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Research Article

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Equilibrium and kinetic studies of adsorption system of chromium ions from aqueous solution using chondruscrispus activated carbon

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ABSTRACT

In the present study, the adsorption carried out to test the suitability of Chondruscrispus powder as an adsorbent for the removal of chromium ions from aqueous solution. The equilibrium studies are systematically carried out in a batch process, covering various process parameters that include contact time, adsorbent size and dosage, initial chromium ion concentration and pH of the aqueous solution. It is observed that adsorption is maximum at pH is 3. From the Langmuir adsorption isotherm, formation of unimolecular layer of adsorbate on adsorbent is verified. Freundlich isotherm also verified, Freundlich plot linearity confirms unimolecular adsorption. Lagergren plot of time in minutes versus t/q gives a straight line and it is confirmed that the kinetics follows the pseudo second order.

Keywords: *Chondruscrispus*, Freundlich isotherm, Lagergren plot.

INTRODUCTION

Removal of heavy metals from industrial wastewater before discharge into the water body is a better prevention of environment. Wastewater of electroplating, zinc based casting industries, storage battery industries, battery manufacturing, metal soldering industries, electroplating, painting, dyeing, ceramics, surface treatment industries, electro- galvanization, textile industries are the main source of heavy metal pollution. Adsorption on activated carbon is a well established technique for the removal of heavy metals present in wastewater [1-3]. The Costs of activated carbon prepared from agricultural waste byproducts are comparatively lower than the commercial activated carbon [4]. Numerous studies have been reported, in the case of adsorption of heavy metals by low cost activated carbons produced from readily available agricultural waste materials, such as cotton seeds, peanut hulls [5] and tamarind nuts [6].

Recently, treatment of industrial waste water through biological agents which include use of microbes, aquatic microphytes and macrophytes known as bioremediation are being used. It is an inexpensive, easy handling and cost effective technology for remediation of contaminated water. A number of aquatic plants have great potential for removal of heavy metals.

In last 2-3 decades chromium toxicity in potable water has rapidly increased [7]. Chromium pollution in fresh water resources occurs naturally from erosion and weathering of chromium containing minerals. The industrial and commercial use of chromium and its compounds in leather tanning, electroplating, ferrochrome, pigmentation and photography has led to increased chromium pollution in fresh water bodies. In Kanpur a large quantity of untreated chromium containing tannery effluent is mixed directly in Ganga and other water bodies daily. It creates a number of environmental and health problems. Irrigation of agriculture lands by chromium contaminated water causes severe of harmful effects on soil fertility. It increases toxicity of soil and decreases the quantity and quality of agro products. Chromium contaminated water causes skin disorders in farmers. If it is used as drinking water, it causes numerous excretory, nervous and digestive system disorders both in human beings and animals. More than 15 villages of Jajmau area of Kanpur are suffered by adverse effects of chromium contamination. The conventional methods of treatment of chromium contaminated water are very expensive. To install the conventional system and operate them with proper maintenance, due to heavy capital investment and high operational cost, they are uneconomical. Therefore it is a need of hour to make emphasis for development of economical, easy handling and cost effective techniques for efficient treatment of industrial waste water. Chromium (VI) in particular is toxic to both plants and animals as a strong oxidizing agent and potential carcinogen [8]. Chromium is released in to air primarily by combustion processes and metallurgical industries. Chrome plating, leather tanning and textile industries release relatively large amounts of Cr (VI) in to surface waters [9]. Cr (VI) has been reported to be a potent carcinogen producing cancer in various parts of the body [10]. Besides this, it acts as irritant to eyes, nose and throat. Chronic exposure may lead to liver and kidney damage. Due to the toxic nature of Cr (VI), various technologies are proposed for the treatment of Cr(VI) rich wastewater. Chromium is one of the widely used heavy metal, which is mainly employed in tanneries and is extremely toxic to living organisms. Hence, the removal of Cr(VI) ions was selected for the present study. Several techniques including ion-exchange, reverse-osmosis precipitation, electro-reduction and cementation are available for the removal of heavy metal ions from waste water. But these methods are found to be more expensive. Since adsorption technique is less expensive and economically feasible, it has been selected for the present study using *Chondruscrispus* as an effective adsorbent. Therefore the objective of the present work was to test the ability of *Chondruscrispus* in removing Cr (VI) ions from aqueous solution, using adsorption technique.

EXPERIMENTAL SECTION

Batch Equilibrium Experiments- Preparation of Adsorbent

Chondruscrispus was collected and sundried. Dry biomass was cut with a knife into irregular shaped particles between 1-3 mm in size. The biomass was then washed with distilled water, filtered and finally dried overnight at 60°C and crushed to an average size of 0-63 μm in a mortar and then activated by 0.1 M H_2SO_4 for 24 hrs and finally carbonized and subsequently used for adsorption experiment.

Batch equilibrium experiments were conducted by adding 100 mg biomass to Erlenmeyer flask containing 50ml of different test solutions at desired pH conditions. The initial solution pH was adjusted by using 0.1 M HCl or 0.1 M NaOH. The flasks were agitated at 150 rpm in a rotary shaker. After 3 hrs of contact time, the biomass was separated from the test solution by filtration. The chromium ion content in the supernatant liquid was determined using photoelectric calorimeter. Prior to analysis, the equipment was initially calibrated using standard chromium ion solution. When necessary, the samples were diluted with distilled water before analysis. The amount of chromium ion adsorbed by biomass was calculated from the difference between the concentration of chromium ion in test solution and the concentration of chromium ion in the supernatant liquid using the following equation.

Percentage of (%) of chromium ion removal

$$= \frac{\textit{Initial Concentration} - \textit{Final Concentration}}{\textit{Initial Concentration}} \, x\, 100$$

$$= \frac{(x - y)}{x} \times 100$$

where x – OD before treatment
y – OD after treatment

Effect of Contact Time and Initial Concentration

To 50 ml solutions of each 10 to 50 ppm of chromium ion solution, 100 mg of *Chondruscrispus* powder was added and left for a period of 3 hours at room temperature (30°C±1) with intermittent shaking. Appropriate control flasks without adsorbent were also maintained. The results of adsorption were recorded to calibrate the equilibrium time. The effect of initial concentration on the removal of chromium ion was observed.

Effect of pH

About 50 ml of 50 ppm chromium aqueous solutions were prepared and the pH values were adjusted by using 0.1 M HCl /0.1 M NaOH. Each solution was treated with 100 mg of the adsorbent and kept for a contact time of 3 hours at room temperature with intermittent shaking. The residual chromium ion concentrations were measured.

Isotherm Studies-Freundlich Adsorption Isotherms

Freundlich proposed the isotherm for dilute and moderately dilute solution. It is represented experimentally by the expression [11].

q_e = $K\ C_e 1/n$

where
q_e = Amount of metal adsorbed at equilibrium (mg/g)
C_e = equilibrium concentration of metal (mg/l)

The modified equation is

$\text{Log } q_e = \log K_f + 1/n \log C_e$

where qe is the amount of chromium ions adsorbed per unit weight of adsorbent (mg/g), K_f is the measure of adsorption capacity and l/n is adsorption intensity; C_e is equilibrium concentration of residual Chromium ion in solution.

Langmuir Isotherm
Langmuir proposed the isotherm for dilute and moderately dilute solution. He considered the formation of uni-molecular layer on the adsorbent surface at low pressure or at moderately high temperature. It is represented experimentally by the expression.

$$\frac{P}{x/m} = \frac{1}{K_1 K_2} + \frac{P}{K_2}$$

Where K_1 and K_2 are proportionality constants
P - initial concentration (C_{eq})
$\frac{x}{m}$ - Amount of metal adsorbed at equilibrium (mg/g), q_e.

A plot of **C_e/q_e** Verses **C_e** will give a straight line. The Slope of this is $\frac{1}{K_2}$ and intercept on the y – axis will give $\frac{1}{K_1 K_2}$.

Fig. 1a. Chondruscripus (Raw) **Fig. 1b.Chondruscripus (Carbonised)**

Kinetic Studies-Lagergren Kinetics
Lagergren also proposed kinetics for the adsorption. According to him, if a plot of time in minutes versus $\log_{10}(q_e - q)$ gives a straight line and it follows the first order kinetics. if a plot of time in minutes versus t/q gives a straight line

and it follows the pseudo second order kinetics[12-13](where q_e–Maximum $\frac{x}{m}$ value at maximum time, q–minimum $\frac{x}{m}$ value at minimum time, x – amount of chromium adsorbed and m–Mass of the adsorbent).

RESULTS AND DISCUSSION

The experimental data obtained from the different batch type experiments in the present investigation was analyzed and interpreted with the help of standard relations existing adsorption ability of the adsorbent *chondruscrispus* material powder.

Batch type experiments

In the present study, *chondruscrispus* was used for the successful removal of Cr ions. Similarly, Kuppusamy et al. (2004) has reported the removal of Chromium using marine green alga Ulva reticulate[14].

Equilibrium time

A plot of time of contact time versus % removal of chromium was plotted. Fig 2 indicated that maximum adsorption has taken place at the 3rd hour, thereafter a marked increase was not observed. Hence, the equilibrium time has been calibrated as 3 hrs. Similarly 6 hrs of equilibrium time was observed by Jasuja *et al* (1997) by using *Ablesmoschus esculentus* plant material [15].

Effect of initial concentrations on metal removal

Percentage of Cr uptake was found to increase with initial adsorbate concentrations (Fig3). This may be probably due to the fact that for a fixed adsorbent dose, the total available adsorption sites remain invariable for all the concentrations checked. Hence the percentage removal of Cr has shown a reduction with the increase in the initial adsorbate concentrations. Manju and Anirudhan (1997) have reported similar results with coconut fibre pith[16].

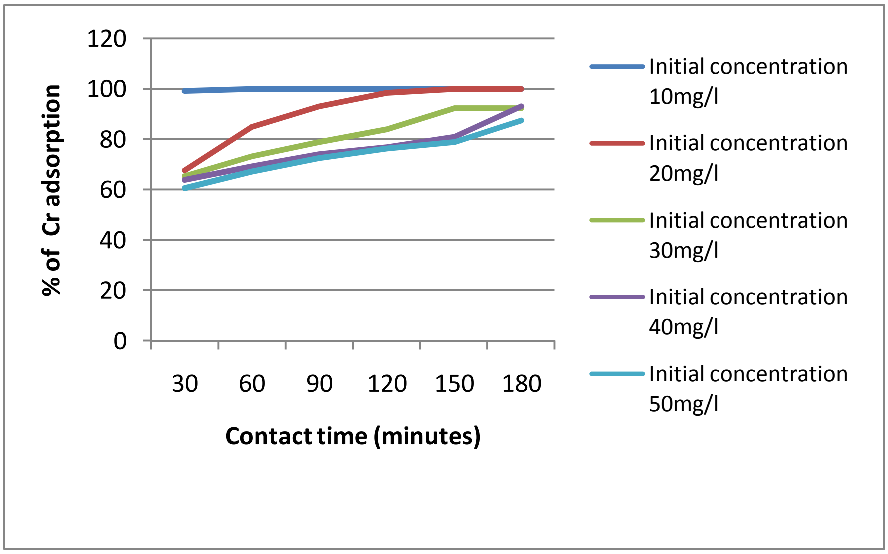


Fig 2. Effect of contact time on removal of chromium using chondruscrispus

Figure 4 shows the effect of pH on the removal of chromium ion. The results showed that adsorption is maximum at pH 3 (Fig.4). This shows that almost acidic pH is preferred for chromium removal using adsorption technique using the adsorbent-chondrus- crispus

Figure 5 represented the effect of contact time on the percentage adsorption of Cr. In these experiments the weight of the adsorbent was 100 mg. The results showed that, time taken for the completion of adsorption was 180 minutes (within 3 hours). Figure 5 gives the effect of dosage of adsorbent on Cr removal. Various amounts of adsorbent - *Chondruscrispus* .*Chondruscrispus* ranging from (50-300mg) were taken. The percentage removal of chromium varied linearly with the amount of the adsorbent *Chondruscrispus* and amount of adsorbate (Cr)

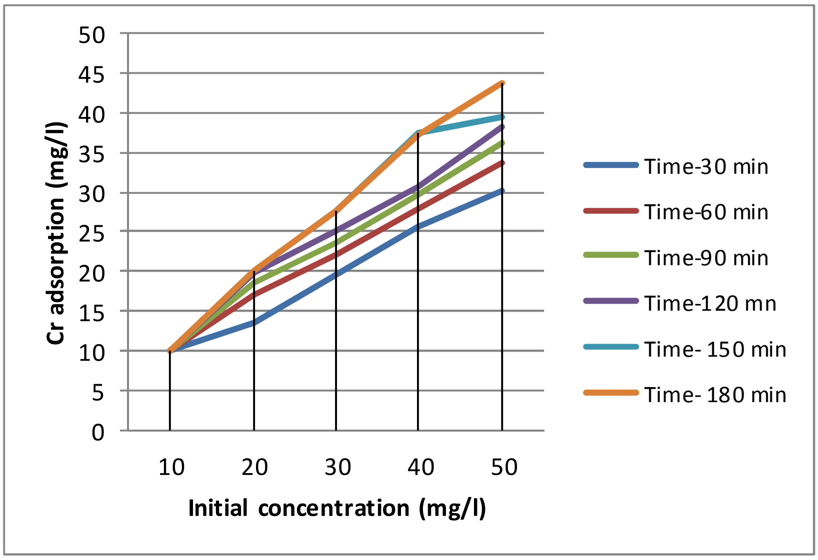


Fig 3. Effect of Initial Concentration on removal of chromium using *Chondruscrispus*
pH = 3; Time : 30 – 180 min; Wt. of adsorbent – 100mg;Temp = 30℃ ±1 & Particle size 0-63 μm

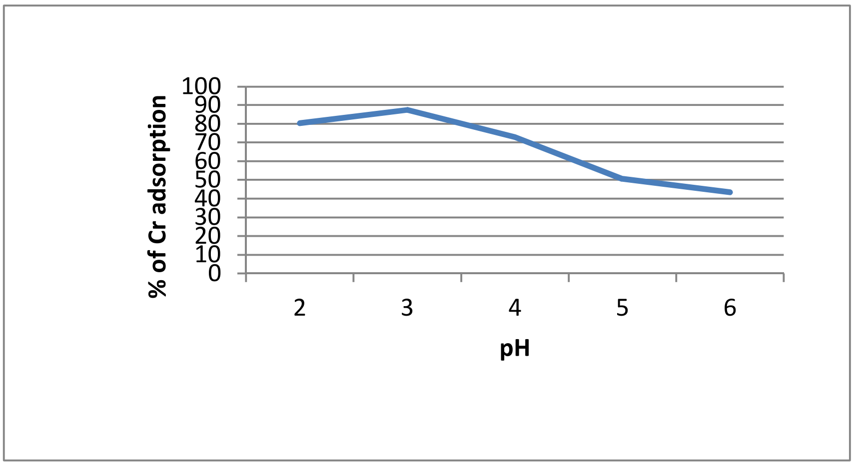


Fig.4. Effect of pH on removal of Chromium using chondruscrispus
Initial con-50mg/l; Time: 3 hrs; Wt. of adsorbent – 100 mg; Temp = 30℃ ±1, & Particle size 0-63 μm

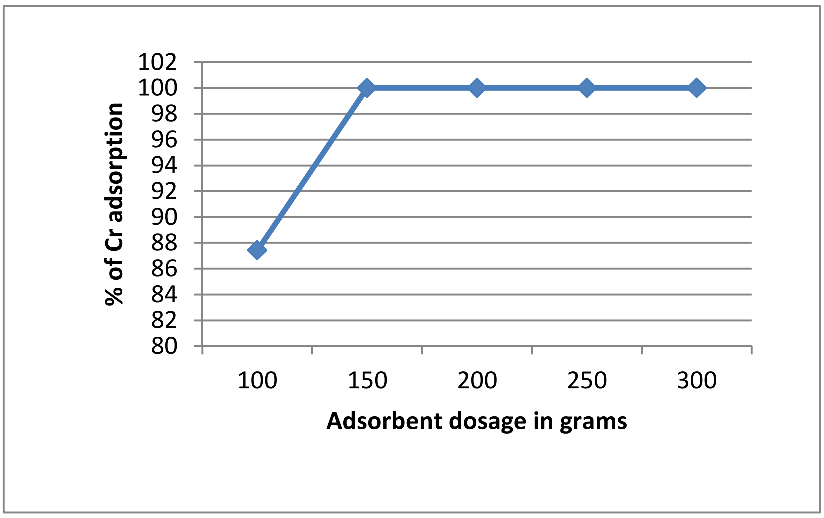


Fig.5. Effect of adsorbent dosage on removal of Chromium using chondruscrispus
pH = 3 ;Time :3 hrs; Temp = 30℃ ±1 ;Particle size 0-63 μ; Initial concentration – 50 mg/l

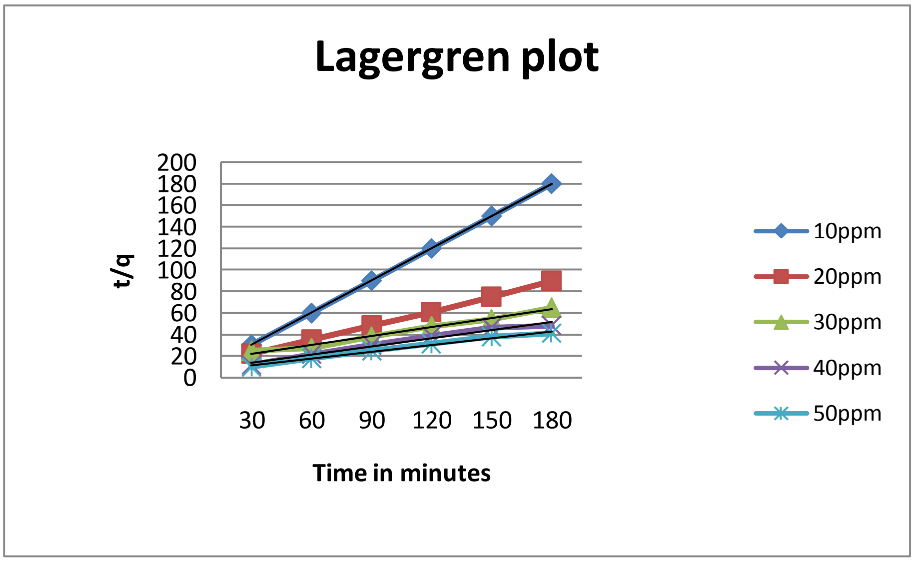
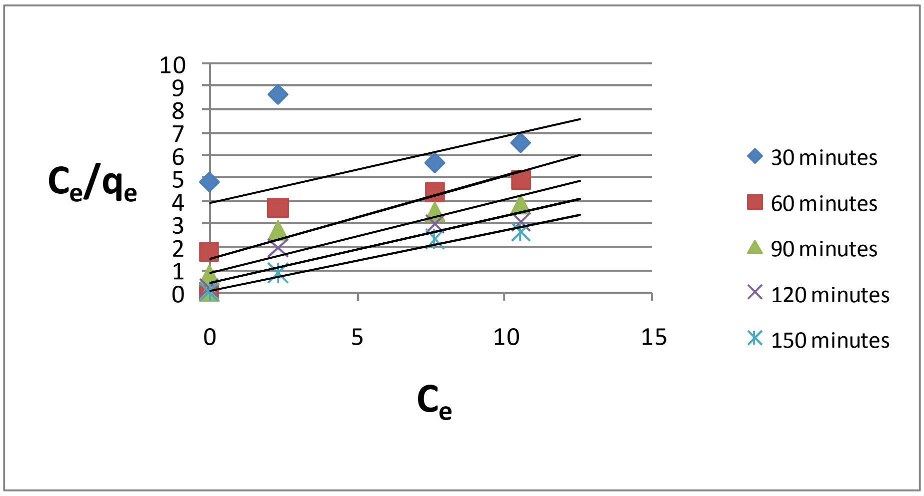


Fig.6. Lagergren adsorption isotherm

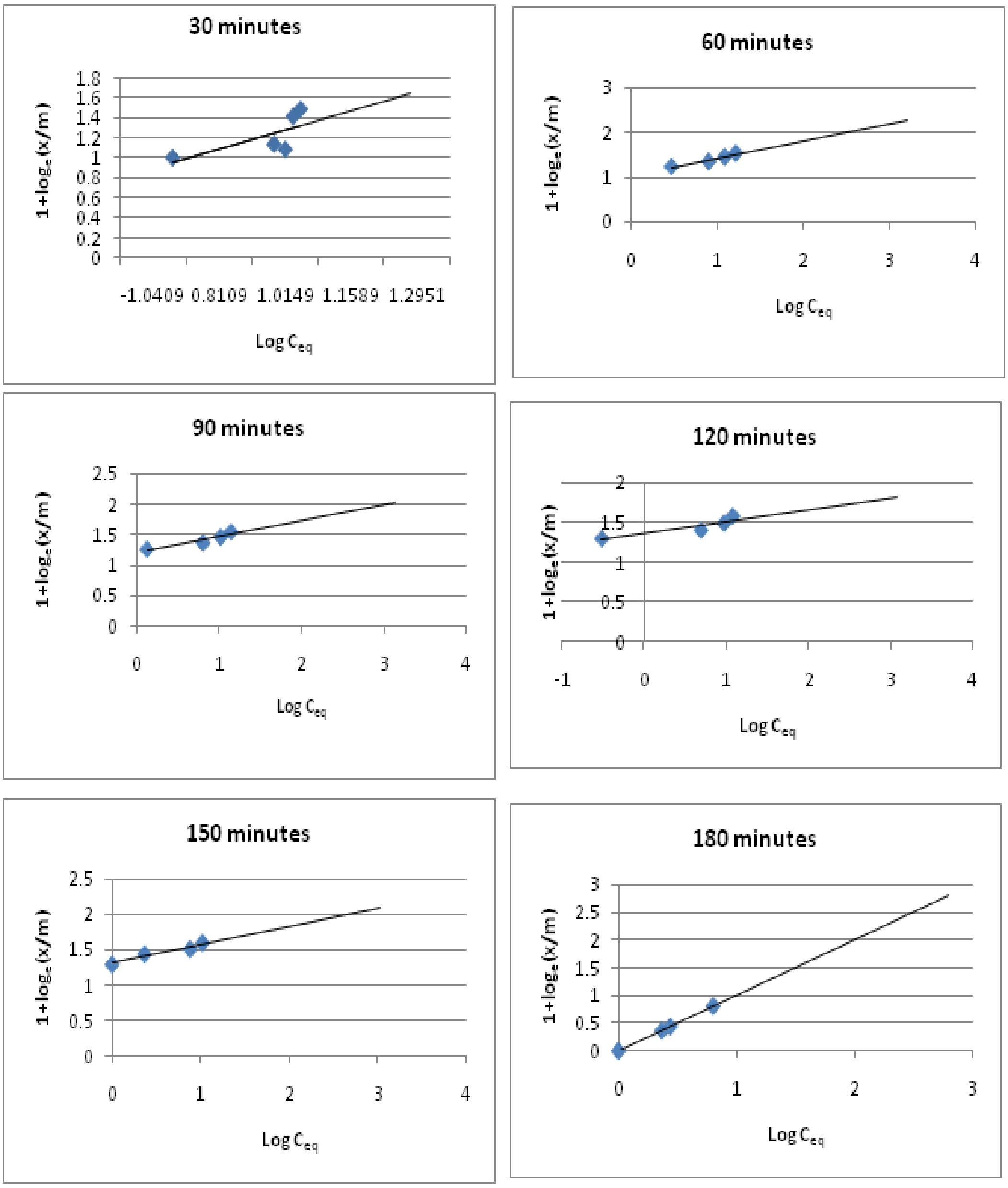
pH = 3; Particle size : 0-63 μm; Wt. of adsorbent = 100mg; Time : 30- 150 minutes Temp = 30℃ ±1



A linear trace for the plot (Lagergren plot) of t/q Vs time shows that the adsorption kinetics follows Pseudo second order kinetics. This is given in Figure 6.From the Langmuir adsorption isotherm, formation of uni-molecular layer of adsorbate on adsorbent can be verified (Fig.7). Freundlich isotherm also verified (Fig.8) Linearity confirms uni-molecular adsorption. Freundlich plot confirmed that the process of adsorption has taken place.

From the present study, it is observed that the percentage of chromium uptake was found to be 87.33% for initial adsorbate concentrations of 10 ppm, 20 ppm, 30 ppm, 40ppm and 50 ppm with adsorbent dosages of 100mg.

Fig.7. Langmuir isotherm



Freundlich biosorption isotherm of chromium at different time

Wt. of adsorbent = 100mg ; pH= 3 ; Particle size : 0-63µ ; Temp = 30°C

Fig.8. Freundlich adsorption isotherm

CONCLUSION

In the present scenario, there is a growing awareness about health hazard caused by metals in general and chromium in particular. Due to the discharge of industrial effluents from chemical industries like tannery, cement, textile, fertilizers, pesticide, electroplating and metal processing, our environment is considerably affected nowadays. Several techniques including cementation, coagulation, precipitation, evaporative – recovery, electro – dialysis and ultra – filtration are widely employed for the removal of metals from waste waters and effluents are found to be uneconomical. On the contrary adsorption technique is preferred over the other treatment process as this process involves less equipment and less operation cost, with high efficiency in achieving the goal. Hence in the present work, adsorption technique was used for chromium removal from waste water samples. From this study, it is concluded that adsorption study can be taken as a model for effluent treatment from waste waters, using a suitable adsorbent like chondruscrispus.

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