

# OPTIMIZATION OF PARAMETERS FOR THE REMOVAL OF CHROMIUM FROM SYNTHESIZED CHROMIUM SOLUTION USING ACTIVATED SODIUM-BENTONITE AS ADSORBENT

Kruthi B S<sup>1</sup>, Rajani M R<sup>2</sup>

Department of Chemical Engineering,  
Dayananda Sagar College of Engineering, Bangalore, Karnataka, India  
kruthisathish@gmail.com, rajanidd@rediffmail.com

**Abstract**— This study aims to employ low-cost adsorbent such as activated Na-Bentonite to remove hexavalent ion of Chromium (VI) from aqueous solution. The cumulative effect of different parameters like initial metal ion concentration, pH, rpm, adsorbent dosage and optimizing the process conditions for the maximum removal of Chromium (VI) was studied using response surface methodology. A 2<sup>4</sup> factorial central composite design using response surface methodology was used to get the mutual interaction between variables and then optimizing it. A Maximum chromium adsorption of 97.39% was achieved at pH 2.4 with adsorbent dosage 3.2 g, initial metal ion concentration of 170 ppm and rotation speed of 180 rpm. The FTIR spectrum of Na-bentonite was used to identify the functional groups. SEM was used to study the changes in morphology of Na-bentonite. The adsorption process has fit freundlich isotherm model and Pseudo-first order kinetics.

**Index Terms**- Sodium-Bentonite, Removal, Chromium, Wastewater, Heavy metals.

## I. INTRODUCTION

With industries growing rapidly, heavy metals are disposed at an increasing rate into the environment and therefore effluent treatment has become one of the most important concern for the industries. Today, heavy metals are released from daily activities of humans like the use of construction materials, cosmetics, medicines, processed foods, fuel sources, agents of destruction, appliances and personal care products. In drinking water, air and soil these metals are found due to the increased use of it. The heavy metals are difficult to degrade unlike organic pollutants [18]. Therefore, chromium effects on human health is widely analyzed by international bodies such as the WHO. For adults, industrial exposure is the common route and for children it is ingestion [13]. The common route of children exposure is due to, hand-to-mouth when it contact with contaminated soil and eating objects that are non-food items like dirt or paint chips [4]. Other routes of exposure is during a radiological procedure, from improper dosage, from a broken thermometer [14] and from a suicide or homicide effort.

It is impossible to prevent the exposure to these heavy metals present in the environment therefore the consumption method should be reconsidered. According to literature survey, various methods are used for treating effluent such as chemical precipitation, carbon adsorption, ion exchange and membrane separation process and many more.

Adsorption is one such modern technology to eliminate toxic metals from wastewater.

Chromium was discovered by Louis- Nicholas Vaughlin in 1797. The name is derived from a Greek word “chroma” meaning “coloured”. Chromium (Cr) is the first element of group 6 and has an atomic number 24. It is a lustrous, brittle, hard and polished metal that appears to be silver-gray in color. When it comes in contact with oxygen a thin layer of oxide is produced. The oxide layer formed is impermeable to oxygen thus protecting the metal below. Adsorption technique, of late has gained attention because of its simple and cost effective nature. To eliminate the heavy metals from wastewater, there are various low cost adsorbents have been employed which include bentonite [17], coip pith [11], expanded perlite [10], fly ash [1], maghnite [19], montmorillonite [8], oak sawdust [3], peat moss [7] and smectite [9]. Bentonite is having large surface area and high cation exchange capacity [6] thus making it a potent adsorbent for the elimination of heavy metals from waste water. The maximum concentration limit for chromium (VI) for discharge into inland surface water is 0.1 mg/l, public sewer is 2 mg/l and marine coastal areas is 1 mg/l [16].

## II. MATERIALS AND METHODS

### A. Materials/Instruments Used

The materials/instruments used for this work were, Atomic absorption spectrophotometer, hot air oven, rotary flask shaker, pH meter, SEM, FTIR.

### B. Sample Collection

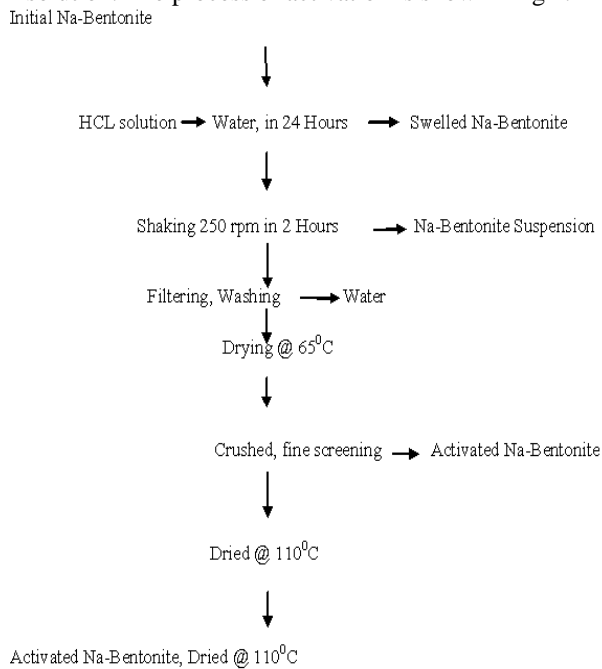
Na-bentonite is collected from Leo Chemiclas, Bengaluru, Karnataka. A sample of Na-Bentonite is shown in Fig 1.



**Fig 1: Sodium-Bentonite**

**C. Process of Sodium-bentonite activation**

The sodium-bentonite is collected and activated with dilute HCL solution. The process of activation is show in Fig 2.



**Fig 2: Activation of Sodium-bentonite**

**D. Preparition of stock solution**

To prepare 1000ppm of stock Chromium solution, 2.83g of potassium dichromate is dissolved in one liter of double distilled water. The stock solution is shown in Fig 3.



**Fig 3: Stock solution**

**E. Central composite design (CCD) and optimization by response surface methodology (RSM)**

The effect of adsorption parameters, initial metal ion concentration, pH, rpm and adsorbent dosage can be well studied by statistically designed experiments using CCD. According to the software, a factorial experimental designs of 2<sup>4</sup> is used with seven replicates at the centre point thus 31 trials were conducted. The experiments with the ranges of initial metal ion concentrations in 50 – 280 ppm, pH in 2-6, rpm in 100-250 and adsorbent dosage in 1 - 5g/100ml was studied coupled to each other and varied simultaneously to cover the spectrum of combinations of variables in the central composite design.

**F. Analysis of sample**

The analysis was carried out based on the experimental data generated by the software for the given range of process parameters. The first sampling was done after 30 min of shaking, which is the first considered contact time for the experiment. Similarly the next sampling was done after 60 min, then after 90 min, 120 min and 150 min, till adsorption equilibrium was reached. For sampling, the supernatant in the conical flask after shaking i.e after chromium adsorption, is collected into sample bottles after each contact time considered. The collected sample was determined by atomic-absorption spectrophotometer. (AAS)

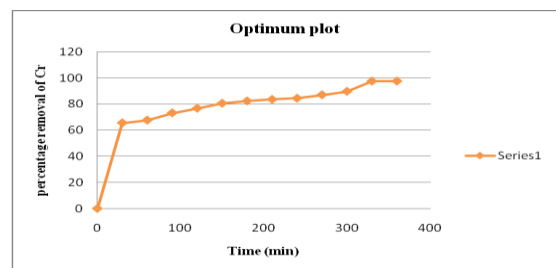
**II. RESULTS AND DISCUSSION**

**A. Optimization of response**

The second degree polynomial equation is solved and the optimum values for the variables are obtained using response optimizer in software. Table 1 gives the optimum values from the software and Fig 5 shows the optimum plot.

**Table 1: Optimum values**

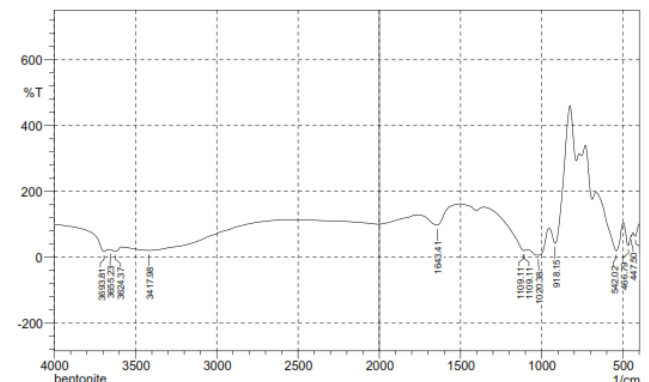
Adsorbent	Initial metal ion Concentration(ppm)	pH	rpm	Ad. dosage(g /100ml)	Y Percentage Removal	D Desirability index
Act. Na-Ben	170.34	2.45	180.38	3.26	97.39	1



**Fig 5: Optimum plot**

**B. Characterization of adsorbent by FTIR Spectrophotometer**

It helps to study the effect of acid attack and the change that have taken place in the structure of bentonite and determination of functional group. Fig 6, 7, 8, shows the interferogram of Na-bentonite, activated Na-bentonite, after Chromium adsorption.



**Fig 6: Interferogram of NA-bentonite**

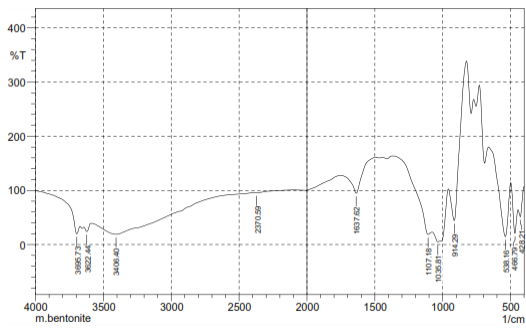


Fig 7: Interferogram of activated Na-bentonite

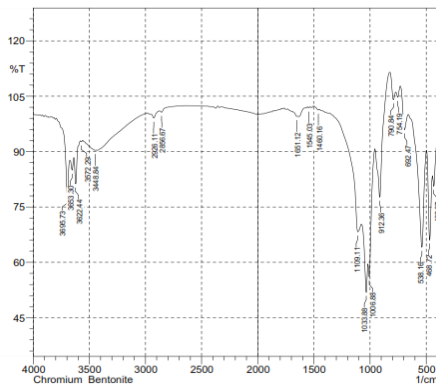


Fig 8: Interferogram for after chromium adsorption on activated Na- bentonite

The FTIR spectra of activated Na-bentonite are carried out in the range from 4000- 400  $\text{cm}^{-1}$  (400 – 1500  $\text{cm}^{-1}$  is bending region and 1600- 4000  $\text{cm}^{-1}$  is stretching region) to see the effect of acid activation on the raw Na- Bentonite. The changes in the functional group indicated the changes occurred during acid activation. The chemical activation or acid activation leads to the formation of amorphous silica, it increases the adsorption sites and also increases the adsorption. Aromatic orthodisubstituted heterocyclic molecules are present which is confirmed from the peaks obtained from IR spectrogram. This suggests that after chromium and nickel adsorption ring cleavage occurs. Thus it can be concluded that the pretreated ester groups are converted into acid groups.

### C. Surface morphology by Scanning Electron Microscopy (SEM)

To study the changes in the surface morphology of Na-Bentonite, SEM was used. Fig 9 and 10 shows the raw and activated Na-bentonite structure, Fig 11 shows the structure for after adsorption of chromium

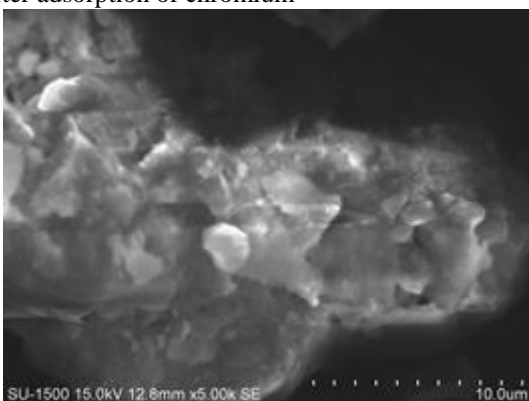


Fig 9: Raw Na-bentonite

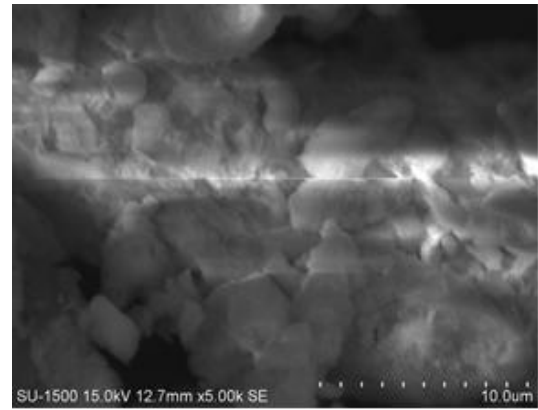


Fig 10: Activated Na-bentonite

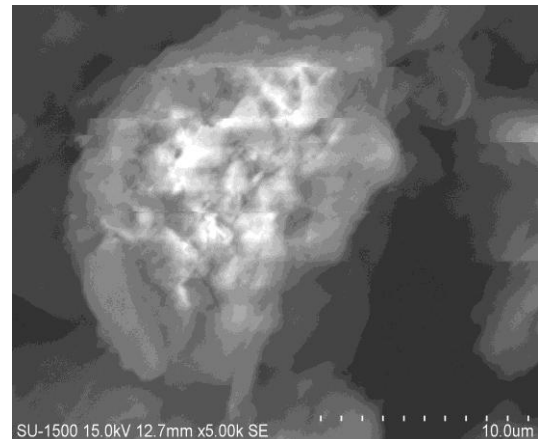


Fig 11: Chromium adsorbed on activated Na-bentonite

The leaching of cations on activation creates voids in the Na-Bentonite and makes the clay surface more porous. Before acid activation, clumps of uneven surface can be seen but after activation surface becomes highly porous with even distribution of pores. As the impurities are removed the exchangeable cations and  $\text{H}^+$  ions replaces forms the smaller pores. These physico-chemical reactions alters the morphology of the NA-bentonite as the pores open up and the clay surface appears to be more porous and homogeneous. Fig 11 shows, pores are occupied by chromium metal ions.

### D. Adsorption isotherms

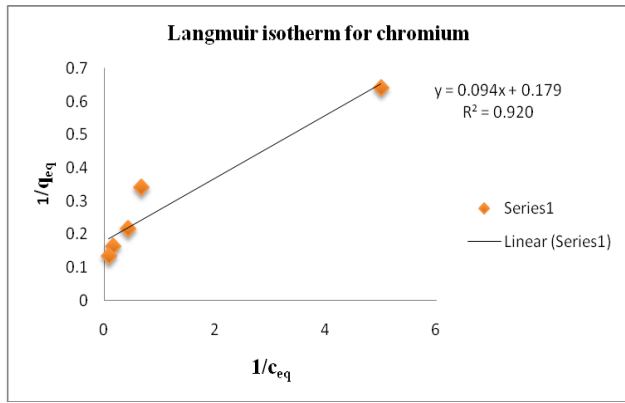
Adsorption isotherm is defined as the equilibrium relationship between the concentration in the adsorbent and the adsorbent in the liquid phase at a particular temperature.

#### a) Langmuir isotherm

This model is applicable to monolayer adsorption whose adsorbent surface consists of equal number of identical sites. The Langmuir isotherm is shown by:

$$C_e/q_e = 1/(bq_m) + C_e/q_m$$

Where,  $q_e$  is the amount of adsorbed metal (mg/g),  $c_e$  is the unadsorbed metal concentration (mg/l),  $q_m$  is the maximum amount of metal per unit weight of adsorbent and  $b$  is constant related to the affinity of the sites. Fig 12 shows the linear plot obtained by plotting  $1/q_e$  versus  $1/c_e$ .

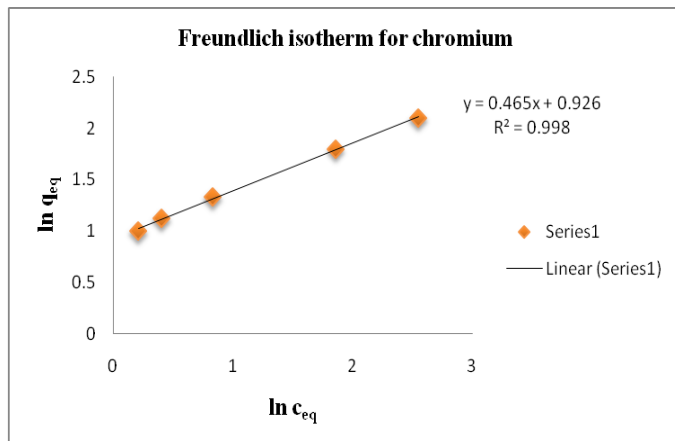


**Fig 12: Langmuir isotherm plots for Chromium adsorption by activated Na-bentonite**

*b) Freundlich isotherm*

This model is applicable for adsorption on heterogeneous surface. Freundlich isotherm is shown by:  $q_e = K_f C_e^n$

Where,  $q_e$  is the amount of adsorbed metal per unit weight of adsorbent,  $c_e$  is the unadsorbed metal concentration in solution at equilibrium and  $K_f$ ,  $n$  are Freundlich constants. Fig 13 shows the linear plot obtained by plotting  $\ln q_{eq}$  versus  $\ln c_{eq}$ .



**Fig 13: Freundlich isotherm plots for Chromium adsorption by activated Na-bentonite**

The above chromium data fits well to Freundlich isotherm indicating heterogeneous adsorption of chromium on activated Na-bentonite. Table 2 shows the  $R^2$  value which is obtained from the isotherm models.

**Table 2: Isotherm values for Chromium by activated Na-bentonite**

Metal ion	Langmuir Isotherm	Freundlich Isotherm
	$R^2$	$R^2$
Chromium	0.920	0.998

*E. Adsorption kinetics*

The adsorption kinetics of Chromium on activated bentonite is studied. The data obtained was studied using Pseudo first-order kinetics and Pseudo second-order kinetics models

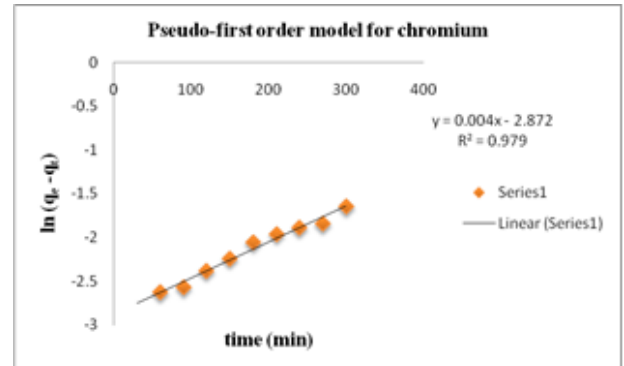
*a) Pseudo-first order kinetics*

It is also known as Lagergren kinetic equation. This model is used to study the system's kinetics behavior.

The following equation is used for this model:

$$\ln(q_e - q_t) = \ln q_e - k_1 t$$

where,  $q_e$  is the amounts of chromium and nickel adsorbed at equilibrium ( $\text{mg g}^{-1}$ ),  $q_t$  is the amounts of chromium and nickel adsorbed at time  $t$  ( $\text{mg/g}$ ),  $k_1$  is the pseudo first order rate constant ( $\text{min}^{-1}$ ) and  $t$  is the time ( $\text{min}$ ). Fig 14 shows the plot obtained by plotting  $\ln(q_e - q_t)$  versus time.



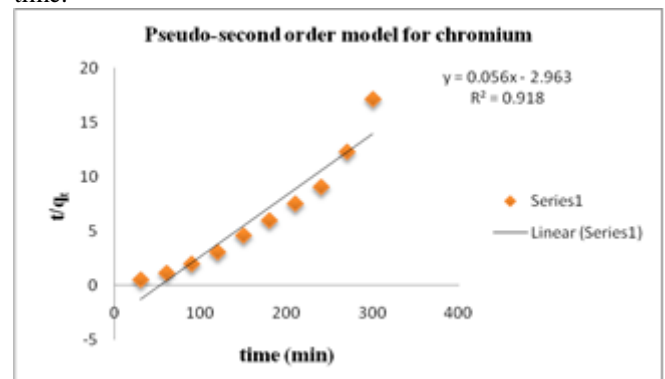
**Fig 14: Pseudo first-order model for adsorption of chromium by activated Na-bentonite**

*b) Pseudo- second order model*

The following equation is used for this model:

$$\frac{t}{q_t} = \frac{1}{k q_e^2} + \frac{1}{q_e} t$$

Where,  $q_t$  is the amount of chromium and nickel adsorbed at equilibrium ( $\text{mg/g}$ ),  $q_e$  is the amount of chromium and nickel adsorbed at time  $t$  ( $\text{mg/g}$ ),  $k_2$  is the pseudo-second-order equilibrium rate constant ( $\text{g mol}^{-1} \text{min}^{-1}$ ),  $t$  is the time ( $\text{min}$ ). Fig 15 shows the plot obtained by plotting  $t/q_t$  versus time.



**Fig 15: Pseudo second-order model for adsorption of chromium by activated Na-bentonite**

The regression study used to examine the Lagergren model and pseudo second order model applicability is  $R^2$ . The values obtained from  $R^2$  shows the models linearity. If the  $R^2$  value is unity then the model is better fit. For the above chromium values fits well to Pseudo first order. Table 3 shows the  $R^2$  which is obtained from the kinetics model.

Metal ion	Pseudo-First order		Pseudo-second order	
	$k_1$	$R^2$	$k_2$	$R^2$
Chromium	0.016	0.979	0.0145	0.918

**Table 3: Kinetics values for chromium by activated Na-bentonite**

### III. CONCLUSION

Studies on adsorption of hexavalent Chromium was carried out by evaluating percentage removal at different conditions and considering initial metal ion concentration, pH, rpm and adsorbent dosage as variables affecting the process, activation with an acid of Na-bentonite were employed. CCD and RSM can be efficiently employed and various statistical parameters like student distribution 't', probability value and regression coefficients are used as standards to certain the significance of the models obtained. The maximum percentage removal of chromium is **97.39 %** at optimum pH 2.4, initial metal ion concentration 170 (ppm) and adsorbent dosage 3.26 g with rpm 180. The Freundlich isotherm model is best suited for the Chromium equilibrium data indicating heterogeneous adsorbent surface. The chromium and values fits well to Pseudo first order.

### IV. ACKNOWLEDGEMENT

We thankfully acknowledge the help from Dr. Ravishankar, Prof. Sikdar D. C, Prof. B.S. Thirumalesh, Department of Chemical Engineering, DSCE, Bangalore, Associate Prof. S. M. Desai, Department of Biotechnology, DSCE, Bangalore, Mr. Devendra G. V, Senior Chemist, GSI, Bangalore, Mr. Sunil and Mr. Ravikumar, Department of Pharmacy, DSCE, Bangalore. We would also like to thank Dr. D. Hemachandra Sagar, Chairman, Dr. D. Premachandra Sagar, Vice-Chairman and Dr. S.C.Sharma, Director, Dayananda Sagar College of Engineering, Bangalore for their encouragement and support for publishing this paper.

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