EFFECTIVE ADSORPTION OF CHROMIUM (VI) FROM AQUEOUS SOLUTIONS USING CHITOSAN

Agnieszka Adamczuk

Department of Inorganic Chemistry, Faculty of Chemistry,
Maria Curie Skłodowska University, Maria Curie Skłodowska Sq. 2, 20-031 Lublin, Poland

Abstract
In this work the adsorption process of chromium on chitosan flakes and powder is presented. The tests in the batch system were studied in equilibrium conditions in order to determine optimum parameters for loading chromium and were compared with those results reported in literature. The parameters investigated in this study included pH, contact time, initial concentration, sorbent dosage and temperature. The above described studies were also carried out for Cr(VI) adsorption in the presence of Cu(II), in order to compare the results with this competing ion. The experimental equilibrium parameters were obtained by fitting the experimental data by the Langmuir and Freundlich models. The process kinetics was evaluated by the pseudo first order, the pseudo second order and the intraparticle diffusion models. It was found that the pseudo second order kinetic model exhibited the highest correlation with the experimental data. Application of the Langmuir isotherm to the systems yielded the maximum sorption capacities of 58.48 mg g⁻¹ and 71.43 mg g⁻¹ for Cr(VI) and 74.63 mg g⁻¹ and 74.07 mg g⁻¹ Cr(VI) in the presence of Cu(II) onto chitosan powder and chitosan flakes, respectively. As follows from the thermodynamic parameters process is favourable, spontaneous and exothermic.

Key words: chitosan, chromium(VI), copper(II), sorption

1. Introduction

Chromium is one of the most common pollutants in the environment. Chromium compounds get into the environment mainly through: electroplating, leather tanning, cement preservations,
paints, pigments, textile, steel fabrication and canning industries (Acosta et al., 2004; Dubey and Gopal, 2007; Hamadi et al., 2001). The guideline value for the total chromium content in drinking water (recommended by the World Health Organization, WHO) is 0.05 mg L\(^{-1}\) and 0.005 mg L\(^{-1}\) in waste waters (Gode and Moral, 2008; Kozlowski and Walkowiak, 2002). Chromium exists in the tree oxidation states in nature i.e. Cr(II), Cr(III) and Cr(VI), however, only the last two are stable (Mohan and Pitman, 2006; Sarin and Pant, 2006). Cr(III) is known as an essential nutrient. However, Cr(VI) is very toxic to living organisms (Lalvani et al., 1998; Selvaraj et al., 2003). Cr(VI) anions, including chromate CrO\(_4^{2-}\) and dichromate Cr\(_2\)O\(_7^{2-}\) are highly mobile in soil and highly soluble in aquatic systems. They are severe contaminants in the environment due to their carcinogenic, mutagenic and teratogenic features in biological systems (Baral and Engelken, 2002). It is known that Cr(VI) is approximately 500 times more toxic than Cr(III) (Dubey and Gopal, 2007; Sarin and Pant, 2006). When chromium enters the human body especially the gastric system, epigastria pain, nausea, vomiting, severe diarrhea and even lungs carcinoma may occur (Beaumont et al. 2008; Russo et al., 2005; Wise et al., 2006; Yao et al., 2008).

The contamination of water by heavy metals such as chromium, copper, cadmium lead and mercury has become an increasing problem in the environment and for human health. Therefore many methods to reduce toxic pollutants have been developed. Lately the most common processes for removal chromium have been: filtration, reverse osmosis (Das et al., 2006), adsorption and chemical reactions i.e. reduction and precipitation (Hagendorfer and Goessler, 2008; Ouejhani et al., 2008), electrodeposition, membrane systems and ion exchange processes (Xing et al., 2007). Conventional methods applied for Cr(VI) removal have many drawbacks. For example, the chemical precipitation produces great amounts of mud and similarly to the chemical reduction, it requires different separation techniques for solutions treatment. The ion exchange and membrane separations are relatively costly, while the electrodeposition method is more energy intensive than other methods (Ouejhani et al., 2008; Xing et al., 2007; Yavuz et al., 2011). Hence, the adsorption is the most popular technique to remove heavy metals from aqueous solutions. The great advantages are variety of adsorbent materials and high efficiency at relatively lower cost (Karthikeyan et al., 2005).

Recently investigations have been carried out for the effective removal of Cr(VI) using biopolymers. Many biopolymers are known to bind metals strongly. One of them is chitosan. Chitosan (2-acetamido-2-deoxy-β-D-glucose-(Nacetylglucosamine) is a partially deacetylated polymer of chitin and is usually prepared from chitin by deacetylation with a strong alkaline solution (Jeauniaux et al., 1989). Chitin is one of the polymers which is produced from wastes from the fishery industry. It is found in the outer skeleton of marine animal (insects, crabs, shrimps and others). It is the second most abundant natural polymer polysaccharide and its annual production is
almost as much as that of cellulose. Main advantages of using chitosan are both its natural origin and low cost of production.

Chitosan is known as an excellent biosorbent for metal ions in acidic or near neutral solutions. This is attributed to: high hydrophilicity due to a large number of hydroxyl groups of glucose units and the presence of a large number of functional groups (acetamido, primary amino and/or hydroxyl groups). The other important advantage of this biosorbent is high chemical reactivity of the above-mentioned functional groups and flexible structure of the polymer chain (Kasaai, 2009). The reactive amino group selectively binds transition metal ions but it does not bind alkali and alkaline earth metal ions (Varma et al., 2004). Additionally, chitosan is only soluble in few dilute acid solutions due to its crystalline character. It is usually used in flaked or powdered forms. Moreover, the modifications to increase its sorption properties are widely known.

In this work, chitosan flakes and powder are applied for chromium(VI) ions removal from aqueous solutions. The adsorption capacity of chitosan towards Cr(VI) was also studied in the presence of Cu(II) ions. In order to optimize the adsorption process, the effects of contact time, initial concentration, chitosan dosage and temperature were evaluated. As for the effect of pH it was found that the efficiency of Cr(VI) removal from aqueous solution is the highest when pH is in the range 3.0-4.0 (below pH 5 almost 90% of active sites are protonated, while at pH 4.0 more than 99% is active) (Schmuhl et al., 2001; Sağ and Aktay, 2002). Also in the paper by Kyzas et al. (2009), it was confirmed that high adsorption percentages were observed in the acidic pH region (more than 70%) and then for higher pH values (pH >6.0), a decrease in sorption is observed. Similar pH behaviour (higher sorption at low pH and lower uptake with the increase of pH) was observed by others.

2. Experimental

2.1. Materials

Chitosan in the form of flakes (high molecular weight) and powder was supplied by Sigma-Aldrich. Both of them were used in experiments without further pretreatment. Its physicochemical properties were presented in (Kolodyńska, 2012). Na₂Cr₂O₇ and CuSO₄·5H₂O were purchased from POCH (Poland). The pH of the solutions was adjusted using 0.1 M NaOH and 0.1 M H₂SO₄. All the reagents used were of analytical grade.

2.2. Methods
The concentration of Cr(VI) was analyzed spectrophotometrically at 546 nm using 1,5-diphenyl carbazide as the complexing agent according to the Pflaum and Howick method as well as by AAS (atomic absorption spectroscopy) method. However, the Cu(II) ion content was determined by AAS method. The amount of Cr(VI) or Cu(II) ions adsorbed was calculated based on the difference in their initial and final concentrations.

2.3. The effect of adsorbent dosage

Tests of adsorption of Cr(VI) onto chitosan adsorbent at different dosages 0.05 g - 0.3 g were carried out at the initial concentrations 0.001 M-0.003 M, 20 ml of solution (pH 4.0) was added to a suitable dosage of chitosan and shaken at 180 min with the shaking speed 180 rpm at 293 K. After this time, the samples were filtered and the concentration of Cr(VI) was analyzed. The studies of the adsorbent dosage for Cr(VI) in the presence of Cu(II) were conducted using the same procedure.

2.4. Kinetics tests

During the investigations of kinetic parameters 20 ml of the Cr(VI) solution at the concentration 0.001 M-0.003 M was added to 0.2 g of the chitosan powder or flakes (pH 4.0, shaking speed 180, temperature 293K). The samples were removed and filtered at different time intervals from 1 to 180 min and the concentration of Cr(VI) was determined. The kinetic tests of adsorption Cr(VI) in the presence of Cu(II) were conducted using the same procedure.

2.5. Adsorption studies

The equilibrium isotherm was determined using the batch studies. In the experiments 20 ml solution of Cr(VI) at the concentration 0.001 M-0.025 M was added to 0.2 g of chitosan powder or flakes samples (pH 4.0, shaking speed 180, shaking time 180 min., temperature from 293 K to 333 K). After adsorption the solution was filtered and the amount of Cr(VI) was determined. The studies of adsorption isotherm for Cr(VI) in the presence of Cu(II) were carried out using the same procedure.

2.6. Calculations
The rate of Cr(VI) and Cr(VI) in the presence of Cu(II) ions is expressed as percentage of the amount of metal ions adsorbed after a certain time related to that required for the state of equilibrium (Eq.1):

\[ S\% = \frac{(c_0 - c_e)}{c_0} \times 100\% \]  

(1)

The chitosan phase concentrations of metal ions at equilibrium, \( q_e \) (mg g\(^{-1}\)) and at time \( t \), \( q_t \) (mg g\(^{-1}\)) were obtained according to (Eqs.2-3):

\[ q_e = (c_0 - c_e) \times \frac{V}{m} \]  

(2)

\[ q_t = (c_0 - c_t) \times \frac{V}{m} \]  

(3)

where: \( c_0 \) is the initial concentration of metal ion in the aqueous phase (mg L\(^{-1}\)); \( c_t \) is the concentration of metal ion in the aqueous phase at time \( t \) (mg L\(^{-1}\)); \( c_e \) is the concentration of metal ion in the aqueous phase at equilibrium (mg L\(^{-1}\)); \( V \) is the volume of the solution (L); \( m \) is the mass of the chitosan (g).

2.7. Apparatus

The concentration of Cr(VI) was analyzed using the Specord M42 spectrophotometer (Carl Zeiss-Jena, Germany) and the total Cr(III,VI) in aqueous solution was analyzed by AAS (atomic absorption spectroscopy). The atomic absorption spectrometer SpectrAA-FS 240 (Varian, Australia) was also used for quantitative determination of the concentration of chromium and copper ions. It was equipped with a deuterium lamp, background correction, hollow cathode lamp for Cu or Cr and an air-acetylene burner.

Scanning electron microscopy images of chitosan before and after the adsorption were obtained at 30.00kV on the field emission scanning electron microscope (Tescan Vega2) after gold plating by using a sputter coater (K-550X, Emitech).

3. Results and Discussion

3.1. The effect of pH

Depending on the Cr(VI) concentration and pH, the Cr(VI) species exist as follows (at 298K) (Kotaś and Stasicka, 2000) (Eqs.4-6):
The main Cr(VI) species in equilibrium in the acidic pH range in diluted solutions are the anions HCrO$_4^-$, CrO$_4^{2-}$. They interact effectively with the protonated amine functional groups of chitosan (Debbaudt et al., 2004; Wan Ngah and Musa, 1998). The species such as Cr$_2$O$_7^{2-}$ and HCr$_2$O$_7^-$ coexist at higher concentrations, above 0.01 M (Fig.1). The pH of the solution strongly influences on the chromium(VI) adsorption on the chitosan surface.

Fig.1. Speciation distribution of Cr(VI) depending on pH (a) and influence of pH on Cr(VI) and Cu(II) adsorption on chitosan (b).

Although there are many examples of metal ions adsorption on chitin as well as on chitosan and its derivatives, and chitosan can be described as an effective metal ions scavenger, the mechanism of adsorption has still not been fully explained. Among others, the chitosan-metal ion adsorption depend on the kind of metal ion, coordination index, hydrolysis constants; precipitation
mechanism, deposition of metal aggregate mechanism, ion exchange and complexation. It was also established that swelling is the first stage of adsorption of metal ions onto chitosan. After that its porous structure disappears and the swollen particles take the form of homogeneous gel material, in which solvent has to diffuse to achieve further swelling until equilibrium is established. Then the metal ions are diffused into the swollen polymer phase and are adsorbed on the polymer by electrostatic attraction in the case of the anions like Cr(VI) and by chelation on the amino groups of the glucosamine unit in the case of cation metal ions such as Cu(II) (Guibal, 2004). As follows from the literature data, Cu(II) is coordinated to the C(1)-alkoxide and the atoms of nitrogen belonging to species of chitosan. The exemplary structures of the formed complexes were presented in Rhazi et al. (2002). In the case of Cr(VI) it was also found that precipitation and reduction of Cr(VI) occurs (Vierra et al., 2011).

3.2. The effect of initial concentration of Cr(VI) and contact time

The adsorption of Cr(VI) onto chitosan strongly depends on the phase contact time. The example of the time curve is shown in (Fig.2). It can be observed that adsorption of Cr(VI) as well as Cr(VI) in the presence of Cu(II) onto both chitosan flakes and powder increase with the contact time for all initial concentrations of Cr(VI). Then the process becomes relatively slower and the equilibrium time conditions are reached after 180 min. Therefore, further batch experiments were carried out at 180 min. as the optimum phase contact time.
Fig. 2. Effect of contact time for the adsorption of Cr(VI) and Cr(VI) in the presence of Cu(II) onto chitosan flakes (a) and chitosan powder (b) at the different initial concentrations (temperature 293 K, pH 4.00).

As it can be observed on SEM images (Fig. 3) that surface morphology after adsorption process changed. However, no differences in results using different forms of chitosan were not reveal.
Fig.3. SEM images chitosan flakes (a) and powder (b) before (a-b) and after the adsorption of Cr(VI) ions at 100X (c-d) and 1500X (e-f) magnification.

3.3. The effect of adsorbent dosage

As for the effect of adsorbent dose on the adsorption efficiency of Cr(VI) and Cr(VI) in the presence of Cu(II), it was found that the adsorption percentage (S%) of Cr(VI) and Cr(VI) in the presence of Cu(II) increased with the increasing amount of adsorbent. It was observed that the maximum adsorption was achieved with 0.2 g (data not presented). The result can be explained by the increase in the surface area (more adsorption sites available) with the increasing adsorbent mass.

3.4. Adsorption kinetics

The mechanism of adsorption depends on the physical and chemical characteristics of the adsorbent. Chitosan powder is characterized by a higher adsorption capacity for both Cr(VI) and Cr(VI) in the presence of Cu(II). Kinetics of chromium adsorption was modeled by the pseudo first order, the pseudo second order and the intraparticle diffusion kinetic equilibrium for the different initial concentrations (c₀).

The pseudo first order kinetic equation proposed by Lagergren (1898) can be represented as (Eq.7):

\[
\log(q_t - q_e) = \log(q_e) - \frac{k_1 t}{2.303}
\]

where: \( q_e \) and \( q_t \) denote the amount of sorption at equilibrium and at time t (mg g\(^{-1}\)) respectively; \( k_1 \) is the rate constant of the pseudo first-order sorption (1 min\(^{-1}\)). Based on the plot of \( \log (q_t-q_e) \) vs. t the kinetic parameters were calculated.
It was observed that for a time greater than 120 min, Cr(VI) concentration became almost stable and that adsorption equilibrium was reached at 180 min. Similar results have been observed for the adsorption of Cr(VI) in the presence of Cu(II) addition.

At the concentration 0.001 M-0.003 M, for the pseudo first order reaction the adsorption constant $k_1$ for Cr(VI) ions is 0.06-0.04 L min$^{-1}$ for chitosan powder and 0.04-0.02 L min$^{-1}$ for chitosan flakes. For Cr(VI) in the presence of Cu(II) this constant is 0.06-0.02 L min$^{-1}$ and 0.07-0.03 L min$^{-1}$, respectively. It can be observed that $k_1$ decreases with the increasing of initial concentration (Table 1). The $R^2$ values show that adsorption of Cr(VI) both onto the chitosan powder and chitosan flakes does not follow the pseudo first order model.

The pseudo second order model is represented as (Eq.8) (Blanchard, 1984; Ho and McKay, 1998):

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2q_e^2}$$

(8)

where: $k_2$ is the rate constant of the pseudo second-order sorption (g/mg$^{-1}$ min$^{-1}$). The kinetic parameters were calculated based on the plots of $t/q_t$ vs. $t$.

**Table 1.** Kinetic parameters for the adsorption of Cr(VI) and Cr(VI) in the presence of Cu(II).

<table>
<thead>
<tr>
<th></th>
<th>The pseudo first-order</th>
<th>The pseudo second-order</th>
<th>Intraparticle</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$C_0$</td>
<td>$q_1$</td>
<td>$k_1$</td>
</tr>
<tr>
<td><strong>Cr(VI) (chitosan powder)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.001 M</td>
<td>0.16</td>
<td>0.60</td>
<td>0.93</td>
</tr>
<tr>
<td>0.002 M</td>
<td>1.21</td>
<td>0.04</td>
<td>0.96</td>
</tr>
<tr>
<td>0.003 M</td>
<td>1.40</td>
<td>0.04</td>
<td>0.91</td>
</tr>
<tr>
<td><strong>Cr(VI)-Cu(II) (chitosan powder)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.001 M</td>
<td>1.26</td>
<td>0.06</td>
<td>0.94</td>
</tr>
<tr>
<td>0.002 M</td>
<td>1.90</td>
<td>0.04</td>
<td>0.80</td>
</tr>
<tr>
<td>0.003 M</td>
<td>0.90</td>
<td>0.02</td>
<td>0.84</td>
</tr>
<tr>
<td><strong>Cr(VI) (chitosan flakes)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.001 M</td>
<td>1.85</td>
<td>0.04</td>
<td>0.97</td>
</tr>
<tr>
<td>0.002 M</td>
<td>1.85</td>
<td>0.03</td>
<td>0.86</td>
</tr>
<tr>
<td>0.003 M</td>
<td>0.89</td>
<td>0.02</td>
<td>0.90</td>
</tr>
<tr>
<td><strong>Cr(VI)-Cu(II) (chitosan flakes)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.001 M</td>
<td>0.12</td>
<td>0.07</td>
<td>0.82</td>
</tr>
<tr>
<td>0.002 M</td>
<td>0.90</td>
<td>0.06</td>
<td>0.80</td>
</tr>
<tr>
<td>0.003 M</td>
<td>0.22</td>
<td>0.03</td>
<td>0.72</td>
</tr>
</tbody>
</table>

The pseudo second order kinetic model is based on the assumption that the rate limiting step may be chemisorption involving valency forces through sharing or exchange of electrons between the sorbent and the sorbate (Sağ and Aktay, 2002). It was found that under the experimental
conditions the pseudo second order model is more accurate to describe sorption kinetics. (Fig.4a-b) illustrates the linear plots of \( t/qt \) vs. \( t \) using the pseudo second-order kinetic model for Cr(VI) and Cr(VI) in the presence of Cu(II) adsorbed onto chitosan powder and chitosan flakes. It is characterized by the \( k_2 \) and \( q_2 \) parameters, but very often the parameter \( h \) (mg/g \( \cdot \)min\(^{-1} \)) is also calculated (Eq.9): 
\[
h = k_2q_2^2
\]  
\hspace{10cm} (9)

**Fig.4.** The pseudo second order plots of Cr(VI) and Cr(VI) in the presence of Cu(II) onto chitosan flakes (a) and powder (b) at the differ initial concentrations (temperature 293 K, pH 4.00).

The obtained data are presented in Table 1. It should be admitted that the mass transfer and sorption are often experimentally inseparable. However, the correlation coefficient \( R^2 \) above 1.00 confirms that adsorption processes followed the pseudo second order kinetics. In contrast to the pseudo first model, it provides good correlation for the adsorption of Cr(VI) and Cu(II) ions. Additionally, the indiscernible change of the pseudo second order rate constants with the particle size was observed for the sorption of Cr(VI) and Cu(II) (chitosan is characterized by the following particle size distribution 0.09-0.42 mm for flakes and 0.06-0.25 mm for powder form).
The linear equation of intraparticle diffusion (Amoyaw et al., 2009) (Eq.10):

\[ q_t = k_i t^{\frac{1}{2}} + C \]  

(10)

where \( k_i \) is the intraparticle diffusion rate constant (mg g\(^{-1}\) min\(^{-1/2}\)), \( C \) is the intercept which reflects the boundary layer effect. The \( k_i \) parameter has been determined from the slope of the linear gradients of the plot \( q_t \) vs. \( t^{1/2} \). The \( R^2 \) values 0.39-0.96 did not yield a good correlation ratio.

3.5. Adsorption isotherms studies

The most popular isotherms, the Langmuir and Freundlich ones have been used to describe the equilibrium of the adsorption. The linear equations of both models are as follows:

a) the Langmuir isotherm model (Jeuniaux et al., 1989) (Eq.11):

\[
\frac{c_e}{q_e} = \frac{1}{q_0 K_L} + \frac{c_e}{q_0} \]

(11)

b) the Freundlich isotherm model (Allen et al., 2004) (Eq.12):

\[
\log q_e = \log K_F + \frac{1}{n} \log c_e 
\]

(12)

where \( q_0 \) is the monolayer sorption capacity of chitosan (mg g\(^{-1}\)) and \( K_L \) is a constant related to the free energy sorption (L mg\(^{-1}\)); \( K_F \) (mg g\(^{-1}\) (L mg\(^{-1}\))\(^{-1/n}\)) and \( n \) are the Freundlich constants, characteristic of the system and the indicators of adsorption capacity and reaction energy, respectively.

The Langmuir isotherm model is representative of monolayer adsorption occurring on the energetically uniform surface on which the adsorbed molecules are not interactive (Baroni et al., 2008; Singh and Pant, 2004). According to this model the equilibrium is attained when the monolayer is completely saturated (Dubey and Gopal, 2007). The obtained adsorption capacities for Cr(VI) and Cr(VI) in the presence of Cu(II) on chitosan are presented in (Figs.5-6).
**Fig. 5.** The Langmuir and Freundlich sorption isotherms of Cr(VI) onto chitosan powder (a) and flakes (b-d) at different temperatures.

**Fig. 6.** The Langmuir and Freundlich sorption isotherms of Cr(VI) in the presence of Cu(II) onto chitosan powder (a) and flakes (b-d) at different temperatures.
The parameter which determines favourable conditions of the Langmuir isotherm and its tendency as an irreversible process used in the adsorption studies is the parameter $R_L$ (Rojas et al., 2005) (Eq. 13):

$$R_L = \frac{1}{1 + K_L c_0}$$

If $R_L < 1$ the process is favourable, if=1 linear and if >1 unfavourable. $R_L$ for the chitosan flakes and the chitosan powder for Cr(VI) is 0.42 and 0.49 (Table 2).

Table 2. Langmuir and Freundlich parameters for adsorption of Cr(VI) and Cr(VI) in the presence of Cu(II) onto chitosan.

<table>
<thead>
<tr>
<th>System</th>
<th>$q_{e,exp}$</th>
<th>Langmuir model</th>
<th>Freundlich model</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr(VI) (chitosan powder)</td>
<td>66.69</td>
<td>$q_0$</td>
<td>$K_L$</td>
</tr>
<tr>
<td>Cr(VI) (chitosan flakes)</td>
<td>42.72</td>
<td>58.48</td>
<td>0.001</td>
</tr>
<tr>
<td>Cr(VI)-Cu(II) (chitosan powder)</td>
<td>65.63</td>
<td>71.43</td>
<td>0.06</td>
</tr>
<tr>
<td>Cr(VI)-Cu(II) (chitosan flakes)</td>
<td>38.23</td>
<td>74.07</td>
<td>0.05</td>
</tr>
</tbody>
</table>

For Cr(VI) in the presence of Cu(II) the adsorption process is also favourable. What is more, the $K_L$ parameter also indicates a favourable process (the higher $K_L$ the more favourable adsorption) (Rojas et al., 2005). $K_L$ has been calculated from the slope of the plot between $(1/q_e)$ vs. $(1/c_e)$. In this study $K_L$ at 293 K for the adsorption of Cr(VI) onto the chitosan powder is 0.001 L mg$^{-1}$ and 0.06 and 0.05 for Cr(VI) in the presence of Cu(II) onto the chitosan powder and flakes, respectively and therefore slightly higher compared to the results obtained by Aydin and Aksoy (2009) where $K_L$ was 0.008 L mg$^{-1}$.

The Freundlich isotherm describes the adsorption on an energetically heterogeneous surface on which the adsorbed molecules are interactive (Debbaudt, 2004; Dubey and Gopal, 2007; Sharma and Weng, 2007). The values of $K_F$ and $n$ were calculated from the slope and intercept of the plot between log $q_e$ vs. log $c_e$. The calculated constants are reported in Table 3. It can be observed that the adsorption isotherms showed good agreement with the experimental data of the Freundlich isotherm. For the values $0.1 < 1/n < 1$ adsorption is favourable (Raji and Anirudhan, 1998). For Cr(VI) adsorption onto the chitosan powder and flakes the n values are equal to 1.21 and 0.78, respectively, for Cr(VI) in the presence of Cu(II) they are equal to 1.97 and 1.95.
The comparison between the determined adsorption capacities of the chitosan flakes and powder towards Cr(VI) ions and other forms of chitosan is presented in (Table 3). It can be observed that the adsorption capacity of both chitosan powder and flakes is equal and also higher than that of some of the biopolymers reported in literature. For example, in the paper by Udaybhaskar et al. (1990) the adsorption capacity for Cr(VI) onto the chitosan powder was 32.00 mg g$^{-1}$ for the initial concentration 50 mg L$^{-1}$ and a slightly lower than the adsorption capacity for Cr(VI) onto the chitosan powder.

Table 3. Comparison of adsorption capacities for Cr(VI) onto adsorbents.

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>Adsorption capacity (mg g$^{-1}$)</th>
<th>pH</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chitosan</td>
<td>22.1</td>
<td>3.0</td>
<td>Aydin and Aksoy, 2009</td>
</tr>
<tr>
<td>Non-cross linked chitosan (powder 0.37 mm)</td>
<td>32.0</td>
<td>4.0</td>
<td>Udaybhaskar et al., 1990</td>
</tr>
<tr>
<td>Plain chitosan flakes</td>
<td>34.4</td>
<td>n.a.</td>
<td>Udaybhaskar et al., 1990</td>
</tr>
<tr>
<td>Cross linked chitosan</td>
<td>50.0</td>
<td>5</td>
<td>Schmuhl et al., 2001</td>
</tr>
<tr>
<td>Cross linked (glutaraldehyde) chitosan (flakes)</td>
<td>215.0</td>
<td>4.0</td>
<td>Rojas et al., 2005</td>
</tr>
<tr>
<td>Chitosan impregnated with microemulsion</td>
<td>85.6</td>
<td>n.a.</td>
<td>de Castro Dantas et al., 2001</td>
</tr>
<tr>
<td>Xanthated Chitosan</td>
<td>625.0</td>
<td>n.a.</td>
<td>Sankararamakrishnan and Sanghi, 2006</td>
</tr>
<tr>
<td>Thio carbamoyl chitosan</td>
<td>434.8</td>
<td>n.a.</td>
<td>Chauhan et al., 2012</td>
</tr>
<tr>
<td>Chitosan coated with poly 3-methyl thiophene</td>
<td>99.0</td>
<td>2.0</td>
<td>Hena, 2010</td>
</tr>
<tr>
<td>Chitosan membranes crosslinked by epichlorohydrin</td>
<td>1400</td>
<td>6.0</td>
<td>Baroni et al., 2008</td>
</tr>
<tr>
<td>Chitosan cross-linked with epichlorohydrin</td>
<td>11.3</td>
<td>3.0</td>
<td>Qian et al., 2000</td>
</tr>
<tr>
<td>Fe-cross linked chitosan complex</td>
<td>295</td>
<td>4.8</td>
<td>Zimmermann et al., 2010</td>
</tr>
<tr>
<td>Metal ion imprinted chitosan</td>
<td>51.0</td>
<td>5.5</td>
<td>Tianwei et al., 2001</td>
</tr>
<tr>
<td>Composite chitosan biosorbent</td>
<td>153.8</td>
<td>4.0</td>
<td>Boddou et al., 2003</td>
</tr>
<tr>
<td>Chitosan/clay nanocomposite</td>
<td>357.1</td>
<td>3.0</td>
<td>Pandey and Mishra, 2011</td>
</tr>
<tr>
<td>Ethylenediamine-modified cross-linked magnetic chitosan resin</td>
<td>48.8</td>
<td>n.a.</td>
<td>Hu et al., 2011</td>
</tr>
<tr>
<td>Chitosan-Fe carbide nanoparticles</td>
<td>32</td>
<td>n.a.</td>
<td>Wu et al., 2007</td>
</tr>
<tr>
<td>Aminated chitosan</td>
<td>28.7</td>
<td>n.a.</td>
<td>Yan et al., 2007</td>
</tr>
<tr>
<td>Chitosan powder</td>
<td>58.5</td>
<td>4.0</td>
<td>This study</td>
</tr>
<tr>
<td>Chitosan flakes</td>
<td>71.4</td>
<td>4.0</td>
<td>This study</td>
</tr>
</tbody>
</table>

n.a. – not available
As mentioned earlier in the literature a few studies report on the adsorption of Cr(VI) mechanism. De Dantas et al. (2001) and Schmul et al. (2001) observed that adsorption is greater at low pH and decreases with increasing pH. At lower pH the adsorbent is positively charged due to the protonation of the amino group, while the sorbate (dichromate ion) exists mostly as an anion leading to the electrostatic attraction between the sorbent and the adsorbate (Boddu et al., 2003). Additionally, hydrogen bonding and weak van der Waals forces should also be taken into account.

It has been proved that Cr(VI) in contact with organic substances or reducing agents, especially in the acidic solutions exhibits a very high positive redox potential (+1.33V) which denotes that it is strongly oxidizing and unstable in the presence of electron donors having lower reduction potential values than those of Cr(VI). Therefore, it is readily and spontaneously reduced to the Cr(III). This results in an increased chromium adsorption in low pH ranges. The reactive OH and NH$_2$ electron donor groups present in the chitosan reduce the toxic Cr(VI) to less toxic Cr(III) which indicates the adsorption coupled reduction (Dambies et al., 2001; Gode and Pehlivan, 2005; Park and Park, 2006; Kyzas et al., 2009). What is more Rojas et al. (2005) observed that at pH ≤ 3.0 Cr(VI) is reduced to Cr(III) and in the range pH ≥ 4.0 only adsorption was observed (as in our paper). Vieira et al. (2011) studied the adsorption and reduction mechanism of Cr(VI), Cu(II) and Hg(II) by using the X-ray photoelectron spectroscopy (XPS). They reported that multivalent nature of chromium(VI) in some cases is hardly stabilized by the functional groups of polymeric matrices. Moreover, due to the irreversible character of the process, Cr(VI) ions can be removed only to some extent by pH changes. By treating with an alkaline solution, elution of the bound Cr(VI) can be accomplished. In the paper by Park et al. (2005) it was reveal that during Cr(VI) reduction, some of the organic carbons of the adsorbent such as biomass were completely oxidized into inorganic carbon i.e. HCO$_3^-$ or CO$_2$.

As for the mechanism, Cr(VI) can be removed from the aqueous solutions through the direct reduction to Cr(III) by contact with the electron-donor groups or by the indirect reduction which consists of the following steps: the binding of the anionic Cr(VI) species to the positively charged groups present on the adsorbent surface, the reduction of Cr(VI) to Cr(III) by the adjacent electron-donor groups and the release of the Cr(III) ions into the aqueous phase due to the repulsion between the positively charged groups and the Cr(III) ions or the complexation of the Cr(III) with the adjacent groups capable of Cr(III) binding (Park et al., 2005).

3.6. The effect of temperature

The adsorption of Cr(VI) onto chitosan at different temperatures shows an increase in the adsorption capacity when temperature is increased. With the increase in temperature from 293 to
313 K, the adsorption capacity increased from 38.08 to 41.16 mg g\(^{-1}\) for the initial concentration of 0.025 M at pH 4.0. For the adsorption of Cr(VI) in the presence of Cu(II) the effect of temperature is similar.

The Gibb’s energy change \(\Delta G^0\) was calculated using (Eq.14) (Rojas et al. 2005):

\[
\Delta G^0 = -RT \ln K_c
\]  

(14)

where \(R\) is the gas constant (kJ mol\(^{-1}\)K\(^{-1}\)), \(T\) is the temperature (K) and \(K_c\) is the equilibrium constant (L mol\(^{-1}\)) determined by (Eq.15) given below:

\[
K_c = \frac{C_a}{C_e}
\]  

(15)

where \(C_a\) (mg L\(^{-1}\)) is the amount of solute adsorbed by the adsorbent at equilibrium and \(C_e\) is the equilibrium concentration (g L\(^{-1}\)). The Gibb’s free energy, standard enthalpy and entropy changes of adsorption process are presented in Table 4. The negative values of \(\Delta G^0\) indicated that the adsorption process was favourable and spontaneous in nature. It can be observed that with the increase in temperature from 293K-333K, the value of \(\Delta H^0\) decreased from -8.26 kJ mol\(^{-1}\) to -10.29 kJ mol\(^{-1}\). Hence the adsorption of Cr(VI) onto chitosan flakes increased at higher temperature (Table 4).

**Table 4.** Thermodynamic data for Cr(VI) adsorption onto chitosan flakes.

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>Temperature (K)</th>
<th>(\Delta H^0) (kJ/mol)</th>
<th>(\Delta G^0) (kJ/mol)</th>
<th>(\Delta S^0) (kJ/mol K)</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr(VI)</td>
<td>293</td>
<td>-8.26</td>
<td>-189.19</td>
<td>4.28</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>313</td>
<td>-9.57</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>333</td>
<td>-10.29</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr(VI)-Cu(II)</td>
<td>293</td>
<td>-8.27</td>
<td>-167.21</td>
<td>4.22</td>
<td>0.85</td>
</tr>
<tr>
<td></td>
<td>313</td>
<td>-9.64</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>333</td>
<td>-10.27</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The values of \(\Delta H^0\) and \(\Delta S^0\) were determined using Van’t Hoff (Eq.16):

\[
\ln K_c = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}
\]  

(16)

\(\Delta H^0\) and \(\Delta S^0\) were obtained from the slope and intercept of the plot of \(\ln K_c\) vs. 1/T (Fig.7).
The negative value of $\Delta H^\circ$ means that the reaction is exothermic. In this study $\Delta G^\circ$ is equal to -189.19 kJ mol$^{-1}$ for the adsorption of Cr(VI) and -167.21 kJ mol$^{-1}$ for that of Cr(VI) in the presence of Cu(II) onto chitosan flakes. The calculated values of $\Delta S^\circ$ for the adsorption of Cr(VI) and Cr(VI) in the presence of Cu(II) are 4.28 kJ mol$^{-1}$K$^{-1}$ and 4.22 kJ mol$^{-1}$K$^{-1}$, respectively. The positive value of entropy also indicates the irreversibility and stability of this process.

It was found that high correlation coefficients from the Langmuir isotherms indicating a reasonable fixed value for the sorption activation energy, could correspond to the chelation bond energy between the metal ion and the lone pair of electrons on the nitrogen. Additionally, high correlation of the linearized Freundlich isotherm indicates more than one mechanism which is associated with the heterogeneity of the surface.

4. Conclusions

The contact time and temperature have great influence on the adsorption onto chitosan powder and flakes, both for Cr(VI) and Cr(VI) in the presence of Cu(II). The kinetic studies have shown that the sorption process is described by the pseudo second order model which is confirmed by the correlation coefficient $R^2$ almost equal to 1.00. Additionally, the adsorption data were fitted well by Freundlich adsorption isotherm. Approximately, 98 % of hexavalent chromium was removed at pH 4.0 within 2 h. The $\Delta H^\circ$, $\Delta G^\circ$ and $\Delta S^\circ$ values showed favourable, spontaneous and exothermic adsorption.

To sum up, chitosan is the efficient biosorbent in Cr(VI) removal from aqueous solutions. It can be used as a low cost attractive alternative for other costly adsorbents as activated carbon.

References:


Hagendorfer H., Goessler W., (2008), Separation of chromium(III) and chromium(VI) by ion chromatography and an inductively coupled plasma mass spectrometer as element-selective detector, *Talanta*, **30**, 656-661.


Lagergren, (1898), About the theory of so called adsorption soluble substances, Kungliga Svenska Vetenskapsakademiens, Handlignar Band **24**, 1-39.


Sağ Y., Aktay Y., (2002), Kinetic studies on sorption of Cr(VI) and Cu(II) ions by chitin, chitosan and *Rhizopus arrhizus*, *Biochemical Engineering Journal*, **12**, 143-153


