

Design, equilibrium and operation for ultrasound assisted batch adsorption of Cr (VI) on some nano-bioadsorbent

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ABSTRACT

Adsorptive removal of chromium species was designed using iron(III) modified cellulose nanocomposite under ultrasound assisted batch operation. The parameters influencing the operational performance were investigated to maximize the efficiency. The process is found to be governed by pH, adsorbent dose, sonication time and initial concentration at fixed temperature. The synthesized adsorbent is found specific for Cr(VI) species. The maximum efficiency was achieved at pH 3.5, dose of 3.0 g/L and sonication time of 30 minutes for each initial concentration at fixed temperature studied. The process was found favorable as the separation factor values were found to be within 0-1. Isotherm fitting of the experimental data indicates that Tempkin model is more suitable than the Langmuir and Freundlich. The thermodynamic parameters such as change in Gibbs free energy, enthalpy and entropy were evaluated. The process is found to be favorable, spontaneous and endothermic in nature. The elution of Cr(VI) was achieved with NaOH solution and the adsorbent can be reused for five successive adsorption-elution cycles.

Keywords: Chromium adsorption, Iron(III) modified cellulose nanocomposite bead, Ultrasound assisted batch operation, Feasibility, Recycling

I. INTRODUCTION

Chromium, particularly in hexavalent state is a critical water contaminant. It finds wide industrial uses in metallurgy, anodizing aluminum, staining glass, leather tanning, wood preservation as well as in organic synthesis. The huge discharge of chromium containing waste water is a real cause of concern throughout the world. While Cr(III) an essential human nutrient and has low migration ability, Cr(VI) accumulates in the food chain and causes severe human health problems ranging from simple skin irritation to lung carcinoma. Due to higher mobility in natural environment Cr(VI) easily enters the groundwater causing water quality degradation. Therefore, treatment via removal of Cr(VI) or reduction to Cr(III) become necessary from environmental view point. As per the World Health Organization the concentration of Cr(VI) in water is recommended below 0.05 mg/L [1, 2].

There are several treatment technologies such as chemical precipitation, electrochemical treatment, photocatalysis, ion exchange and adsorption, the later is simple and cost effective utilizing low cost adsorbents

[3]. Natural polysaccharides as the precursor of the synthetic adsorbents gain progressive demand in water treatment, particularly for removal of metals. Cellulose being the most abundant natural biopolymer may show the potential for such purposes. However, modification of cellulose becomes necessary as cellulose itself has poor adsorption capacity compared to synthetic polymeric adsorbents [4-6].

In the present study effort has been made to synthesize modified cellulose nanocomposite bead via impregnation of Fe(III) on cellulose. Impregnation of metal on cellulose modifies the adsorption capacity while the bead nature improves durability, mechanical strength, hydrophilicity and density [7]. Equilibrium study in ultrasound assisted batch operation was carried out and the optimum condition was established for the influence of operational parameters during adsorption. The interference of other ions commonly present in the wastewater is studied. Isotherm studies were made to study the feasibility of the operation. Desorption of Cr(VI) from the used adsorbent was made using alkali treatment. The suitability of the adsorbent was tested by repeated use.

II. EXPERIMENTAL

1. Materials

All the chemicals and solvents used are of analytical grade (Merck, India). Cellulose powder (Loba Chemie, India) was used for preparation of cellulose bead. Chromium(VI) stock solution ($1.0 \cdot 10^{-3}$ M) was prepared by dissolving appropriate amount of $K_2Cr_2O_7$ in deionized water and working solutions were prepared by proper dilution of the stock solution. Iron impregnation of cellulose bead was made with $Fe(NO_3)_3 \cdot 9H_2O$ solution (10% W/V).

2 Preparation of FeCNB

Cellulose nanocomposite bead was prepared from cellulose powder using the method described by Santra et al [8]. The cellulose (Cell) was first converted into cellulose xanthate using NaOH and CS_2 . The mixture was further added to a mixture of 6.0% NaOH for dissolution and kept for 8 h when a gel is formed. The gel was subsequently added to methanol with constant vigorous stirring.

The resulting spherical white beads (CNB) were washed with distilled water and air dried. CNB was taken in a conical flask, shaken with $Fe(NO_3)_3 \cdot 9H_2O$ solution (10%) at a speed of 100 rpm for 2 h. The iron(III) impregnated cellulose nanocomposite bead was appeared as brown in color.

3 Ultrasound assisted batch operation

Batch experiments were conducted for static operation in an ultrasonic bath (30 cm x 20 cm x 30 cm) at frequency of 22.5 kHz, power of 120W and total acoustic power of 1.52 W/cm^2 . Influence of pH, FeCNB dosage, initial Cr(VI) as well as total chromium (Cr(T): Cr(III)+ Cr(VI)) concentration, sonication time and agitation speed at fixed temperature on the adsorption behavior were investigated. The solution after equilibrium was filtered through Whatmann 41 filter paper and the Cr(VI) concentration was determined spectrophotometrically using 1,5- diphenylcarbazide as the complexing agent and Cr(T) using AAS. Desorption of Cr(VI) after adsorption onto FeCNB was carried out by equilibrating with NaOH solution of definite strength.

All the experiments were carried out in triplicate and the mean of the quantitative results were taken. A control run without FeCNB was carried out to find any precipitation of chromium.

The amount of Cr(VI) uptake by FeCNB was determined using the mass balance equation.

$$q_t = V (C_0 - C_t) / W \quad (1)$$

Adsorption percent (R) is calculated from the following equation:

$$R = (C_0 - C_e) / C_0 * 100 \quad (2)$$

where, q_t is the amount (mg/g) of Cr(VI) adsorbed at time t, C_0 , C_t and C_e are the chromium concentration (mg/L), initial, at time t and equilibrium time respectively, V is the volume of the solution (L) and W is the weight of FeCNB (g).

Adsorption isotherm is useful to describe nature of interaction of the solute with adsorbent and hence for designing the process as a unit operation. Adsorption efficiency of FeCNB at equilibrium was evaluated considering Langmuir, Freundlich and Tempkin isotherm models.

III. RESULTS AND DISCUSSION

1. Characterisation of FeCNB

The surface characterization of FeCNB was made using FT-IR, SEM, EDS and XRD. The thermal stability was established from TGA. The physical characteristics are evaluated from swelling factor, bulk density and pore volume. The FT-IR spectrum of FeCNB shows characteristics vibrational peaks of cellulose (O-H stretching and bending, C-H symmetrical stretching and bending, C-C, C-OH, C-H ring stretching) with additional bands at 514, 552, 575 nm corresponding to symmetric Fe-O stretching, O-Fe-O bending. [9, 10]. The bands are found shifted to 561, 588 nm with concomitant appearance of a new band at 913 nm due to Cr=O stretching [11] after Cr(VI) adsorption, indicating adsorption potential of FeCNB for Cr(VI). EDS shows the presence of C, O, H and Fe in FeCNB and C, O, H, Fe as well as Cr in CrFeCNB. This attributes impregnation of iron on CNB and adsorption of chromium on FeCNB. The XRD pattern of FeCNB

shows poor crystallinity and suggested a state between amorphous and semi crystalline nature. All diffraction peaks are consistent with the standard structure of maghemite (JCPDS card No. 39-1346) [12]. TGA provides temperature induced mass losses at multiple steps. In the first step at around 150°C the mass loss may corresponds to moisture or physisorbed water. The mass loss at temperature 250 to 275°C is due to minor decomposition and that above 350°C for major decomposition of the beads. The degree of swelling, bulk density and porosity of FeCNB were found to be 18.74, 0.93 g/mL and 46.83% respectively. SEM study at different magnifications indicates spherical nanonature of both CNB and FeCNB.

2. Influence of variables in batch operation

The influence of operational variables on adsorption of hexavalent chromium (S) and total chromium (T) was modeled for ultrasound assisted batch operation. The range of operation variables studied are: pH (2-10), dose (0.5-5.0 g/L), initial concentration (100-300 mg/L), sonication time (10-60 min) and agitation speed (50-150 spm) at constant temperature.

The influence of pH was studied with both Cr(VI) and total chromium Cr(T) in figure 1. The pH dependent adsorption is primarily due to the surface properties of the adsorbent and the forms of the solute species [13]. It is observed that the adsorption efficiency is higher at acidic pH (3-6) than at alkaline pH. It is interesting to found that adsorption extent of Cr(T) on FeCNB does not differ from that of Cr(VI), which indicates that FeCNB is specific for adsorption of Cr(VI) only. The decrease in adsorption beyond pH 6 is due to the repulsive nature of negatively charged FeCNB in abundant OH⁻ environment.

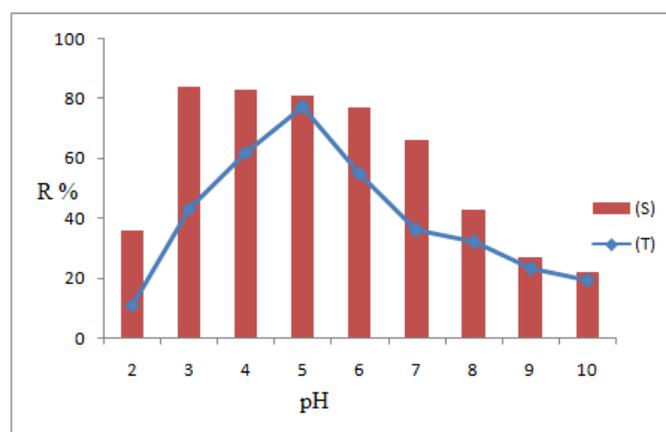


Figure 1. Influence of solution pH

Investigation on the influence of FeCNB dose reveals that adsorption efficiency increases with increasing FeCNB dose and reaches maxima after the optimum dose. It is expected that availability of the number of active sites on FeCNB surface increases as the dose increases. The saturation of adsorption extent even with increase of dose beyond equilibrium is thought to be due to either aggregation or overlapping of active surface sites [14]. Highest adsorption corresponds to 3.0 g/L of FeCNB for both Cr(T) and Cr(VI) (Fig 2). However, due to poor stability of cellulose bead it was not used for adsorption.

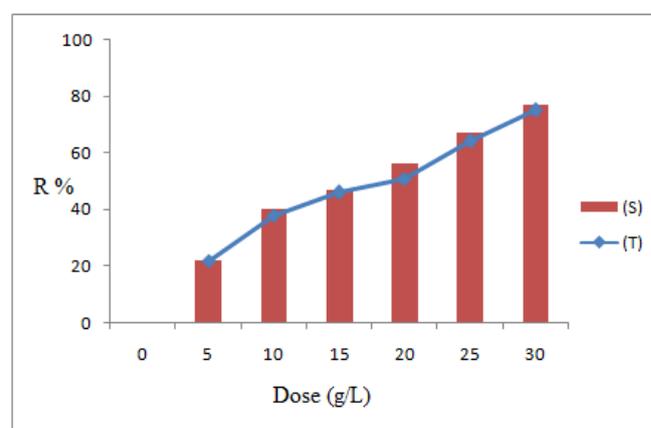


Figure 2. Influence of FeCNB dose

In order to achieve equilibrium for solute-FeCNB interaction the sonication period was varied. With progress of time initially the rate of adsorption is more which slows down gradually and reaches maxima near equilibrium. At the initial stage increase of adsorption is due to availability of more vacant adsorption sites and high solute concentration gradient between the adsorbent surface and bulk solution which is assisted more under

ultrasound power [15]. Thus equilibrium is established quickly. The behavior of Cr(T) and Cr(VI) adsorption with progress of adsorption for a fixed adsorbent dose is shown in figure 3. With progressive adsorption the vacant sites get occupied and become exhausted near the equilibrium. Beyond the equilibrium a flat plateau was observed.

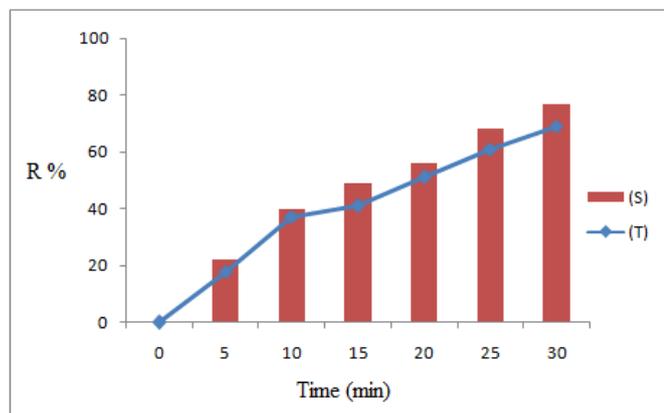


Figure 3. Influence of contact time

The agitation speed during ultrasound assisted adsorption was varied from 50-200 spm to study the adsorption behavior of hexavalent and total chromium (Figure 4). It is found that while agitation speed does not influence the adsorption percent of hexavalent chromium, adsorption of total chromium vary irregularly. This behavior may be due to resistance in mass transfer from solution bulk to adsorbent surface prior to establishment of the equilibrium.

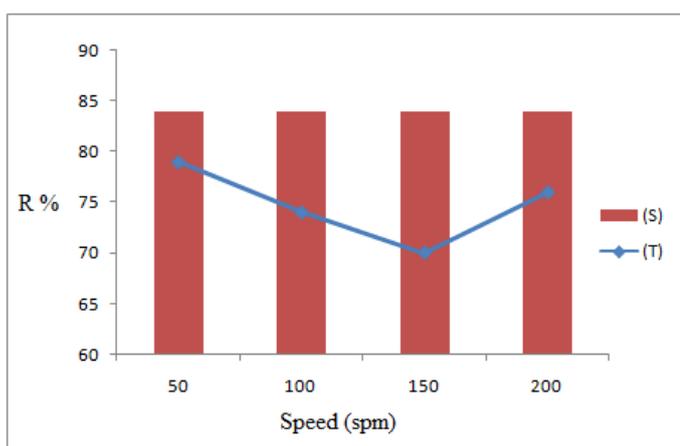


Figure 4. Influence of agitation speed

In order to find the effect of initial chromium concentration on adsorption efficiency solute concentrations ranging from 100-300 mg/L was varied (Figure 5). Due to the more availability of surface active sites of FeCNB compared to the solute species at lower

initial concentration percent adsorption increases [16]. The adsorption efficiency of Cr(T) and Cr(VI) was found almost similar.

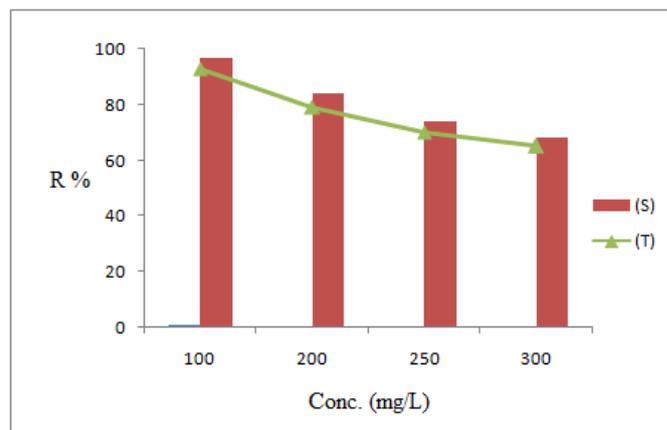


Figure 5. Influence of initial concentration

Influence of interfering ions

The role of common anions present in the effluents such as nitrate, chloride and sulfate on Cr(VI) adsorption is studied. It shows non significant influence of the anions upto 10 times of load of Cr(VI). However, AsO_4^{3-} , PO_4^{3-} show decrease of adsorption percent of Cr(VI) due to their competitive nature for FeCNB adsorption sites. In presence of bicarbonate Cr(VI) adsorption lowers down to 27.9% due to increase of solution pH from 3.8 to 7.9.

3. Adsorption isotherm, feasibility factor and thermodynamic parameters

The Langmuir isotherm was used to estimate the monolayer adsorption capacity on homogeneous adsorbent sites [17] and is given in linear form as:

$$C_e/q_e = 1/q_{max} K_L + C_e/q_{max} \quad (3)$$

where, q_{max} (mg/g) and K_L (L/mg) are maximum Cr(VI) capacity and adsorption intensity respectively. Freundlich adsorption was employed to estimate the adsorption intensity of the adsorbent towards heterogeneous adsorbent sites [18] and is given in linear form as:

$$\ln q_e = \ln K_F + (1/n) \ln C_e \quad (4)$$

where, K_F (L/g) and $1/n$ are the distribution coefficient and a correction factor, respectively and C_e is

equilibrium concentration of Cr(VI) (mg/L). Temkin isotherm assumes that the heat of adsorption of the solute decreases linearly with the progressive filling of vacant adsorption sites [19] and is represented as:

$$q_e = (RT/B_T) \ln A_T + (RT/B_T) \ln C_e \quad (5)$$

where, B_T (kJ mol^{-1}) represents the heat of adsorption and A_T ($\text{dm}^3 \text{g}^{-1}$) the equilibrium binding constant corresponding to the maximum binding energy. The isotherm constants are evaluated and the model q_e values are calculated. Adsorption isotherm plot from the model and experimental values are shown in the Figure 6 to find the best fit model.

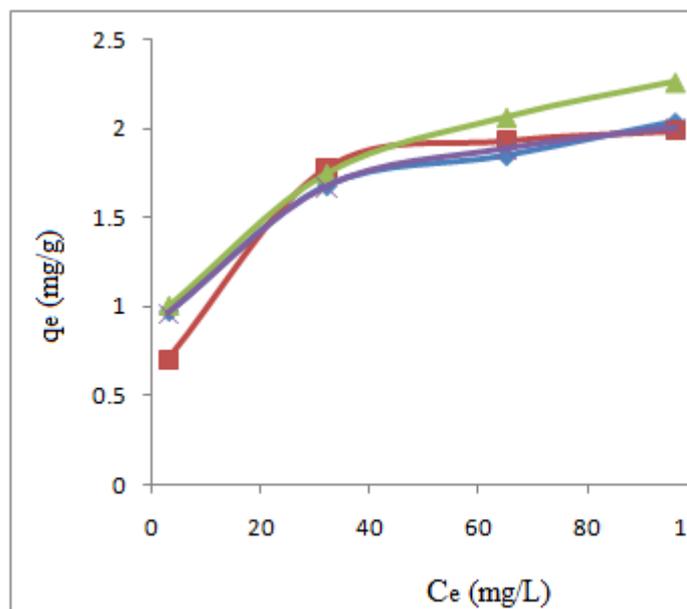


Figure 6. Fitting of experimental and model isotherm data

It is found that Temkin isotherm model is most suited one than the Langmuir and Freundlich model as confirmed by the higher regression coefficient value (R^2) and lower Chi square (χ^2) value. It is found that for Tempkin: $R^2 = 0.9998$, $\chi^2 = 0.001$; for Langmuir: $R^2 = 0.9971$, $\chi^2 = 0.005$ and for Freundlich: $R^2 = 0.8946$, $\chi^2 = 0.022$. Thus the order of fitting of isotherm model is Tempkin > Langmuir > Freundlich. In order to study the feasibility of ultrasound assisted adsorption separation factor (R_L), a dimensionless quantity, was estimated from,

$$R_L = 1 / (1 + K_L \cdot C_0) \quad (6)$$

where, K_L is the Langmuir constant and C_0 is the initial Cr(VI) concentration in solution. The nature of the isotherm was indicated from R_L value [20], as favorable ($0 < R_L < 1$), irreversible ($R_L = 0$), unfavorable ($R_L > 1$) or linear ($R_L = 1$). In the present case SF values at three different temperatures and concentrations are found to lie between 0-1 indicating a favorable case of Cr(VI) retention on FeCNB. Thermodynamic parameters such as change in free energy ΔG (kJmol^{-1}), ΔH (kJmol^{-1}) and ΔS ($\text{kJmol}^{-1}\text{K}^{-1}$) are found to be -4.49, 95.77 and 33.31 respectively as evaluated from the following equations.

$$-\Delta G = RT \ln K_c \quad (7)$$

$$R \ln K_c = -\Delta H / T + \Delta S \quad (8)$$

The negative free energy change indicates that the operation is spontaneous; the positive value of free energy change indicates that the process is endothermic and the positive value of entropy change indicates that the process is aided by increased randomness.

4. Desorption and regeneration of FeCNB

Regeneration of adsorbent for repeated use has an important significance in economical and environmental point of view. In the present case regeneration of FeCNB was done by 0.2M NaOH solution and the adsorption-elution process was repeated. It is observed (Figure 7) that adsorption capacity of the regenerated FeCNB remained unaltered upto four cycles and declined gradually afterwards. While in first cycle 98.8% removal was achieved in the fifth cycle removal efficiency was 91.4%, which further decreases to 83.31% in the sixth cycle. Thus FeCNB can be used in column operation for adsorption of Cr(VI) at least up to five repeated operations.

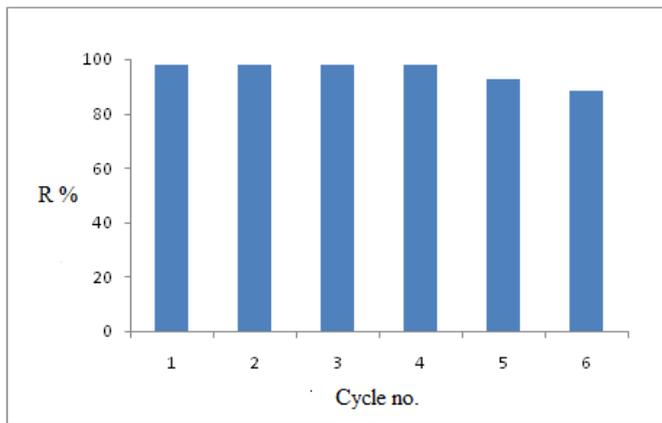


Figure 7. Recycling characteristic of FeCNB

5. Application in real sample

The physicochemical parameters of the effluent from a typical electroplating industry are presented in Table 1. The value of each parameter is the mean of three replicate analyses. In a typical study 10 mL of the sample was treated with FeCNB maintaining the optimum condition of FeCNB dose and contact time in batch operation. It is observed that 86% of chromium removal takes place lowering to the level recommended by the WHO. The simple operation, low amount of adsorbent and sufficient quick operation makes the synthesized adsorbent a good one for removal of chromium from effluent.

Table 1. Physicochemical parameters of electroplating industry wastewater

Parameter	Value
Color	Yellowish brown
Temperature	32 ⁰ C
pH	4.32
EC	2.14 mS/cm
BOD	89 mg/L
COD	225 mg/L
TS	742 mg/L
TDS	678 mg/L
Chloride	195 mg/L
Sulfide	17 mg/L
Chromium (total)	180 mg/L

IV. CONCLUSION

In this study, iron (III) modified cellulose nanocomposite bead was synthesized and adsorption

efficiency of chromium under ultrasound assisted batch operation. The influence of operational variables on adsorption percent for hexavalent and total chromium was investigated. It is found that FeCNB is specific for adsorption of Cr(VI). The process obeys Temkin isotherm model than Langmuir or Freundlich, The process is spontaneous, feasible, endothermic and random. Elution of chromium can be effected with NaOH solution and the bead can be reused for multiple operation. Moreover, FeCNB can effectively remove chromium from electroplating wastewater.

V. ACKNOWLEDGEMENT

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