International Research Journal of Multidisciplinary Science & Technology
www.irjmrs.com ISSN: 2455-930X

KINETIC MODEL STUDIES ON REMOVAL OF HEXAVALENT CHROMIUM – SUGARCANE BAGASSE POWDER

D. Sivakumar[1], D. Shankar[2], R. Mahalakshmi [3], K. Deepalakshmi [4]

[1, 3 & 4] Department of Civil Engineering, Vel Tech High Tech Dr.RangarajanDr.Sakunthala Engineering College Avadi 600 062,Chennai, Tamil Nadu, India

[2]Department of Pharmaceutical Chemistry, K.M. College of Pharmacy, Uthangudi 625 107, Madurai, Tamil Nadu, India

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ABSTRACT—*In the present study, chromium (VI) was re from tannery industry wastewater using the method called adsorption methods. The experimental investigations have been carried out by using sugarcane bagasse powder as adsorbent for different dosages, different temperatures and different agitation speeds against different pH. The experimental results were validated with the treatment efficiency on other parameters. In this study, maximum removal of chromium (VI) from tannery industrial wastewater was found to be 86.9 %. In order to validate the experimental data, verification test was conducted on removal other parameters available in tannery industry wastewater against the same optimum process parameters value. From the validation test, it was found that the maximum removal was occurred at the identified optimum process parameters value. In order to investigate the consistency, experimental data were fitted with pseudo-first order and pseudo-second order. Based on the kinetic model studies, the equilibrium experimental data fitted well with pseudo-second order kinetic model than pseudo-first order kinetic model for elucidating the mechanism of Cr(VI) removal by sugarcane bagasse powder in a tannery industry wastewater.*

Keywords—Tanneryindustrywastewater, Sugarcanebagasse, Chromium (VI), Process parameter

1. INTRODUCTION

Chromium is one of the heavy metals used by modern industries like plastic, pigment, wood preservative, electroplating, leather tanning, cement, mining, dyeing and fertilizer. The wastewater from these industries contains both Cr(III) and Cr(VI). Among them, Cr(VI) is highly toxic, which is carcinogenic that cause lung cancer, as well as kidney, liver and skin damage in human beings and Cr(III) is an essential micronutrient in trace amounts necessary for carbohydrate, lipid and protein metabolism. In addition to chromium, wastewater generated from these industries contains much higher concentrations of properties like total dissolved solids, suspended solids, phenols, chlorides, ammonia, and other heavy metals. The discharged wastewater is generally contaminated the surface water and groundwater, results increased water pollution [6]. As per WHO, 1996 [24], the maximum permissible limit of chromium content in drinking water is 0.05 mg/L. In recent years, increasing awareness of water pollution and its far reaching effects has prompted concerted efforts towards pollution abatement.

There are several processes that can be adopted for the treatment of tannery wastewater such as such as reduction followed by chemical precipitation, sedimentation, electrochemical processes [9,12], ion exchange, biological operations, bioremediation [7,8,10,17,18,22], biosorption [4,13,23], cementation, coagulation / flocculation [17], filtration and membrane processes, and solvent extraction.

But due to certain limitations the above mentioned methods are less effective in producing results. So, therefore an alternative method was pursued to treat the effluent coming from the tannery industry. The process is known as adsorption and it has gained a lot of attention in the recent past [2,3,5]. The adsorbent prepared from biomaterial has large surface area and micro porous character nature have made them potential adsorbents for the removal of heavy metals from industrial waste water [11,14-16,19-21].

This study mainly focused on removal of Cr(VI) rather than Cr(III) from tannery industry wastewater using *sugarcane bagasse* powder. In order to investigate the consistency, experimental data obtained in this study were validated with the removal of other parameters in a tannery industry wastewater against the identified optimum process parameters value and experimental data obtained in this study were fitted with pseudo-first order and pseudo-second order.

2. MATERIALS AND METHODS

2.1 Adsorbent Preparation

The sugarcane bagasse powder was selected as adsorbent for the method. The raw sugarcane bagasse was collected and washed with water initially to remove particulate material from their surface. After that, they were dried in sun drying method for a period of 2 days and dried in an oven at 50 ^{o}C for a period of 60 min. The dried materials were ground using a mixer. The grounded sugarcane bagasse (powder) were then

sieved through sieves to get uniform geometrical size of 1 mm size.

$$\frac{(C_1-C_2)}{C_1} \times 100$$

2.2 Collection of Wastewater Sample

For the present study, the wastewater samples were collected from tannery industrial estate of Pallavaram ('originally PallavaPuram), which is a town and a second-grade municipality located in the suburbs of Chennai. It forms a part of the TambaramTaluk of Kanchipuram District and is located 17 kilometres from Chennai city. Pallavaram is known for its cantonment and bustling residential colonies. The latitude and longitude are 12 58' 34'' and 80 11' 01'' respectively. The samples were collected with the help of air tight sterilized bottles, took to the laboratory and then they were stored for analyzing Cr(VI).

2.3 Experiment al Arrangement

The primary focus of the present study is to reduce the Cr(VI) concentrations in a tannery industrial wastewater using *sugarcane bagasse* powder as an adsorbent with different dosages, different agitation speeds, different temperatures against different pH.This method consists of batch experiments involving variations in dosages of 20, 40, 60, and 80 g, variations in temperature such as 30, 40, 50 and 60 ^{o}C, varying speeds of 25, 50, 75 and 100 rpm. Tannery industry wastewater was taken in 4 glass beakers of 250 ml capacity and was kept on the magnetic stirrer apparatus for different dosages, different temperatures and different agitations speeds against the different pH. The initial concentration of Cr(VI) in tannery industrial wastewater was found to be 480 mg/l, which was found using UV Spectrophotometer [1].

The treated samples were filtered and the settled particles were removed. After treating by adsorption processes, clear samples after settlement (24 hours) were further tested by a digital spectrophotometer to find out the reduction in concentrations of chromium in the wastewater. The adsorption removal percentage of Cr(VI) in a tannery industry wastewater by *sugarcane bagasse* powder was calculated by using the following formula:

Percentage Removal = (1)

in which C1 is the concentration of Cr(VI) in mg/l before treatment with *sugarcane bagasse* powder and C2 is the concentration of Cr(VI) in mg/l after treatment with *sugarcane bagasse* powder.

2.4 Kinetic Models

Many kinetic models propose to elucidate the mechanism of solute adsorption and potential rate controllingstep. The experimental data obtained from batch studies were fittedto the pseudo first order and pseudo second order models for determining the suitability of*sugarcane bagasse* powder for removing Cr(VI) in mg/l in a tannery industry wastewater.

The pseudo-first order equation of Lagergren is generally

$$\frac{t}{q_t} - \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad -\frac{k_1}{2.303} t$$

expressed a

in which, qt is the sorption capacity at equilibrium (mg/g), qt is the sorption capacity at time 't' (mg/g), k1 is the first-order rate constant (min^{-1}) and 't' is time (min). Hence, a linear trace is expected between the two parameters, log(qe-qt) and 't', provided the adsorption follows first order kinetics. The values of k1 and qe can be determined the slope and intercept.

The pseudo-second order kinetic rate equation is expressed as

$$\frac{t}{q_t} - \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$

in which, k2 is second order rate constant (mg g^{-1} min^{-1}). A plot of t = qtand 't' should give a liner relationship if the adsorption follows second order. qe and k2can be calculated from the slope and intercept of theplot.

3.RESULTS AND DISCUSSIONS

In the present study, Cr(VI) in the tannery industrial wastewater was reduced using the method called adsorption methods. The selected process parameters are different dosages, different temperatures and different agitation speeds, but conducted against different pH. The results are presented below.

3.1 Effect of Temperature

The Fig. 1 shows the effect of temperature on adsorbent variation in tannery industry wastewater at a temperature 30, 40, 50 and 60 ^{o}C for the adsorbent dosage 20 g, the agitation speed of 50 rpm against the pH of 3, 4, 5, 6 and 7 respectively.

From Fig. 1, it may be observed that the percentage removal of chromium for the adsorption method with a temperature 30, 40, 50 and 60 ^{o}C was found to be 41.6, 59.6, 71.6 and 64.3 % against the pH 3 respectively. Similarly, the percentage removal of chromium was found to be 43.2, 61.3, 76.8 and 69.6 % respectively for the temperature of 30, 40, 50 and 60 ^{o}C against the pH 4. The percentage removal of chromium was found to be 38.2, 55.2, 67.8 and 60.8 % respectively for the temperature of 30, 40, 50 and 60 ^{o}C against the pH 5.

Further, the percentage removal of chromium was found to be 35.0, 51.3, 65.8 and 57.5 % respectively for the temperature of 30, 40, 50 and 60 ^{o}C against the pH 6. The percentage removal of chromium was found to be 32.0, 47.5, 63.4 and 53.5 % respectively for the temperature of 30, 40, 50 and 60 ^{o}C

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www.irjmrs.com ISSN: 2455-930X

against the pH 7.

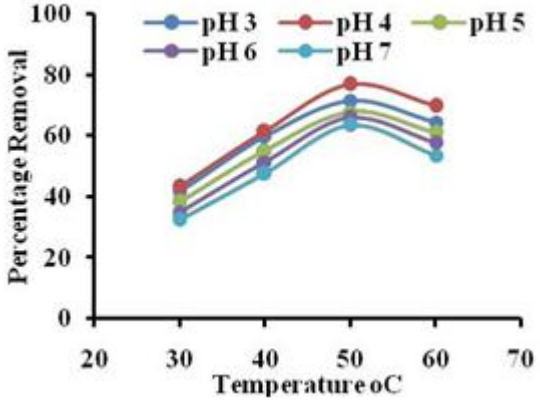

Fig. 1 The effect of temperature on Cr(VI) removal in a tannery industry wastewater using *sugarcane bagasse* for different pH against agitation speed of 50 rpm and adsorbent dosage 20 g

In addition, from Fig. 1, it was found that the maximum adsorption percentage amount of Cr(VI) in tannery industrial wastewater is 78.2 % by adsorption method for the temperature of 50 °C, which was also observed at a pH of 4.

3.2 Effect of Agitation Speed

The Fig. 2 shows the effect of agitation speed in a tannery industry wastewater. The selected agitation speeds are 25, 50, 75 and 100 rpm, against the adsorbent dosage 20 gand optimum temperature of 50 °Cand for the different pH of 3, 4, 5, 6 and 7 respectively.

From Fig. 2, it may be observed that the percentage removal of chromium by the *sugarcane bagasse* powder with an agitation speed of 25, 50, 75 and 100 rpm was found to be 43.5, 62.3, 74.8 and 65.1 % against the pH 3 respectively. Similarly, the percentage removal of chromium was found to be 44.1, 63.3, 82.6 and 72.6 % respectively for an agitation speed of 25, 50, 75 and 100 rpm against the pH 4. The percentage removal of chromium was found to be 40.2, 58.2, 69.8 and 62.8 % respectively for an agitation speed of 25, 50, 75 and 100 rpm against the pH 5.

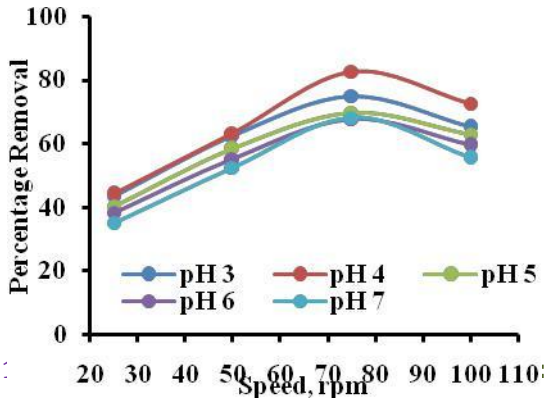

Fig. 2The effect of agitation speed on Cr(VI) removal in a tannery industry wastewater using *sugarcane bagasse* for different pH against optimum temperature of 50 °C and adsorbent dosage 20 g

Further, the percentage removal of chromium was found to be 38.2, 55.2, 67.8 and 59.5 % respectively for an agitation speed of 25, 50, 75 and 100 rpm against the pH 6. The percentage removal of chromium was found to be 35.0, 52.5, 68.2 and 55.5 % respectively for an agitation speed of 25, 50, 75 and 100 rpm against the pH 7.

In addition, from Fig. 2, it was found that the maximum adsorption percentage amount of Cr(VI) in a tannery industrial wastewater is 83.8 % by adsorption method for the agitation speed of 75 rpm, which was also observed at a pH of 4. Thus, the optimum agitation speed found in this study is 75 rpm.

3.3 Effect of Adsorbent Dosage

The Fig. 3 shows the effect of adsorption dosage in a tannery industry wastewater. The selected adsorbent dosage are 20, 40, 60 and 80 g, against the optimum temperature of 50 °C and optimum agitation speed of 75 rpm and for the different pH of 3, 4, 5, 6 and 7 respectively.

From Fig. 3, it may be observed that the percentage removal of chromium by the *sugarcane bagasse* powder with adsorbent dosage of 20, 40, 60 and 80 g was found to be 45.9, 66.2, 77.3 and 68.9 % against the pH 3 respectively. Similarly, the percentage removal of chromium was found to be 48.1, 69.8, 86.9 and 74.1 % respectively for the adsorbent dosage of 20, 40, 60 and 80 g against the pH 4. The percentage removal of chromium was found to be 43.2, 62.3, 74.3 and64.2 % respectively for the adsorbent dosage of 20 40, 60 and 80 g against the pH 5.

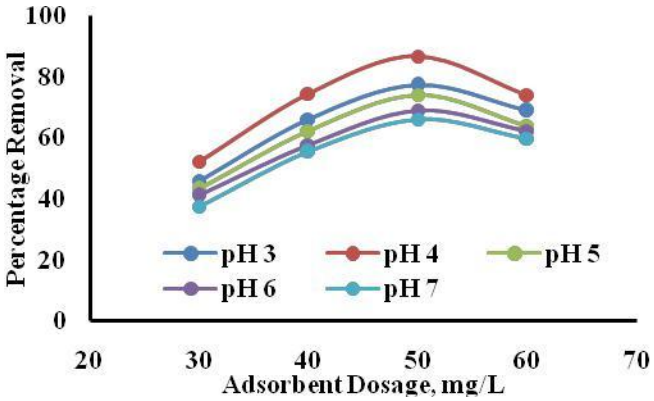

Fig. 3The effect of Adsorbent Dosage on Cr(VI) removal in a tannery industry wastewater using *sugarcane bagasse* for

different pH against optimum temperature of 50 °C and agitation speed of 75 rpm

Further, the percentage removal of chromium was found to be 41.2, 57.8, 69.1 and 62.4 % respectively for the adsorbent dosage of 20, 40, 60 and 80 g against the pH 6. The percentage removal of chromium was found to be 37.6, 55.5, 66.3 and 58.9 % respectively for the adsorbent dosage of 20, 40, 60 and 80 g against the pH 7.

In addition, from Fig. 3, it was found that the maximum adsorption percentage amount of Cr(VI) in a tannery industrial wastewater is 86.4 % by adsorption method for the adsorbent dosage of 60 g, which was also observed at a pH of 4. Thus, the optimum adsorbent dosage found in this study is 60 g.

3.4 Validation Test

In order to verify the experiments conducted for the removal of Cr(VI) in a tannery industry wastewater, a separate experiments were conducted for removing various other parameters present in the tannery industry wastewater at an optimum temperature of 50 °C, optimum agitation speed of 75 rpm, optimum adsorbent dosage of 60 g and optimum pH of 4. The results of the verification test are presented in the Fig. 4.

From the Fig. 4, it may be observed that the maximum removal of BOD, TDS, EC, COD is obtained at the same optimum temperature, optimum adsorbent dosage, optimum agitation speed and optimum pH. Thus, this study proved that the *sugarcane bagasse* powder is effectively used for removal of Cr(VI) present in the tannery industry wastewater, in addition toother parameters also.

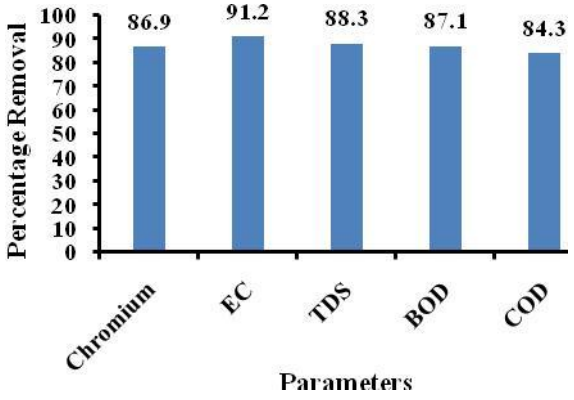

Fig. 4 Maximum Removal Percentage for Various Parameters in the Tannery Industry Wastewater at Optimum Temperature, Adsorbent Dosage, Agitation Speed and pH.

3.5 Kinetic Models Fit

From Fig. 5, it can be observed that adsorption of Cr(VI) by *sugarcane bagasse* powder occurred very rapidly within the first 30 min and equilibrium occurred after 90 min. It may also be found from the maximum removal of Cr(VI) occurred for the concentration of 30 mg L^{-1}(4^{th} dilution ratio) by *sugarcane bagasse* powder. Thus, an optimum concentration for which the maximum removal of Cr(VI) was found to be 86.9 % in 30 mg L^{-1} concentration.

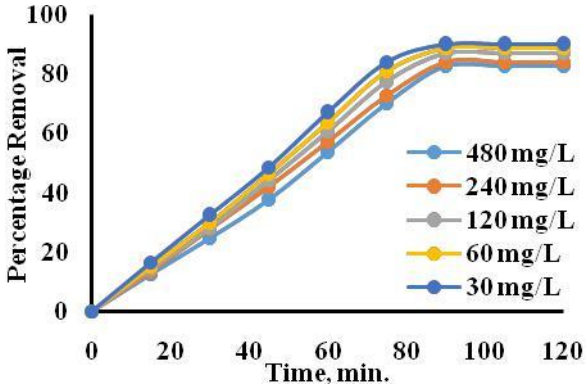

Fig. 5 The equilibrium study conducted at different concentration against Cr(VI) removal in a tannery industry wastewater using *sugarcane bagasse* for the optimum adsorbent dosage 60 g, optimum temperature of 50 °C, optimum pH of 4 and optimum agitation speed of 75 rpm

In order to investigate the consistency, experimental data were fitted with pseudo-first order and pseudo-second order. The plots of the two kinetic equations for removing Cr(VI) by *sugarcane bagasse* powder at various initial concentrations are shown in Figs. 6 and 7.

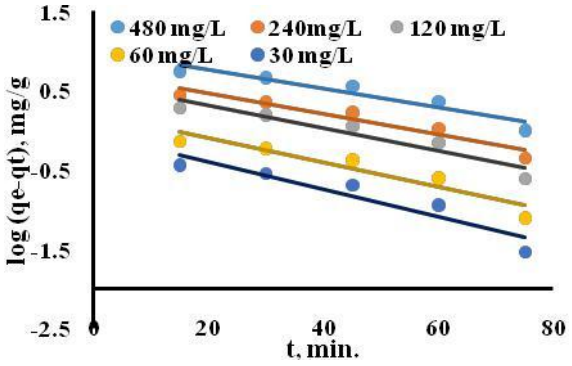

Fig. 6 Pseudo First order kinetic model

From Fig. 6, it may be found that the pseudo first-order rate constant k1 for removing Cr(VI) by *sugarcane bagasse* powder ranges between 0.029 and 0.041 min^{-1}. The correlation coefficient R^2 found to range from 0.845 to 0.946.

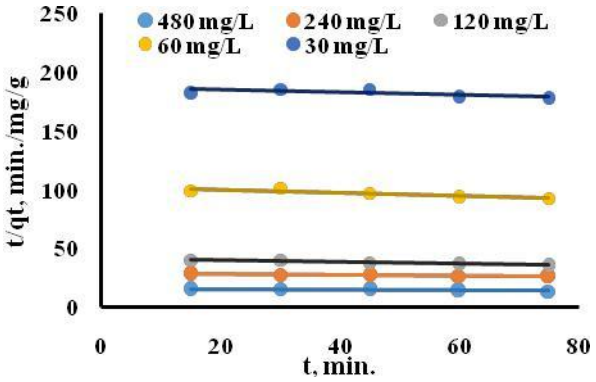

Fig. 7 Pseudo Second order kinetic model It was found that the values for rate constant (k2) of pseudo-second order kinetic model for removing Cr(VI) by *sugarcane bagasse* powder ranges from 0.000064 to0.00056 kg $mg^{-1}min^{-1}$(Fig. 7). The correlation coefficient R^2 found to range from 0.899 to 0.994.

Results from Figs. 6 and 7, indicated that equilibrium experimental data fitted well with pseudo-second order kinetic model than pseudo-first order kinetic model. Thus, the study informed that pseudo-second order kinetic model was used to elucidate the mechanism of Cr(VI) removal by *sugarcane bagasse* powder in a tannery industrywastewater.

4. CONCLUSIONS

In the present study, experiments have been conducted for removal of Cr(VI) in tannery industrial wastewater using *sugarcane bagasse* powder as an adsorbent. The ability of *sugarcane bagasse* powder as an adsorbent for removing Cr(VI) in the tannery industrial wastewater, the experiments were conducted with varying adsorbent dosages, temperatures and agitation speeds against different pH. The results showed that the maximum percentage removal of Cr(VI) in the tannery industrial wastewater at the temperature, agitation speed and adsorbent dosage of 50 ^{o}C, 75 rpm and 60 g respectively and the maximum percentage removal of Cr(VI) in the tannery industrial wastewater is 86.9 % at a pH of 4. The experimental investigation was verified and the results of the verification tests also showed that the maximum removal of other parameters in a tannery industry wastewater was also occurred at the same optimum adsorbent dosage, temperature, agitation speed and pH values. Checked the consistency of experimental data obtained in this study with pseudo-first order and pseudo-second order. Based on the kinetic model studies, the equilibrium experimental data fitted well with pseudo-second order kinetic model than pseudo-first order kinetic model for elucidating the mechanism of Cr(VI) removal by *sugarcane bagasse* powder in a tannery industrywastewater. Thus, the *sugarcane bagasse* powder as adsorbent was used effectively for removing Cr(VI) in the tannery industrial wastewater.

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