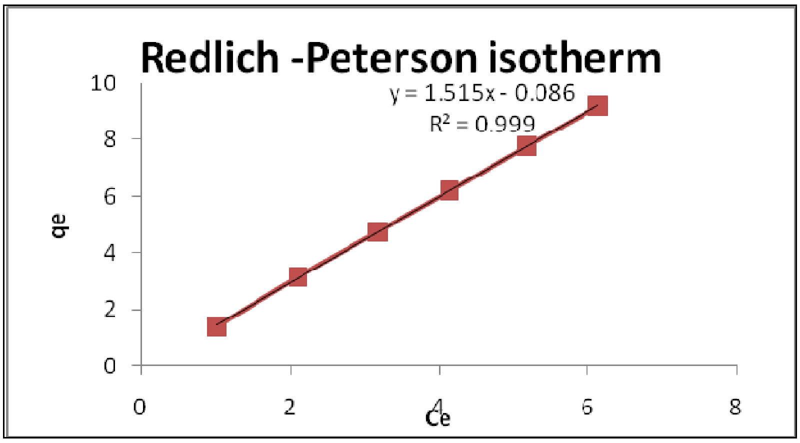

Figure-9 Redlich –Peterson isotherm

Khan isotherm
The simplified Khan model can be expresses as follows

$$q_e = \frac{q_m b_k C_e}{(1 + b_k . C_e)^{a_k}}$$

Where b_k is the Khan model constant; ak Khan model exponent [20].

From the results qm and bk values found 5.5 mg/g and 0.505 respectively .as similarly observed for Redlich – Peterson isotherm, the simplified Khan model also agrees well with the parameter models based on the determination of coefficients R2 = 0.873 .

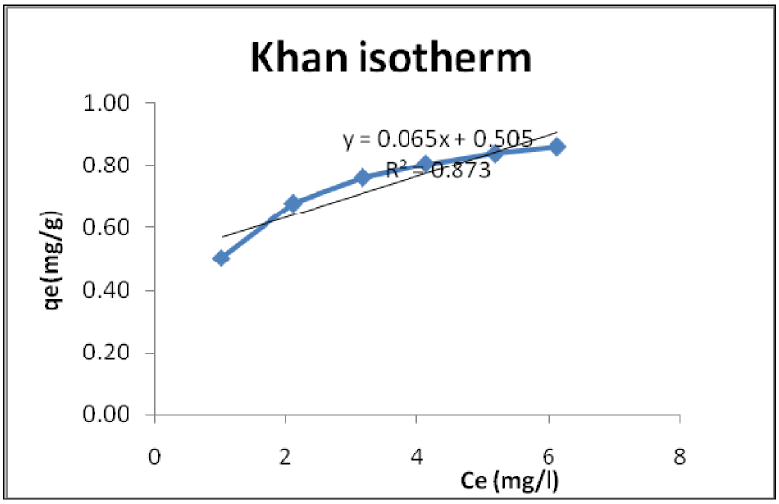

Figure-10 Khan isotherm

Table-1 Adsorption isotherm parameters

Langmuir	**Q_o**	**k_L**	**R^2**	
	0.515	0.086	0.998	
Freundlich	**k_f**	**n**	**R^2**	
	1.14	2.22	0.993	
Temkin	**a_t**	B	**b_t**	**R^2**
	0.283	1696	1.46	0.950
Redlich-Peterson	**k_{RP}**	**p_e**	**g**	**R^2**
	1.5	0.08	1	0.999
Khan	**q_m**	**b_k**	**a_k**	**R^2**
	4.5	0.065	0.505	0.873

IR Study

Fourier transform infrared spectroscopy (FTIR) was used to Shimadzu Fourier transform infrared spectroscopy determine the vibration frequency changes in the functional groups of carbons. The spectral of carbon were measured within the range of 400-4000/cm wave number. Some fundamental FTIR frequencies of Chlorella Vulgaris observed for before and after adsorption are shown in Figure 11 that the adsorption frequencies are shifted to higher wave numbers with the adsorption of chromium in Chlorella Vulgaris. From these findings it is presumed that the chromium is incorporated within the adsorbent through interaction with the active functional groups.

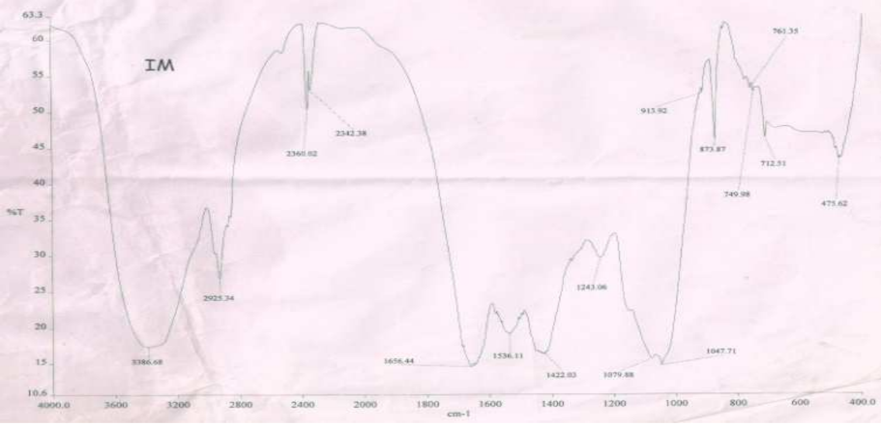

Figure-11 FTIR Result for chlorella vulgaris

SEM analysis:

The surface morphology of the activated carbon was examined using scanning electron microscopy (SEM), the corresponding SEM micrographs being obtained using at an accelerating voltage of 20 kV (Hitachi SE 900) at1, 500 × magnification (Figure 12). At such magnification, the Chlorella Vulgaris particles showed rough areas of surface within which micropores were clearly identifiable.

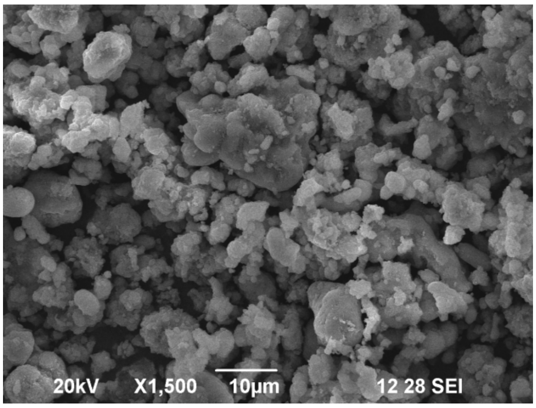

Figure -12 SEM results for Chlorella vulgaris

CONCLUSION

- Chlorella vulgaris is a cheap and effective adsorbent for the removal of chromium ion from wastewater without requiring any pretreatment.
- Experiment results showed that maximum removal of chromium ion by chlorella vulgaris at optimium condition(3 pH, 60 min. contact time 60mg/ 50ml of 100ppm concentration) 99.75% was obtained.
- The experimental data correlated reasonably well by the Langmuir, Freundlich, Temkin, Redlich- Peterson, Khan adsorption isotherms and the isotherm parameters were calculated.
- These experimental studies on adsorbents would be quite useful in developing an appropriate technology for the removal of heavy metal ions from contaminated industrial effluents.

Acknowledgement

The authors wish to express the gratitude for the support and financial help given by Department of Science and Technology, New Delhi for their support under Net Work Programme of Bio-Alge Carbon Sequestration research under the title “Carbon Sequestration and cultivating algae for green bio-fuel Production”.

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