



Adsorption Dynamics of Chromium (VI) Ions onto Activated Carbon Prepared using Microwave from Silk Cotton Fruit Walls (*Ceiba pentandra*L.)

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Abstract

Heavy metal ion pollution due to the presence of Chromium (VI) in the environment has become a serious concern because of rapid industrialization. The acute toxicity of chromium to aquatic life, human and the stringent effluent standard to be met by industries as specified by regulatory organizations has necessitated the development of innovative, effective and economical methods for treating Chromium bearing wastewater. Present investigation is the evaluation of adsorption capability of activated carbon prepared from fruit walls of Silk Cotton (*Ceiba pentandra*L.) using Chromium (VI) ion as model adsorbate. ZnCl₂ is used as activating agent and micro wave heating is adopted to prepare the activated carbon. Batch mode adsorption experiments were carried out to assess the effects of the system variables such as contact time, adsorbent dosage, pH and initial metal ion concentration. Experimental data obtained were fitted with linearised forms of Lagergren, Ho and Webber Morris pseudo first order, pseudo second order and intra particle diffusion kinetic models respectively. The statistical tool Sum of Squared Error (SSE) inferred that for second order kinetic model was more suitable to describe the above adsorption. The intra particle diffusion is found to be the rate determining step.

Keywords: Activated carbon; Adsorption; *Ceiba pentandra*L.; Cr (VI) ions; Kinetics; Microwave; Zinc chloride.

1. INTRODUCTION

The discharge of metal ions in industrial effluents is of great concern because their presence and accumulation have a toxic or carcinogenic effect on living species (Ko *et al.* 2000). Especially Chromium compounds are widely used in chemical manufacture, leather, textile and other industries. Chromium ions exist in two common oxidation states, Chromium (III) and Chromium (VI). The former is an essential metal while the latter is toxic. So removal of Chromium (VI) is an important one. Common treatment technologies used in the removal of heavy metals from waste effluents are electro deposition, ion exchange, chemical precipitation, reverse osmosis, membrane separation and adsorption (Popuri *et al.* 2009). Except adsorption, other methods do not seem to be economically feasible for such industries because of their relative high costs (Quek *et al.* 1998). Adsorption is found to be cheap, effective and easy to adopt (Zhang *et al.* 2011; Shah *et al.* 2012). Many types of adsorbents have been used for the removal of Cr(VI), including: biomass, such as *Mucorhiemalis* (Shroff and Vaidya, 2011), *Schizosaccharomyces pombe* (Durmaz-Sam *et al.* 2011), chitosan (Repo *et al.* 2010), rice husk

(Bansal *et al.* 2009), red pine sawdust (Gode *et al.* 2008), almond green hull (Ahmadpour *et al.* 2009), *Sargassum wightii* (Vijayaraghavan *et al.* 2006) and activated carbon (Anupam *et al.* 2011). Activated carbon is a form of carbon that has been processed to make it extremely porous and thus to have a very large surface area available for adsorption or chemical reactions.

Present study is undertaken to evaluate the efficiency of activated carbon prepared from fruit walls of Silk cotton (*Ceiba pentandra*L.) by microwave assisted method. Investigations have been carried-out to evaluate the adsorption of Cr (VI) ions onto the prepared carbon.

2. MATERIALS & METHODS

2.1 Preparation of adsorbent through microwave method

50 g of the fruit wall powder was soaked with 60 % ZnCl₂ solution. The slurry was allowed to stand as such at ordinary conditions of temperature and pressure for a day to ensure the access of the ZnCl₂ into the material. Then

the slurry was subjected to microwave heating for 10 min with the power of 600 watts. Thus the carbonized samples were washed with 0.5 M HCl followed with hot distilled water and cold distilled water until the pH of the washings reach 7. Then the carbon was filtered and dried at 378 K. Thus obtained carbon from the fruit walls of silk cotton was designated as Microwave assisted Zinc chloride Activated Silk cotton Carbon (MWZASC). The carbon was ground well and the particle size ranging from 53 to 105 μm was taken for further study.

2.2 Preparation of stock Solution

1000 mg/L Cr(VI) stock solution was prepared by dissolving 2.828 g of Potassium dichromate (AR grade) in 1000 mL of double distilled water. The experimental solutions were prepared by proper dilution.

2.3 Adsorption experiments

The effect of parameters such as initial concentration Cr (VI), adsorbent dose and contact time was studied by batch mode technique because of its simplicity. Pre-determined dose of the adsorbent was taken in 250 mL iodine flask and 50 mL and pre-determined concentration of the Chromium solution was poured into the flask and the desired pH of the solution was brought by adding Con. HCl or 01 N NaOH solution. The content of the flask was agitated using rotary shaker with 130 rpm for pre-determined duration. Then the adsorbents were then separated by centrifugation and concentration of the centrifugate was determined spectro photometrically by diphenyl carbozide method. The percentage removal of the Cr (VI) from the solution and the quantity adsorbed by the adsorbent were calculated by the following equations.

$$\% \text{ Removal} = (C_0 - C_f) 100 / C_0 \quad (1)$$

where C_0 and C_f are the initial and final concentrations (mg/L) of the solutions respectively.

$$\text{Quantity adsorbed per gram } q_t(\text{mg/g}) = (C_0 - C_t) V / M \quad (2)$$

Where C_0 and C_t were the metal ion concentration (mg/L) at initial and at time 't' respectively, V was the volume of solution (mL) and M was the mass of the adsorbent (g).

2.3.1 Diphenyl carbozide method

0.25% (W/V) solution of diphenyl carbozide was prepared in 50% (V/V) acetone. 1 mL of the sample solution was pipette out into 25 mL standard flasks. To this 1 mL of 6 N H_2SO_4 was added followed by 1 mL of diphenyl carbozide and the total volume was made up to 25 mL using double distilled water. Concentration of Cr(VI) was estimated by the intensity of the reddish brown color developed due to complex formation using Systronics Double Beam UV-visible Spectrophotometer: 2202 at the wave length of 540 nm (Ramesh *et al.* 2014).

3. RESULT & DISCUSSION

3.1 Effect of pH

The effect of pH was studied by shaking 20 mg/50 mL of adsorbent with 20 mg/L chromium (VI) ion solution for 2 hrs for the initial pH values between 2 and 10. The results were shown in Fig. 1.

The adsorption capacities of Chromium (VI) ions onto MWZASC decreased significantly with the increase of pH value and the maximum removal was attained at pH 2.0. The reason for the high percent of removal of Cr (VI) at lower pH range was explained as below. The Cr (VI) exists in different forms such as HCrO_4^- , $\text{Cr}_2\text{O}_7^{2-}$ and CrO_4^{2-} ions in aqueous solution and the stability of these forms is dependent on pH of the system. The active form of Cr (VI) ion adsorbed is HCrO_4^- ions. This form is stable only at lower pH which leads to high removal of chromium (Ramesh *et al.* 2014). Hence further experiments were carried out at pH 2.

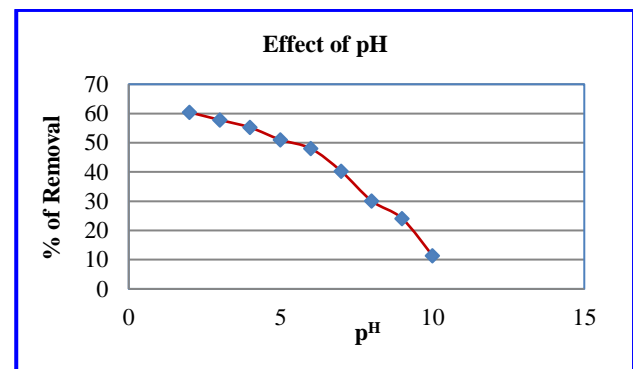


Fig. 1: [Cr(VI)]:20 mg/L Dose:25 mg/L Time:2 hrs Temp:305 K

3.2 Effect of dosage

The adsorption of Cr (VI) onto MWZASC was studied by varying the dose of the adsorbent from 5 mg/50 mL to 50 mg/50 mL by taking 20 mg/L of Cr (VI) ion solution. Contact period was maintained for 2 hrs. The percentage of removal of adsorbate from aqueous solution increased with an increase of carbon dose which is shown in the Fig. 2. This is due to the increased carbon surface area and the availability of more adsorption sites (Priya and Santhi, 2014). Based on these results, the remaining parts of the experiments were carried out with the adsorbent dose of 20 mg/ 50 mL of Chromium (VI) ion solution.

3.3 Effect of contact time and initial concentration

The effect of contact time on the percentage removal of Cr (VI) ion from aqueous solution was studied by taking 12 mg/L, 16 mg/L, 20 mg/L and 24 mg/L solutions as initial concentrations which is shown in Fig. 2. Majority of adsorption found to occur within 20 minutes. The rate of percentage removal was found to decrease afterwards and attained equilibrium around 50 min.

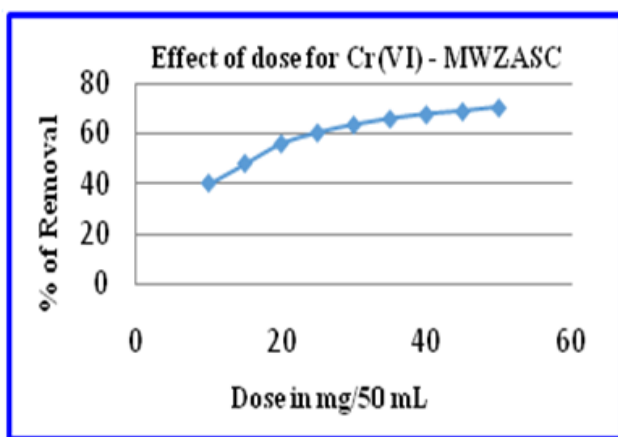


Fig. 2: [Cr (VI)]:20 mg/L pH: 2 Time: 2 hrs Temp: 305 K

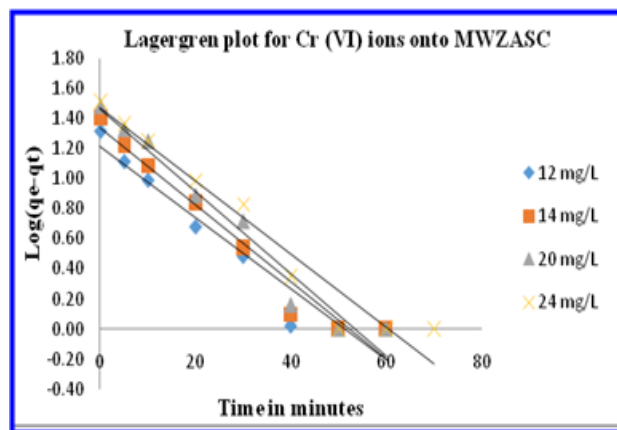


Fig. 4: Lagergren plot for Cr(VI) ions onto MWZASC

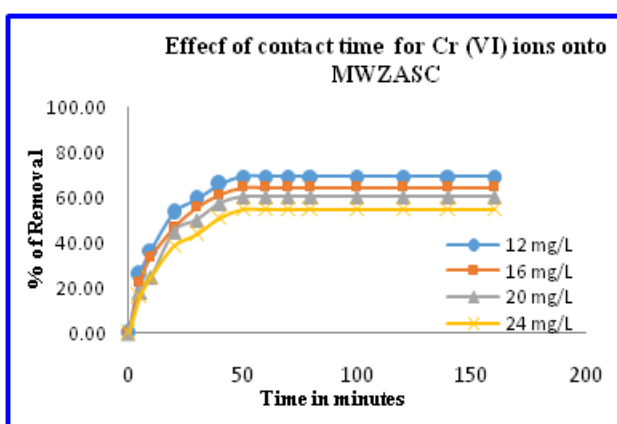


Fig. 3: Dose: 25 mg/L pH: 2 Temp: 305 K

The Lagergren model and Ho model were used in describing the adsorption kinetics of Cr (VI) ion onto MWZAS are shown in Fig. 4 and Fig. 5 respectively and values of concerned parameters are given in Table 1 and Table 2.

Table 1. First order kinetics parameters

Conc. (mg/L)	k_1 (min^{-1})	$q_e(\text{exp})$ (mg/g)	$q_e(\text{pr})$ (mg/g)	SSE	R^2
12	0.0556	20.80	16.21	1.77	0.9405
16	0.0592	25.75	21.87		0.9582
20	0.0631	30.20	28.84		0.9639
24	0.0560	33.00	29.51		0.9515

3.4 Kinetic models

3.4.1 Pseudo First order kinetic model

Lagergren (1898) developed the linearised form of Pseudo first order kinetic model equation which is given below

$$\text{Log}(q_e - q_t) = \text{log } q_e - k_1 / 2.303 \times t$$

Where, q_e and q_t are the quantity of metal ion adsorbed (mg/g) at equilibrium and at time t (min), respectively. k_1 is the pseudo first order rate constant of adsorption. The values of k_1 and predicted equilibrium adsorption capacity $q_{e(\text{pr})}$ were calculated from the slope and intercepts of the linear plots respectively.

3.4.2 Pseudo Second order kinetic model

HO *et al.* (1996) developed the linearised form of pseudo second order reaction rate equation which is given below

$$t/q_t = 1/k_2 \cdot q_e^2 + 1/q_e t$$

The predicted equilibrium adsorption capacity ($q_{e(\text{pr})}$) and the pseudo second order constants k_2 ($\text{g} / (\text{mg} \cdot \text{min})$) can be determined from the slope and intercept of plot of t/q_t versus t .

Table 2. Second order kinetics parameters

Conc. (mg/L)	K_2 ($\text{g}/(\text{mg} \cdot \text{min})$)	$q_e(\text{exp})$ (mg/g)	$q_e(\text{pr})$ (mg/g)	SSE (%)	R^2
12	0.0140	20.80	21.98	1.03	0.9978
16	0.0106	25.75	27.32		0.9973
20	0.0104	30.20	32.57		0.9946
24	0.0097	33.00	35.71		0.9955

3.4.3 Test for kinetics models

The Sum of Squared Error (SSE) is statistical tool which has been used in literature to test the validity of kinetic models. The sum of squared error is given as follows;

$$\text{SSE} = \frac{\sum [(q_e)_{\text{exp}} - (q_e)_{\text{pr}}]^2}{N}$$

Where N is the number of data points.

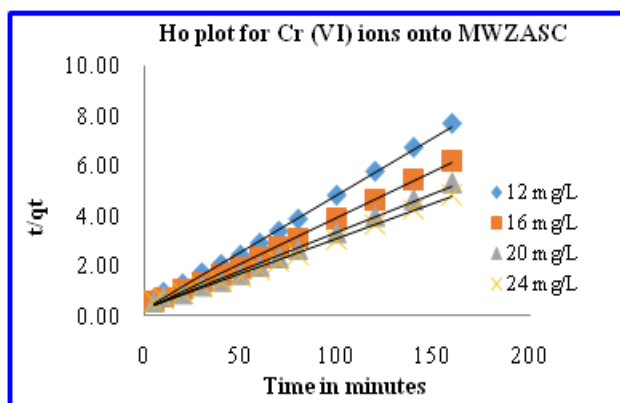


Fig. 5: Ho plot for Cr(VI) ions onto MWZASC

Experimental $q_{e(exp)}$, predicted $q_{e(pr)}$ and SSE for the pseudo first order and pseudo second order kinetics are given in Table-1 and 2. It shows that $q_{e(exp)}$ is close to $q_{e(pr)}$ obtained from pseudo second order kinetics. It can be seen that SSE (%) value is lower for the pseudo second order kinetic model than that of pseudo first order kinetic model. This confirms the applicability of the pseudo second order kinetic model. The determination regression coefficient (R^2) for pseudo first order model ranged between 0.9405 and 0.9639, whereas these values for the pseudo second order model were ranged between 0.9946 and 0.9978. It indicates that the experimental data best fitted into pseudo second order model.

3.4.4 Intra particle diffusion

Intra particle diffusion equation is given by Weber–Morris (Weber and Morris, 1963) which is given below:

$$q_t = k_p t^{1/2} + C$$

Where k_p is the intra-particle diffusion rate constant. Plot of q_t versus $t^{1/2}$ contains multi linearity describing different steps involved in the adsorption process. The values of intra particle diffusion constant k_p calculated (Fig. 6 & 7) are presented in Table 3. Increase of k_p values with the increase of initial concentration infers that pore diffusion limits the overall rate of the Chromium (VI) ion adsorption.

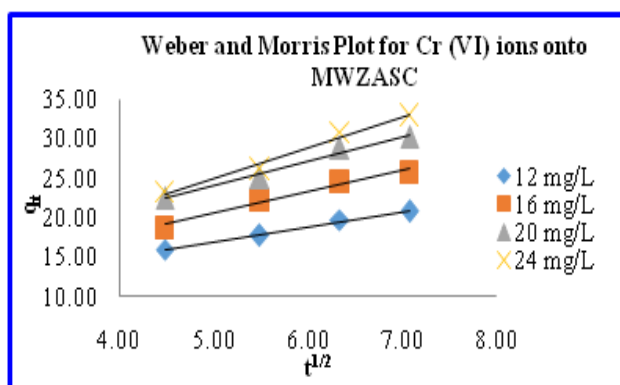


Fig. 6: Weber and Morris Plot for Cr (VI) ions onto MWZASC

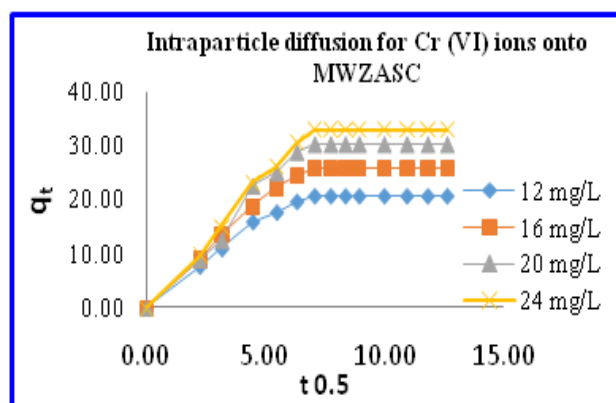


Fig. 7: Intraparticle diffusion for Cr (VI) ions onto MWZASC

Table 3. Intra particle diffusion - Cr (VI) ions onto MWZASC

Temperature (K)	Conc. (mg/L)	k_p (mg/g.min)	R^2
305	12	1.8999	0.9829
	16	2.7165	0.9787
	20	3.1076	0.9808
	24	3.8969	0.9861

4. CONCLUSION

The following conclusions drawn from the above study:

- i) The kinetic studies indicated that the equilibrium time required for the adsorption of Chromium (VI) ion from aqueous solution was 50 minutes.
- ii) The Lagergren pseudo first order reaction rate and Ho's pseudo second order reaction rate models described the adsorption data adequately with good and statistically significant regression coefficient. The Ho's model represented the adsorption kinetics better than the Lagergren model.
- iii) Adsorption capacity decreased with increase of pH of the solution
- iv) The optimum pH for Chromium (VI) ion adsorption from the aqueous solution is 2.

The kinetic parameters evaluated will be useful to environmental engineers to design effluent treatment plant for the removal of Cr (VI) ions.

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CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest.

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