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## Kinetic and Equilibrium Studies For the Removal of Chromium Using Eggshell Powder.

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### ABSTRACT

Removal of toxic metals from wastewater occurs by either biological methods or physicochemical methods (e.g., adsorption, oxidation-reduction, chemical coagulation, ozone treatment, and membrane filtration). Low cost adsorbents have gained attention over decades as a means of achieving very high removal efficiency to meet discharge standards. The eggshell in a powdered form is a potentially useful material for the removal of toxic metal from industrial wastewater. It is suggested that the work is designed to increase the scale of egg shell application to cope with the removal of chromium under industrial conditions should be initiated. The principal component of the shell is calcium carbonate which comprises more than 90% of the carbon material. Powdered egg shell has a substantially larger capacity to remove the toxic metals by adsorption. The performance analysis was carried out as function of various operating parameters such as contact time, initial concentration, adsorbent dose, and particle size. The parameters affecting kinetics and equilibrium of Cr<sup>+6</sup> adsorption onto egg shell powder was studied, Detailed data analysis indicated that the adsorption of chromium followed Freundlich isotherm and Langmuir isotherm.

**Keywords:** EggShell; Chromium; Langmuir model; Freundlich model.

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## INTRODUCTION

The studies made on investigation of economic and effective methods for the removal of heavy metals have resulted in the development of new separation technologies. Biological treatment, ion exchange, coagulation, electrochemical operation and filtration are commonly applied to the treatment of industrial effluents [1, 2]. However technical and economic factors limit the feasibility of such processes. Then the search for new technologies has directed the attention towards biosorption. Biosorption is a process that uses inexpensive biomaterials to sequester metals from aqueous solutions and the biomaterial used in this process is termed as biosorbent. The main advantages of this method are effectiveness in the reduction of the concentration of heavy metal ions to permissible levels using low cost biomass materials, low operating cost, minimal volume of chemical disposable, regeneration of the biosorbent biological sludge and high detoxifying efficiency of very dilute effluents [3].

The by-products from agriculture, food and pharmaceutical industries provide economically viable sources of biosorbent and makes the biosorption an inexpensive alternative treatment method. Recent research on biosorption has shown that biomaterials containing acidic groups such as hydroxyl and carboxyl were effective in binding metal cations [4].

The term biosorption commonly refers to the passive binding of metal ions or radioactive elements by dead biomass. The focus in early studies has been exclusively on the toxicological aspects of biosorption. Biosorption removal of toxic heavy metals is especially suited as a 'polishing' waste water treatment step because it can produce close to drinking water quality from initial metal concentrations of 1-100 mg/L to final concentrations less than 0.01-0.1 mg/L [6, 7].

Removal of toxic metals from industrial waste water is essential from the standpoint of environmental pollution control. Among all toxic heavy metals mercury, lead, chromium and cadmium are in the lime light due to their major impact on environment. Chromium (VI) is one of them and its permissible limit in drinking water is 0.05 mg/lit and when present above the permissible limit, it causes various types of acute and chronic disorders like vomiting, nausea, hemorrhage, acute diarrhea and abnormalities related to genetic cycle causing mutations [8-10]. Owing to the different toxicities of Cr(VI), there is a great interest in the speciation and determination of chromium species in environment [11-13]. Most of the methods suffer from drawbacks such as high operational costs, incomplete removal or disposal of the residual metal sludge. The eggshell in a powdered form is a potentially useful material for the removal of toxic metal from industrial wastewater. Powdered egg shell has a substantially larger capacity to remove the toxic metals by adsorption.

## MATERIALS AND METHODS

### Preparation of adsorbent egg shell

Adsorbent Egg Shell was collected from poultry farm nearby Tenali. Primarily Egg Shell was washed thoroughly with distilled water. Further it was treated with sodium hydroxide for about 5 hours and washed with distilled water for 2 to 3 times, later it was treated with sulphuric acid for about 4-5 hours and again washed with distilled water and dried at 60°C for 1 hour in oven. Then the adsorbent Egg Shell was crushed by using crusher and the crushed particles are screened to different sizes by using screen analysis. Finally, the obtained particles of Egg Shell were stored in air tight bottles until required.

### Preparation of Stock Solution

Stock solution of Chromium concentration 1000 mg/l was prepared by dissolving appropriate amount of  $K_2Cr_2O_7$  powder in 1 lit. of distilled water. The stock solution was then appropriately diluted to get the test solution of desired Chromium concentration varied between 20 to 100 mg/l.

**RESULTS AND DISCUSSION**

**Effect of contact time**

To study the effect of contact time 0.5 grams of 0.052mm size adsorbent is taken in 30 ml of aqueous solution of initial Chromium concentration 20 mg/l, at known pH 6.8, temperature of 30°C and the shaking was provided for 150 minutes. The experiment was repeated for different time intervals like 15, 30, 45, 60.....150 minutes at constant agitation speed 160 rpm. From the fig.1, observed that with increasing time the percentage adsorption increases, but initially the adsorption rate is high and with the increase in time the rate of adsorption decreases because active sites are initially high and as the time increases active sites of adsorbent decreases.

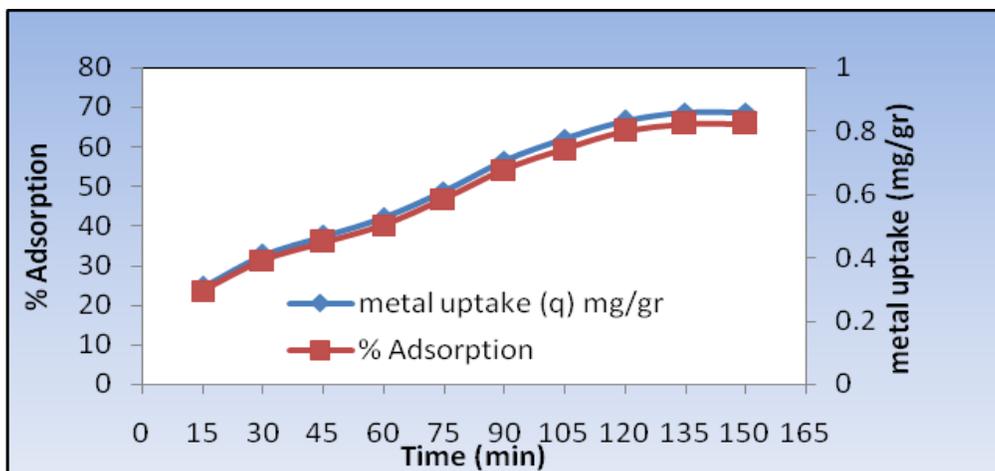


Figure 1: Effect of contact time

**Effect of Concentration**

It was observed from figure 2, the adsorption at various concentrations that present the percentage of the adsorption decreased with increases in initial chromium concentration, but the actual amount of chromium adsorbed per unit mass of adsorbent increased with increases in chromium concentration. This means that the adsorption is highly dependent on initial concentration of chromium.

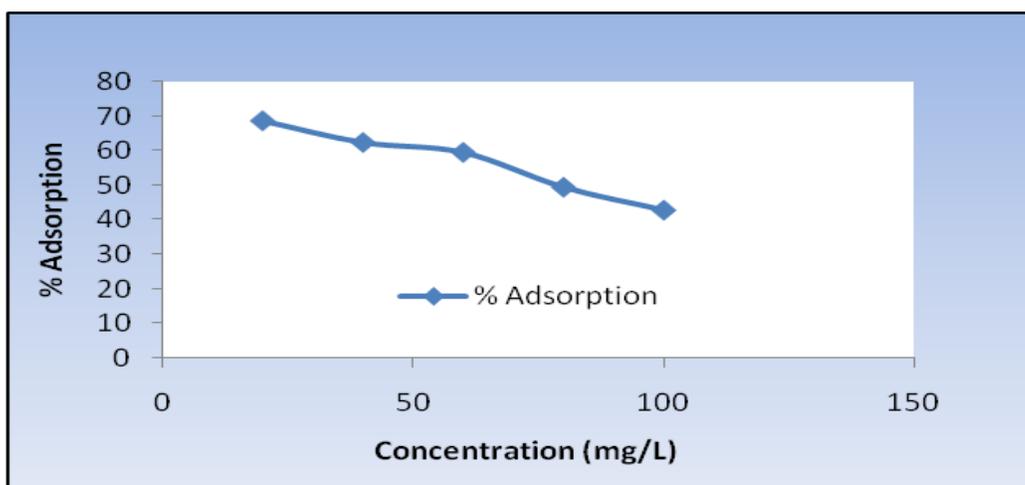


Figure 2: Effect of concentration

**Effect of Dosage**

From Fig.3, It was observed that the experimental results of adsorption at 20 mg/lit concentration that percentage of adsorption increased with increases in amount of adsorbent dosage. It means numbers of active sites are increases with increasing dosage.

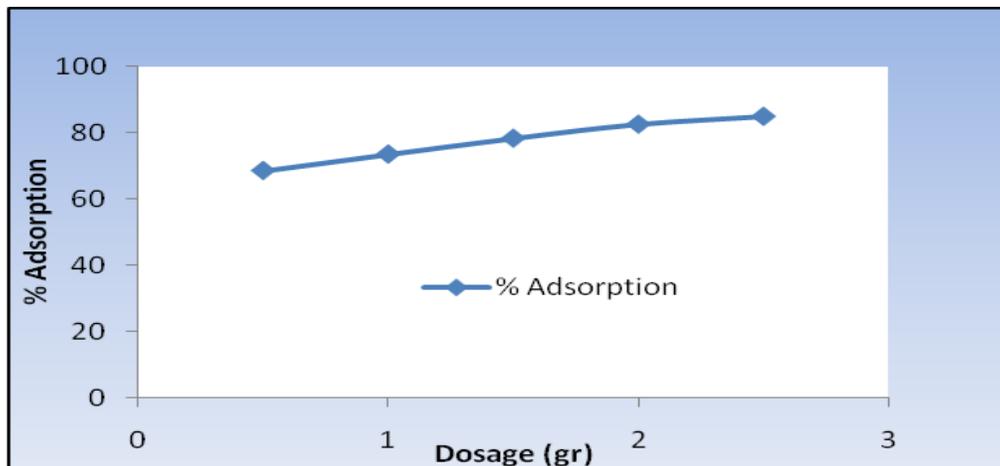


Figure 3: Effect of Dosage

**Effect of Particle size**

It was observed from Fig.4, the experimental results of adsorption at 20 mg/lit concentration that percent adsorption decreases with increases in adsorbent particle size. It means that the surface area decreases with increasing particle size.

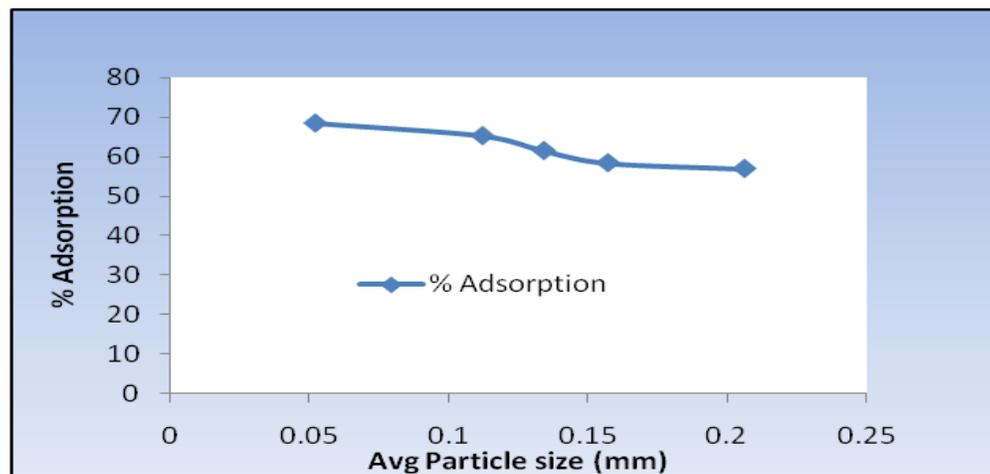


Figure 4: Effect of particle size

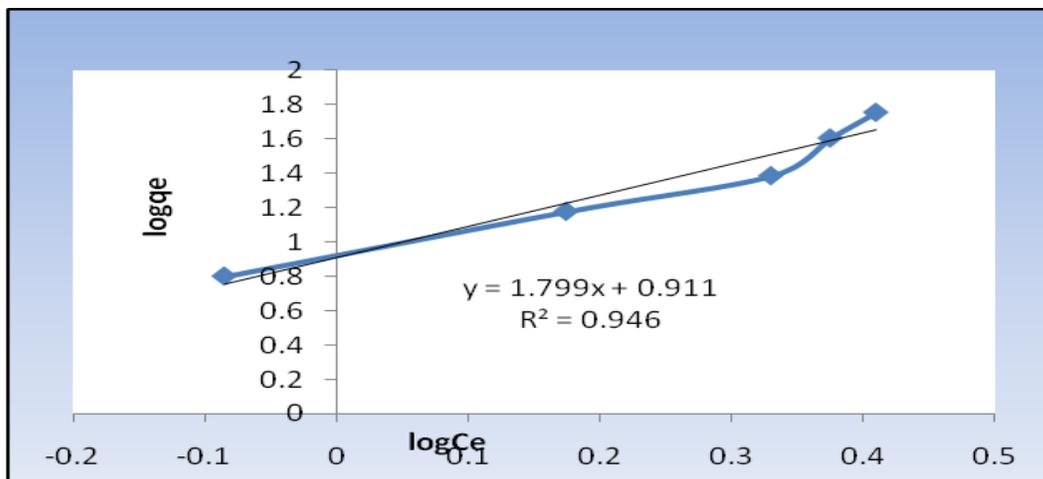


Figure 5: Freundlich Isotherm

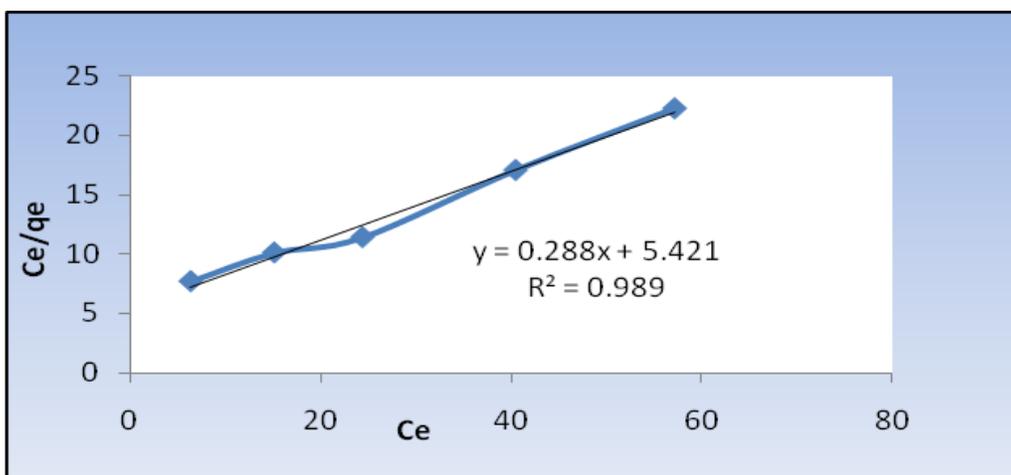


Figure 6: Langmuir Isotherm

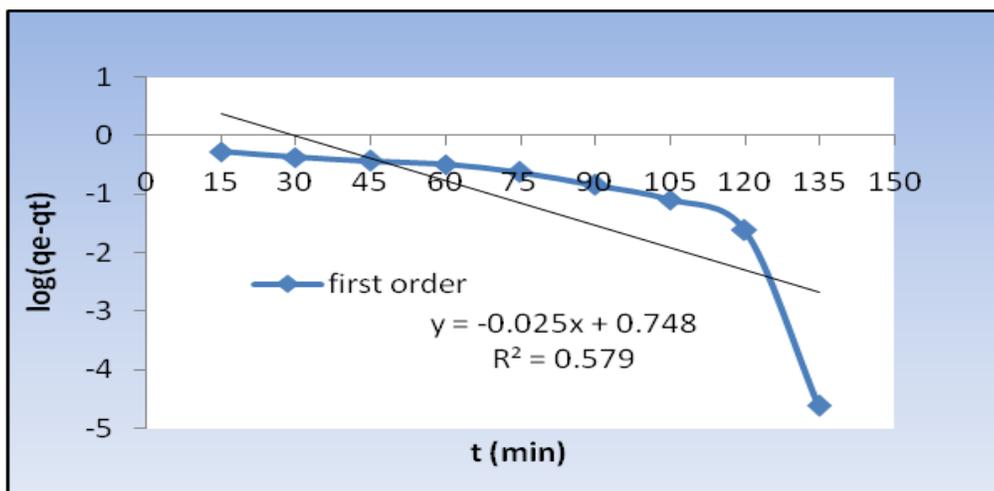


Figure 7: First order kinetics

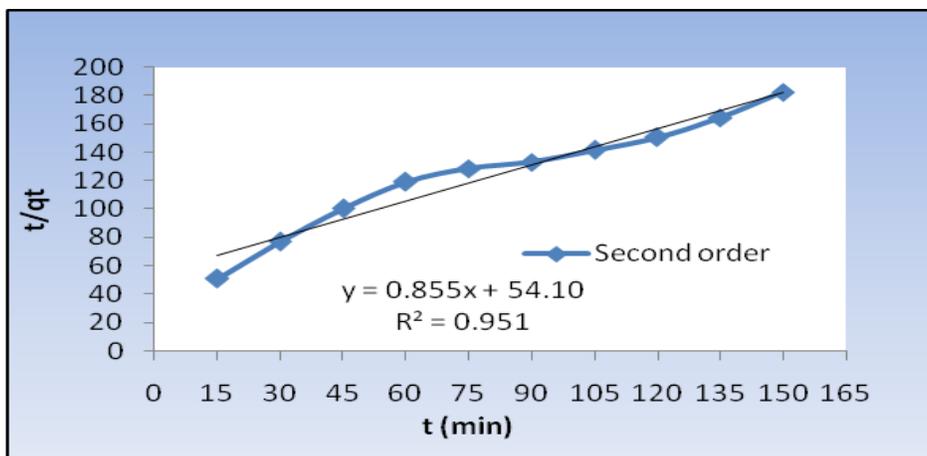


Figure 8: Second order kinetics

**Freundlich Isotherm**

Freundlich isotherm gives the relationship between equilibrium liquid and solid phase capacity based on the multilayer adsorption properties consisting of heterogeneous surface of the adsorbent. This isotherm is derived from the assumption that the adsorption sites are distributed exponentially with respect to the heat of adsorption. The linear form of Freundlich isotherm is

$$\text{Log}q_e = \text{Log}K_f + n\text{Log}C_e \text{ [15–16].....(i)}$$

where  $q_e$  is the amount adsorbed at equilibrium (mg/g),  $K_f, n$  are the Freundlich constants,  $1/n$  is the heterogeneity factor which is related to the capacity and intensity of the adsorption and  $C_e$  is the equilibrium concentration. The values of  $K_f$  and  $n$  can be obtained from the slope and intercept of the plot of  $\text{log}q_e$  against  $\text{log}C_e$ .

**Langmuir Isotherm**

Langmuir isotherms assume monolayer adsorption onto a surface containing finite number of adsorption sites of uniform strategies of adsorption with no transmigration of adsorbate in the plane of surface. The linear form of Langmuir isotherm equation is given as;

$$\frac{C_e}{q_e} = \frac{C_e}{q_0} + \frac{1}{q_0 b} \text{ [15–16].....(ii)}$$

Where  $q_0$  and  $b$  are Langmuir constants related to adsorption capacity and rate of adsorption respectively. A plot of  $(C_e/q_e)$  versus  $(C_e)$  for chromium adsorption onto egg shell is presented in the figure 6. The Langmuir constants  $b$  and  $q_0$  are obtained from the graph. The  $R^2$  value of 0.9985 indicated that the adsorption data of chromium onto egg shell best fitted the Langmuir isotherm model.

The constants of both Freundlich and Langmuir were specified in table 1.

Table 1: Isotherm constants

| Freundlich Isotherm |       |                | Langmuir Isotherm |                |                |
|---------------------|-------|----------------|-------------------|----------------|----------------|
| Kf                  | n     | R <sup>2</sup> | B                 | q <sub>0</sub> | R <sup>2</sup> |
| 0.2517              | 0.385 | 0.9646         | 0.2178            | 0.9208         | 0.9985         |

**KINETIC STUDIES**

The adsorption kinetic study is quite significant in wastewater treatment as it describes the solute uptake rate, which in turn controls the residence time of adsorbate uptake at the solid-solution interface. Dosage study is an important parameter because it determines the capacity of adsorbent for a given initial concentration of the chromium solution. In this present investigation, the kinetics of the adsorption systems were studied by plotting the amount of chromium adsorbed on the adsorbent with time for different adsorbent dosages at a constant initial concentration (20mg/l). This model represents the initial stages where rapid adsorption occurs, but cannot be applied for the entire adsorption process. Furthermore, the correlation coefficient  $R^2$  are relatively low for 1<sup>st</sup> order reaction so this cannot be applied to the process. The  $R^2$  value obtained in 2<sup>nd</sup> order reaction is higher than 1<sup>st</sup> order reaction so the adsorption of chromium onto adsorbent can be applied in second order reaction. The rate constants of both first order and second order were specified in table.2. [17-18]

**Table 2: Kinetic study constants**

| Concentration ppm | First Order |          |        | Second Order |          |       |
|-------------------|-------------|----------|--------|--------------|----------|-------|
|                   | $K_1$       | $q_e$    | $R^2$  | $K_2$        | $q_e$    | $R^2$ |
| 10                | 0.036848    | 1.083927 | 0.6497 | 0.725163     | 0.011199 | 0.974 |

**CONCLUSIONS**

The observed results were analytically discussed on the study of removal of chromium from the aqueous solution of  $K_2Cr_2O_7$  using egg shell adsorbent.

- Adsorption of chromium on to egg shell powder showed that a contact time of 135 minutes was sufficient to achieve equilibrium.
- Adsorption of chromium decreases with increase in the initial concentration of chromium.
- Adsorption of chromium decreases with increasing particle size of egg shell powder.
- The amount of adsorbate adsorbed increases with the increasing the adsorbent dose.
- The experimental data gave good fit with Langmuir isotherm & the adsorption coefficient agreed well with condition of favorable adsorption.
- The 2<sup>nd</sup> order rate equation is best fitted with the adsorption process compared to 1<sup>st</sup> order rate equation.

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