



# CHROMIUM ADSORPTION KINETICS FROM AQUEOUS METAL SOLUTIONS USING CHITOSAN

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**Keywords:** chitosan; intraparticle diffusion rate model; adsorption; chromium(VI); hazardous; wastewater

The paper discusses the kinetics of chromium(VI) ions adsorption from aqueous solutions using chitosan at 25 °C and pH 5. The intraparticle diffusion rate constants ( $K_{id}$  and  $C_i$ ) determined for chitosan are 0.487 mg g<sup>-1</sup> min<sup>-1(1/2)</sup> and 11.66 mg g<sup>-1</sup> respectively. The results show that the intraparticle diffusion model fits the sorption of chromium(VI) with higher coefficient of determination ( $R^2$ ), thereby indicating the intraparticle diffusion may be rate limiting step for chromium(VI) adsorption. The results from this study indicate that chitosan is a good adsorbent for the removal of chromium(VI) from wastewater.

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## Introduction

Heavy metal ions are toxic pollutants, some of these are cumulative poisons capable of being assimilated, stored and concentrated by organisms that are exposed to low concentration of these substances for long period or repeatedly for short period.<sup>1</sup> The anthropogenic sources of heavy metals include waste from the electroplating and metal finishing industries, metallurgical industries, tannery operations, chemical manufacturing, mine drainage, battery manufacturing, leachates from landfills and contaminated groundwater from hazardous waste sites.<sup>2,3</sup> The use of chromate and dichromate in metal plating and as corrosion control agents in cooling waters is quite extensive. It is well known that chromium(VI) is toxic to living systems and must be removed from wastewater before it can be discharged. Current treatment for the removal of chromium(VI) involves acid catalyzed chemical reduction to chromium(III). The chromium(III) is then precipitated as hydroxide at alkaline conditions using either caustic or lime.<sup>4</sup> Unfortunately this method is expensive and requires the use of contaminating products for desorption of metals for cleaning up of the inorganic matrix. Physico-chemical methods presently in use have several disadvantages such as unpredictable metal ion removal, high reagent requirements, formation of sludge and its disposal in addition to high installation and operational costs.<sup>5</sup> Natural materials that are available in large quantities or certain waste from agricultural operations may have potential to be used as low cost adsorbents, as they represent unused resources, widely available and are environmental friendly.<sup>6</sup> In recent years studies on polymers, which bind metal ions, have increased significantly. Studies on the polymer metal complexes are of great practical importance. Complexing ability of polymers is used in nuclear chemistry, electrochemistry, hydrometallurgy and environmental protection. Of particular significance among many methods of metal ion separation is one which combines two processes: complexing of polymer with metal ions and ultra-filtration of the complexes through membranes of appropriate selectivity. Chitosan is a natural product derived from chitin, a polysaccharide found in outer skeleton of crustacean shells, shell fish like shrimp, prawn, crab etc., and also obtained from fungal sources. Chitin is

the second most bountiful natural polysaccharide after cellulose on earth. Chitosan is a linear polymer of  $\beta(1-4)$  linked 2-amino-2-deoxy- $\beta$ -D-glucopyranose and is easily derived by N-deacetylation, to a varying extent that is characterized by the degree of deacetylation (DDA) and is consequently a copolymer of N-acetylglucosamine and glucosamine units.<sup>7,8</sup> Chitosan forms chelates with metal ions by releasing hydrogen ions.<sup>9</sup> Chitosan has undoubtedly been one of the most popular adsorbents for the removal of metal ions from aqueous solution and is widely used in waste treatment applications.<sup>10-13</sup> Chitin and its de-acetylated derivatives, chitosan, have unique properties, which make them useful for a variety of applications.<sup>14-16</sup> The traditional source of chitin is selfish waste from shrimps, Antarctic krill, crab and lobster processing.<sup>17,18</sup> Chitosan is a natural, cationic, hydrophilic, nontoxic, biocompatible and biodegradable polysaccharide suitable for application in biosorption of heavy metal. Chitosan is slightly soluble at low pH and poses problems for developing commercial applications. It is also soft and has a tendency to agglomerate or form a gel in aqueous solution.<sup>14</sup> Low pH would favour protonation of the amino sites resulting in a reversal of charge and would greatly diminish the metal chelating ability of chitin and chitosan. This suggests that a neutral pH more of the metal ions should be adsorbed by chitosan. The amino sugars of chitin and chitosan are the major effective binding sites for metal ions, forming stable complexes by co-ordination.<sup>19</sup> The nitrogen electrons present in the amino and N-acetyl amino groups can establish dative bonds with transition metal ions. Some hydroxyl groups in these biopolymers may function as donor. Hence, deprotonated hydroxyl groups can be involved in the co-ordination with metal ions.<sup>20</sup>

In this study, chitosan is used to remove chromium(VI) from wastewater. A kinetic study was carried out for chromium(VI) removal from aqueous metal solution by using chitosan.

## Experimental

### Adsorbent and reagents

Chitosan (India Sea Food, Kochi M.W. 10<sup>7</sup>), Potassium dichromate ( $K_2Cr_2O_7$ ) (Qualigens, India), hydrochloric acid (HCL) (Merck, Limited, Mumbai, India), Sodium hydroxide (NaOH) (Thomas baker (Chemicals) Pvt. Limited, Mumbai,

India], demonized water. All the reagents used were of good quality grade. Standard stock solution ( $1000 \text{ mg L}^{-1}$ ) of chromium(VI) was prepared by dissolving salt of  $\text{K}_2\text{Cr}_2\text{O}_7$  in deionized water and required concentration of chromium(VI) ions was prepared by diluting stock solution with deionized water.

### Kinetics of metal sorption

Kinetic sorption studies for chromium(VI) were carried out for chitosan at pH 5, temperature  $25^\circ\text{C}$  for initial concentration  $10 \text{ mg L}^{-1}$ . 300 mL of standard solution of metal was transferred into various 500 mL flask. The fixed amount of chitosan (1.0 g) was weighed into the flasks and agitated in a shaker for the different contact time (5, 10, 15, 20, 30, 40, 100, 160 and 180 min.). After each agitation time, the content of each flask was centrifuged and the residual concentration of metal in supernatant solution was analyzed using atomic absorption spectrophotometer (ECIL-4141). Blank solutions were also prepared and analyzed.

### Data analysis

The amount of chromium(VI) adsorbed ( $a_t$ ) in  $\text{mg L}^{-1}$  from each metal solution by chitosan at time  $t$  was calculated by using the following equation:

$$a_t = C_0 - C_t \quad (1)$$

The percentage of metal removed (%  $R$ ) from the aqueous solutions by the chitosan was calculated using equation:

$$R = \frac{C_0 - C_t}{C_0} \times 100 \quad (2)$$

where,  $C_0$  and  $C_t$  are the initial metal ion concentration and metal ion concentration at time  $t$  respectively in  $\text{mg L}^{-1}$ .

### Adsorption dynamic

Adsorption kinetics of chromium(VI) on chitosan was evaluated using the intraparticle diffusion model.<sup>21,22</sup> Weber-Morris found that in many adsorption cases, solute uptake varies almost proportionally with  $t^{1/2}$  rather than with the contact time  $t$ .

$$q_t = k_{id}t^{0.5} + C_i \quad (3)$$

where,

$k_{id}$  ( $\text{mg g}^{-1} \text{min}^{-1/2}$ ) = measure of diffusion coefficient.

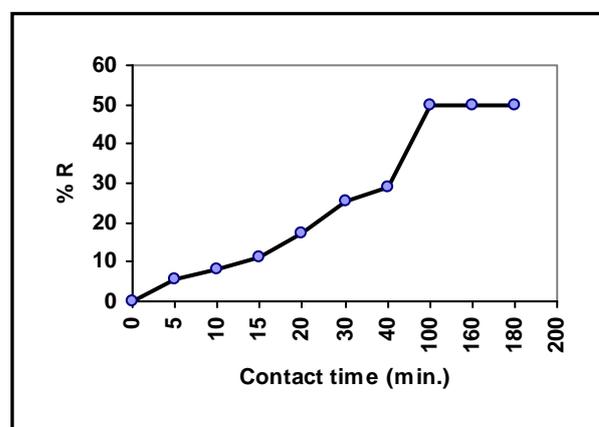
$C_i$  = intraparticle diffusion constant i.e. intercept of the line ( $\text{mg g}^{-1}$ ). It is directly proportional to the boundary layer thickness.

The plots of  $q_t \sim t^{1/2}$  gave a straight line are shown in Fig. 1 and is not going through the origin represents that the adsorption kinetics may be controlled by film diffusion and intraparticle diffusion simultaneously.

## Results and discussion

### Sorption kinetics

Kinetics of metal sorption governs the rate, which determines the residence time and it is one of the important characteristics defining the efficiency of an adsorbent.<sup>23</sup> Sorption kinetics can be controlled by several independent processes that could act in series or in parallel, such as bulk diffusion, external mass transfer (film diffusion), chemical reaction (chemisorptions) and intraparticle diffusion.<sup>24</sup> From the Fig. 1, it can be determined that the adsorption of metal was quite rapid initially, however the adsorption rate becomes slower with passage of time up to 100 min. The initial faster rate of removal of metal ions may be due to the availability of the uncovered surface area of the adsorbent, since adsorbent kinetics depends on the surface area of the adsorbent.<sup>25</sup>



**Figure 1.** Effect of contact time on % removal of chromium(VI) by chitosan

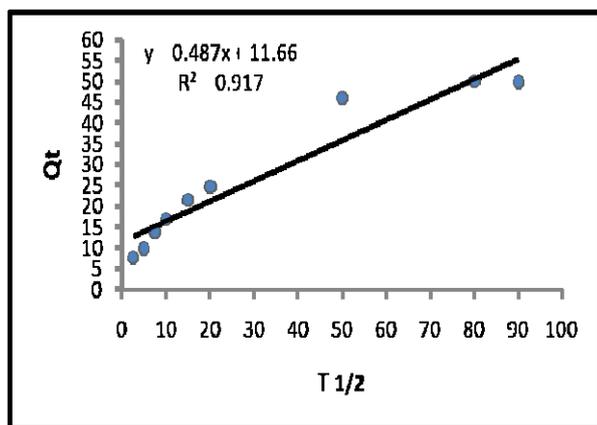
### Kinetic modeling

Kinetic equations have developed to explain the transport of metals onto various adsorbents. These equations include the pseudo first order equation<sup>26</sup>, the pseudo second order equation<sup>27</sup>, the Elovich equation<sup>28</sup> and the intraparticle diffusion model.<sup>22</sup> These kinetic models are only concerned with the effect of the observable parameters on the overall rate of sorption.<sup>29</sup> However for this study the intraparticle diffusion model was chosen to analyse the rate of sorption of chromium(VI) on chitosan.

**Table 1.** Intraparticle diffusion model rate constant (Eq.3) for chromium(VI) using chitosan as adsorbent at  $25^\circ\text{C}$

| Kinetic model Relationship | $R^2$ | Constants         | Values   |
|----------------------------|-------|-------------------|--|
| $y=0.487x+11.66$           | 0.91  | $k_{id}$<br>$C_i$ | $0.487 \text{ mg g}^{-1} \text{min}^{-1/2}$<br>$11.66 \text{ mg g}^{-1}$ |

Figure-2 presents the intraparticle diffusion kinetic model for chromium(VI) ions. Linear regression ( $R^2$ ) is frequently used to determine the best fitting kinetic model for metal sorption. In this study kinetic of chromium(VI) ions was evaluated using the intraparticle diffusion model. The coefficient of determination ( $R^2$ ) was used as the fitting parameter.



**Figure 2.** Intraparticle diffusion kinetic model for chromium(VI) ions

Table 1 represents the values of the parameters calculated from the linearized form of the intraparticle diffusion model equation. The  $R^2$  values for chromium(VI) ions can be stated that sorption of chromium(VI) on chitosan, to a certain extent and can be explained by using the intraparticle diffusion model. It therefore, means that for sorption of chromium(VI), intraparticle diffusion may be the rate-limiting step since it obeys the intraparticle diffusion model. It has been reported that sorption of chromium(VI) follows the intraparticle diffusion model.<sup>30</sup>

## Conclusion

This study indicated that chitosan is a good adsorbent for removal of chromium(VI) from aqueous solutions. The kinetics of the adsorption of metal was rapid in the initial stage followed by slow rate. The adsorption data showed that the applicability of the intraparticle diffusion model for chromium removal.

## Acknowledgements

The authors are thankful for the financial assistance received from the University Grants Commission (UGC).

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Received: 31.03.2013.

Accepted: 05.05.2013.