Chapter 12
An Insight into the Adsorption Mechanism of Hexavalent Chromium onto Magnetic Pine Cone Powder

Immaculate L. A. Ouma, Eliazer B. Naidoo and Augustine E. Ofomaja

Abstract The remediation of hexavalent chromium [Cr(VI)] contaminated water has been a challenge due to its high toxicity and mobility in the environment. Adsorption has so far been the most promising method for the treatment of chromium containing water due to the availability of low cost materials capable of chromium sequestration. The mechanism for hexavalent chromium removal has however not been fully understood with many studies pointing to a reduction-coupled mechanism. In this study, a composite material consisting of agricultural waste material (pine cone) and magnetite nanoparticles was used for the remediation of hexavalent chromium contaminated water with a focus on the removal mechanism and adsorbent regeneration studies. The mechanism was identified to be adsorption-coupled reduction where Cr(VI) was reduced on the adsorbent surface to the less toxic trivalent chromium [Cr(III)] before being adsorbed. The adsorbed chromium was successfully desorbed using NaOH allowing for concentration and chromium recovery. The adsorbent material was applied in three adsorption-desorption cycles without a significant loss in adsorption capacity.

Keywords Adsorption · Chromium · Magnetite · Mechanism · Pine cone · Regeneration

12.1 Introduction

Among the pollutants found in water, heavy metals are of concern because they are non-biodegradable, hence leading to accumulation in the environment. Even at low concentrations these metals may interfere with normal biological processes, hence

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becoming toxic resulting in either heavy metal poisoning or genetic disorders. The removal of these metal species from water is therefore critical to the general availability of clean water for human and animal consumption. Chromium is a highly soluble metal pollutant with strong oxidizing properties which can cause irritation in plant and animal tissues [1–3]. It has several uses including metal plating, leather processing, surface treatments and in refractories [3, 4]. It exists in six oxidation states with the trivalent [Cr(III)] and hexavalent [Cr(VI)] states being the most prevalent in water [5]. Trivalent chromium is an essential nutrient while the hexavalent form is toxic, carcinogenic, teratogenic and mutagenic to living organisms [1, 6]. The maximum levels permitted for chromium in water are 5 mg L^{-1} and 0.05 mg L^{-1} for Cr(III) and Cr(VI)respectively [5, 6]. The removal of chromium from contaminated water has been investigated over the years with different methods being reported for water treatment. All these methods are aimed at reducing the level of pollutants to produce water suitable for human consumption or agricultural use. The methods for remediation of Cr(VI) contaminated water include oxidation, coagulation-flocculation, ion exchange, membrane separation and adsorption among others [7, 8]. Among these methods, adsorption has been considered the most favorable due to its low operation cost and versatility. However, the mechanism of hexavalent chromium adsorption is still not well documented. In our previous work we described the adsorption of Cr(VI) onto FTP-MNP, a composite biosorbent made from pine cone powder and magnetite nanoparticles with detailed characterization of the prepared adsorbent and analysis of the adsorption parameters [9]. This study therefore proceeds by providing an insight into the adsorption mechanism of Cr(VI) remediation using FTP-MNP and the regeneration efficiency of the adsorbent material.

12.2 Experimental

12.2.1 Materials

Sodium hydroxide (NaOH, >98%) and potassium dichromate ($K_2Cr_2O_7$, >99%) were purchased from Associated Chemical Enterprises (South Africa). Ammonium hydroxide (NH_4OH, 25%) was supplied by Labchem (South Africa). Hydrochloric acid (32%) and ferrous sulphate ($FeSO_4{\cdot}7H_2O$, >98%) were supplied by Merck. Ferric chloride ($FeCl_3{\cdot}6H_2O$, >99%) and sodium arsenite ($NaAsO_2$, >90%) were purchased from Sigma-Aldrich. All chemicals were used without any further purification. All syntheses were carried out under nitrogen atmosphere with vigorous stirring to ensure uniform dispersions.

12.2.2 Methods

The synthesis of the composite material is described in detail in our previous work [10]. Briefly, the material was prepared in a single step co-precipitation method where 1.5 g of Fenton's treated pine cone powder was added to degassed water followed by the addition of ferrous and ferric salts and precipitation with ammonium hydroxide at 60 °C under nitrogen atmosphere.

12.2.2.1 Determination of Cr(VI) Adsorption Mechanism

To determine the effect of solution pH, solutions of 100 mg L^{-1} Cr(VI) were prepared in separate volumetric flasks and the solution pH in each flask was varied between 2 and 12 using 0.01 HCl and 0.01 M NaOH. 0.5 g of the adsorbent was introduced into a separate sealable flask containing 100 cm^3 of each solution and agitated for 2 h. The solution pH and redox potential before and after adsorption were determined on a Crison Basic 20 pH meter.

12.2.2.2 Desorption and Regeneration

To determine the most appropriate solvent for desorption, 0.1 L of 200 mg L^{-1} solution of Cr(VI) was contacted with 1 g of the adsorbent material for 2 h. After adsorption, the adsorbent was filtered, washed with deionised water and dried overnight. The chromium loaded adsorbent was then shaken in either deionised water (H_2O), 0.1 M acetic acid (AA), 0.1 M hydrochloric acid (HCl) or 0.1 M sodium hydroxide (NaOH) for 2 h and filtered to obtain the supernatant solution while the spent adsorbent was washed and dried for reuse. The residual solutions after adsorption and desorption were both analysed for Cr(VI) content.

Cr(VI) concentration was determined spectrophotometrically following the diphenyl-carbazide method at a wavelength of 540 nm [11]. Total chromium concentration was determined on a Shimadzu AA 7000 Atomic Absorption Spectrophotometer with an air/acetylene flame and wavelength of 357.9 nm. Cr(III) concentration was determined as the difference between total chromium and Cr(VI) concentrations. X-ray photoelectron spectroscopy (XPS) studies were performed using XPS microprobe (PHI 5000 Scanning ESCA Microprobe ULVAC-PHI Inc) with Al Kα radiation ($h\nu = 1486.6$ eV).

12.3 Results and Discussion

During the removal of hexavalent chromium from solution, mechanistic pathways have been proposed based on two principles namely: (i) electrostatic attraction of negatively charged Cr(VI) ions in solutions to the adsorbent surface, and (ii) reduc-

tion of Cr(VI) to Cr(III) followed either by adsorption or repulsion by the adsorbent surface. The mechanism for chromium removal from aqueous solutions by biomaterials has been determined to be by direct and indirect reduction [12]. In the direct reduction mechanism, Cr(VI) is reduced to Cr(III) by the electron donating groups of the biomaterial. The indirect reduction mechanism is a three step process in which anionic Cr(VI) ions bind to cationic groups on the biomaterial surface, Cr(VI) ions are then reduced to Cr(III) by adjacent electron donating groups followed by either the release of Cr(III) into the solution due to repulsion or complexation with adjacent groups [12]. The proposed mechanisms each lead to the consumption of hydrogen ions therefore raising the solution pH during adsorption. Both mechanisms have been shown to describe the adsorption of Cr(VI) on lignocellulosic biosorbents and iron oxide nanoparticles [13, 14]. To determine which of the mechanisms was responsible for the removal of Cr(VI) from solution, the parameters associated with each mechanism were considered. These parameters include the change in hydrogen ion (H^+) concentration, change in the oxidation-reduction potential (ORP) of the solution and the total amount of chromium ions (total Cr) left in the solution after adsorption.

12.3.1 Change in H^+ Concentration

The adsorption of hexavalent chromium is highly dependent on solution pH and has been reported to be favoured by its high redox potential (+1.3 V) at acidic pH [5]. The optimum pH for Cr(VI) adsorption was found to be pH 2 where $HCrO_4^-$ is predominant [9]. This species has low adsorption free energy and is therefore favourably adsorbed at low pH when the adsorbent surface is positively charged allowing for electrostatic attraction with the anionic species [15]. Reduction of Cr(VI) to Cr(III) in the presence of organic matter and magnetite results in the consumption of hydrogen ions as shown in Eqs. 12.1 and 12.2 [16, 17]. Cr(VI) can be reduced by electron donor groups on the biomass which have a lower reduction potential than that of Cr(VI) (1.3 V) [13].

$$HCrO_4^- + \textit{Organic matter} + H_3O^+ \rightarrow Cr^{3+} + H_2O + CO_2 \tag{12.1}$$

$$6Fe_3O_4 + 8H^+ + 2HCrO_4^- \rightarrow 9\gamma - Fe_2O_3 + 2Cr^{3+} + 5H_2O \tag{12.2}$$

At low solution pH the change in hydrogen ion concentration was high due to large amounts of Cr(VI) being either bound or reduced by the adsorbent (Fig. 12.1). As the solution pH was raised the change in H^+ was reduced and the amount of Cr(VI) removed was lowered.

In both the electrostatic attraction and adsorption coupled reduction mechanisms, removal of Cr(VI) is favoured at lower solution pH due to the presence of high concentrations of hydrogen ions. The consumption of hydrogen ions also causes the solution pH to increase during the reduction of Cr(VI) to Cr(III) [18]. The change

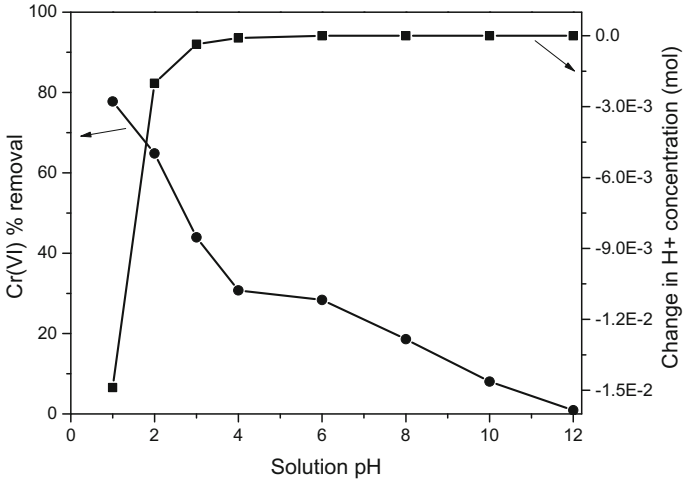

Fig. 12.1 Effect of solution pH on Cr(VI) removal and change in H^+ concentration

in H^+ concentration was therefore not sufficient in determining whether the adsorption of Cr(VI) onto FTP-MNP proceeded through either electrostatic attraction or reduction to Cr(III).

12.3.2 Cr(III) Concentration After Adsorption

The amount of Cr(III) ions in solutions was determined to confirm whether the reduction in Cr(VI) concentration was due to electrostatic attraction or conversion to Cr(III). In the electrostatic attraction mechanism, only Cr(VI) ions are expected to be present in solution since there is no reduction expected to take place. In the reduction coupled adsorption however, Cr(III) ions are present in the solution. This is a result of the reduction process which may be followed by some of the formed Cr(III) ions being adsorbed while others are repelled back into the solution by positive charges on the adsorbent surface. Therefore, the total amount of chromium in solution is the sum of Cr(VI) and Cr(III) in the solution. In the case of complete reduction from Cr(VI) to Cr(III) as reported by Sanghi et al., the chromium left in solution only consist of Cr(III) ions [19].

Throughout the studied pH range there was some amount of Cr(III) ions remaining in the solution after adsorption (Fig. 12.2). The highest amount of Cr(III) was observed at lower solution pH due to the presence of high amounts of H^+ ions aiding in the reduction of Cr(VI) to Cr(III). However, at high solution pH the amount of Cr(III) was lower due to repulsion of Cr(VI) anions from the negatively charged adsorbent surface, therefore resulting in low reduction. Some of the formed Cr(III) ions were not adsorbed due to repulsion of the cations by the positively charged

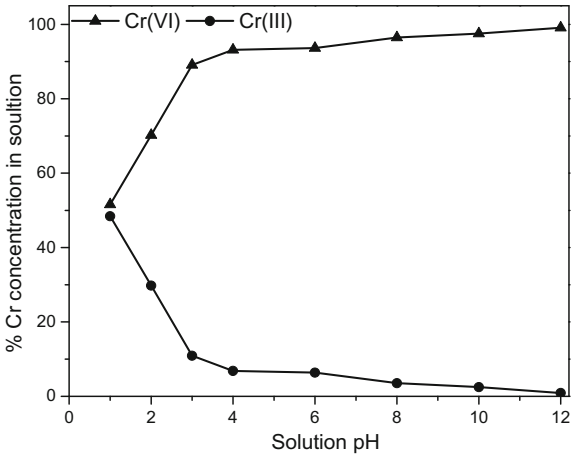

Fig. 12.2 Cr(VI) and Cr(III) concentration in solution after adsorption

adsorbent surface, leading to higher amounts of Cr(III) in solution at low solution pH since there was maximum reduction at low pH following higher redox potentials.

12.3.3 Change in Redox Potential

The difference in oxidation reduction potential (ORP) of the solution before and after adsorption was determined in order to confirm Cr(VI) reduction to Cr(III). A reduction in ORP indicates Cr(VI) reduction as observed by Yu et al., when nanoscale zero-valent iron particles which have a strong reductive capacity were introduced into Cr(VI) wastewater [18]. During Cr(VI) adsorption onto FTP-MNP the difference between the final and initial ORP of the solution increased with increasing pH (Fig. 12.3). This was because of decreased Cr(VI) reduction as the pH of the solution increased with greater decreases in ORP being observed at lower pH where higher Cr(VI) reduction was expected. Similar trends have been reported for Cr(VI) reduction by magnetite indicating that reduction to Cr(III) decreases as pH increases [20, 21].

12.3.4 XPS Analysis

The XPS spectra of FTP-MNP before and after Cr(VI) adsorption were studied to determine the changes in surface states resulting from the adsorption process. The survey spectrum of the chromium loaded adsorbent showed that all peaks from the

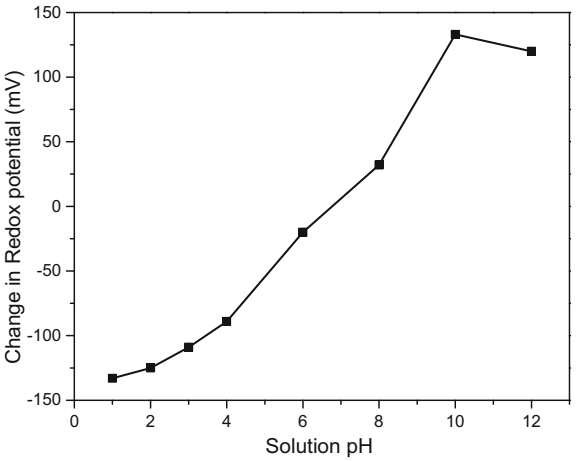

Fig. 12.3 Change on redox potential with solution pH

pristine adsorbent were retained with the introduction of a new peak at approximately 580 eV assigned to Cr2p (Fig. 12.4) [15].

The O1 s peak in Fig. 12.5a was slightly shifted from 529.4 to 529.9 eV after Cr(VI) adsorption indicating that oxygen containing groups were involved in the binding of Cr(VI) to the FTP-MNP surface. The Cr2p band (Fig. 12.5b) consisted of two peaks at 587 and 575 eV which were assigned to $Cr2p_{1/2}$ and $Cr2p_{3/2}$ representing Cr(VI) and Cr(III) respectively [15]. The presence of both peaks suggested that Cr(VI) was

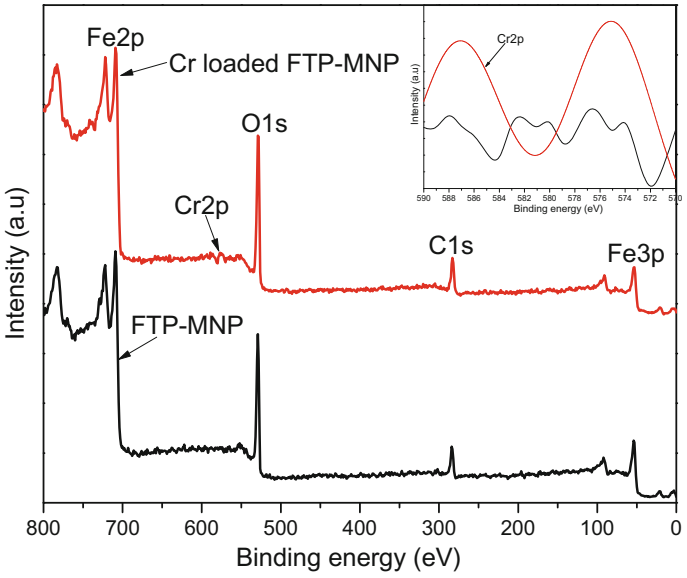

Fig. 12.4 XPS full spectra before and after Cr(VI) adsorption (Inset: Cr2p peak comparison)

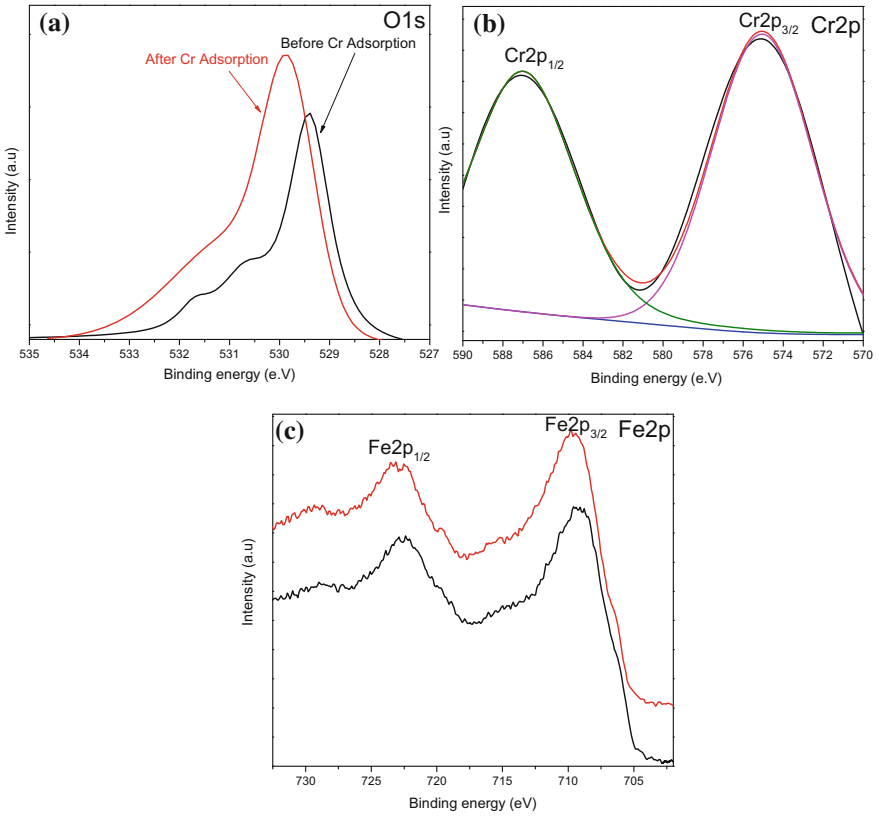

Fig. 12.5 XPS spectral comparisons of FTP-MNP before and after Cr(VI) adsorption

adsorbed and later reduced to Cr(III) on the adsorbent surface [22]. The reduction of Cr(VI) to Cr(III) at acidic pH or in the presence of organic matter follows a redox reaction (Eq. 12.3) [15]:

$$HCrO_4^- + 7H^+ + 3e^- \rightarrow Cr^{3+} + 4H_2O \tag{12.3}$$

The binding energies for $Fe2p_{1/2}$ and $Fe2p_{3/2}$ showed no significant shift after chromium adsorption at energies of 722.6 and 709.3 eV in the pristine adsorbent and 722.9 and 709.6 eV in the chromium loaded adsorbent (Fig. 12.5c). The constant binding energies for Fe2p indicate that there was no Cr substitution in the iron phase of the adsorbent and the magnetite phase was retained throughout the adsorption process [14, 22].

12.3.5 Desorption and Adsorbent Regeneration

Regeneration of spent adsorbents is important in making the adsorption process more economical [23]. In order to determine the reusability of the adsorbent it is important to establish the most suitable eluent solution to desorb the bound adsorbate from the adsorbent surface. Desorption studies are important in the practical considerations of adsorbents for water treatment [24]. Desorption of Cr(VI) was tested using four eluents namely deionised water (H_2O), 0.1 M acetic acid (AA), 0.1 M hydrochloric acid (HCl) and 0.1 M sodium hydroxide (NaOH). The adsorption of Cr(VI) was pH dependent, therefore desorption was also affected by the pH of the eluent solution. The percentage efficiency of desorption was calculated using Eq. 12.4 and the results are presented in Fig. 12.6a [25]. The efficiency of the eluents was in the order H_2O < AA < HCl < NaOH and NaOH was therefore considered the best eluent and was used in the determination of adsorbent reusability. The presence of OH^- ions from NaOH led to the formation of soluble sodiumchromate which was released into the solution [26].

$$Desorption\ (\%) = \frac{amount\ desorbed}{amount\ adsorbed} \times 100 \tag{12.4}$$

The reusability of the adsorbent was studied by consecutive adsorption-desorption cycles (Fig. 12.6b). After each adsorption, the loaded adsorbent was shaken with the eluent solution, then filtered and washed with deionised water and dried before being contacted with the adsorbate solution. After three cycles the adsorbent retained >85% of its initial adsorption capacity. FTP-MNP was therefore favourable for Cr(VI)

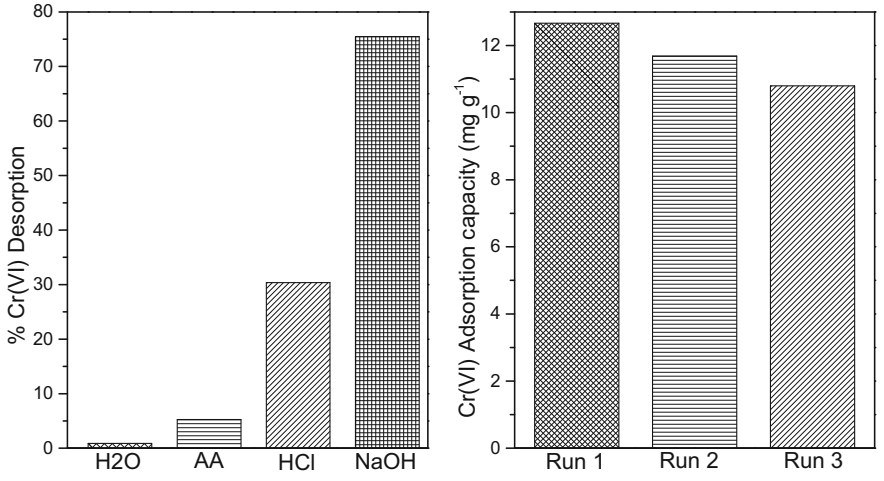

Fig. 12.6 **a** Desorption efficiency using different solvents and **b** reusability of FTP-MNP for Cr(VI) adsorption

adsorption and can be applied in up to three cycles therefore increasing its cost efficiency.

12.4 Conclusion

The adsorption of hexavalent chromium was optimum at low solution pH where electrostatic attraction was responsible for the binding of anionic chromium species to the adsorbent surface. Hydrogen ions were used up during both Cr(VI) binding and reduction to Cr(III) resulting in an increase in solution pH after adsorption. The presence of Cr(III) ions after adsorption and a change in redox potential further confirmed that Cr(VI) was reduced to Cr(III) during the adsorption process. XPS analysis further indicated that Cr(VI) ions were bound to the adsorbent surface as well as Cr(III) therefore confirming that the mechanism of Cr(VI) adsorption onto FTP-MNP was via adsorption coupled reduction. The adsorbed Cr(VI) was successfully desorbed using 0.1 M sodium hydroxide and the adsorbent was reused twice, losing less than 15% of its initial capacity.

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