

A Novel Technique for Hexavalent Chromium Reduction

Mohammed S. El-Ali Al-Waqfi¹ and Basim Ali Telfah²

¹Technical Monitoring & Auditing Manager, Ministry of Water & Irrigation, Amman-Jordan

²Former Secretary General, Ministry of Water & Irrigation, Amman-Jordan

Received 30 June, 2017; Accepted 6 Feb, 2018

Abstract

This study presents a novel technique for the reduction of Cr(VI) to Cr(III) in an acidic aqueous medium. This technique is a batch treatment that utilizes an iron rotating disc as the reductant metal. The removal of the Cr(VI) under various conditions, including retention time, rotation rate, ion initial concentration and the initial pH of the solution, was investigated in this study. The effect of the shape of the rotating iron piece on the Cr(VI) reduction was also examined. It was found that the efficiency of removal of Cr(VI) initially, increased with increasing rate of rotation, retention time and the surface area of the disc until the dichromate ions were totally consumed or a state of equilibrium was reached. Conversely, the removal efficiency of Cr(VI) was found to decrease with the increasing of the solution pH and the initial concentration of Cr(VI). Almost the complete removal of Cr(VI) was achievable in a retention time of fifteen minutes at pH being 1.5 and the initial concentration reaching 100 ppm. Practically, the removal of the Cr(VI) become independent of the rotation rates above 600 rpm with the retention time being more than fifteen minutes. The use of a fan-shaped iron piece, unexpectedly, showed insignificant advantages over the rotating disc as the retention time increased.

© 2018 Jordan Journal of Earth and Environmental Sciences. All rights reserved

Keywords: Cr (VI); Reduction; Low-cost reductants; Iron rotating disc

1. Introduction

Chromium is an inorganic pollutant of a prime concern to scientists and engineers working in the field of the environment and the conservation of water resources. It can exist in several forms; the most common and stable ones are Cr(VI) and Cr(III) as in dichromates ($\text{Cr}_2\text{O}_7^{2-}$) and chromium hydroxide ($\text{Cr}(\text{OH})_3$). Chromium can make its way into waters and soils through chemical spills or inadequately treated industrial wastewaters. Cr(III) and Cr(VI) significantly differ in their toxicities, mobilities, and (bio)availabilities. Cr(III) is vital for glucose metabolism in our bodies. While it is essential in animal food, it is harmful to plants only at very high concentrations [Moore and Ramamoorthy, 1984], on the other hand, hexavalent chromium is exceptionally toxic to humans as well as to animals and plants. Also, Cr(VI) is considered by the US Toxicology Program as a pulmonary carcinogen. Unlike Cr(III), which is relatively immobile and can simply be precipitated as hydroxide, Cr(VI) is easily transported through soils and aquatic environments [Richard and Bourg, 1991]. Furthermore, Cr(VI) is a strong oxidizing agent and can be absorbed through the skin. Despite their toxicity, Cr(VI) compounds are still extensively used in a wide range of industries (such as the tannery, corrosion inhibitors, stainless steel, inks, dyes, electroplating, etc) due to the good qualities and advantages of its applications.

The reduction of Cr(VI) to Cr(III) by S(IV) and Fe(II) followed by the precipitation of $\text{Cr}(\text{OH})_3$ has been the most commonly used technology for the elimination of hexavalent chromium encountered in industrial wastewaters. Evaporative recovery of concentrated hexavalent chromium wastes was also proved, technically and economically, to be a viable

treatment alternative. However, the increasingly stringent effluent standards made some industries utilize ion exchange for the disposal-off Cr(VI)-containing wastewaters. Lately, The application of other processes such as electrochemical and electro reduction of Cr(VI) using an iron metal has been extensively investigated (Eary and Ray, 1988; Cantrell et al., 1995; Powell et al., 1995; Sedlak and Chan, 1997; Blowes et al., 1997; Buergeand and Hug, 1997a; Beukes et al., 1999; Huang et al., 2008; Shamra et al., 2008; Yang et al., 2008; Abdo and Sedahmed, 1998; Demirbas et al., 2004.; Junyapoon and Weerapong, 2006; Chen et al., 215; Igcalinos and Besagas, 2016;). The reduction rates and the subsequent precipitation as hydroxide were adequately rapid and may, therefore, offer a practical treatment option for the industry (Gould, 1982; El-Shazly et al., 2005; Zhu et al., 216).

The currently used processes for the electrochemical reduction of Cr(VI) by iron, mostly employ the metal in the form of wool, chips or shots (small spheres) contained in packed columns, rotating chambers or tumble barrels. In such equipment, the iron surface is vulnerable to become covered with the metal oxidation secondary products as well as the settleable materials present in the effluents treated. Packed columns are, in particular, prone to clogging and flooding complications. Several workers have reported the formation of magnetite (Fe_3O_4), green rust ($\text{Fe}_4\text{Fe}_2(\text{OH})_{12}\text{SO}_4\cdot\text{H}_2\text{O}$), goethite (FeOOH) and ferric hydroxide ($\text{Fe}(\text{OH})_3$) on the metal surface (Mackenzie et al., 1999; Scherer et al., 1998; Pratt et al., 1997; Lee et al., 2003; Ponder et al., 2000; Kendelewicz et al., 2000; Gilmore et al., 1998; Buerge and Hug, 1999 b). Furthermore, these equipments are relatively difficult to design and are associated with high power consumption and

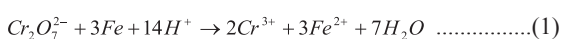
* Corresponding author. e-mail: Mahammad_Al-waqfi@mwi.gov.jo

cost.

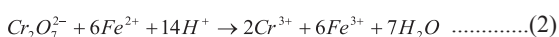
In view of the drawbacks associated with such techniques, an attempt was made to develop an easy, and efficient, as well as potentially economical method for the treatment of Cr(VI) which can be scaled up to suit the needs of small industrial firms, meeting at the same time the strict effluent standards. An iron-rotating disc was, therefore, chosen as the reductant metal. In addition to the elimination of the likely clogging problems associated with some of the current techniques, the rotating disc also provides a stirring action to the treated solution promoting the mass transfer of the fresh reactants to the metal's surface and the released ferrous ions to the bulk of the solution. The stirring action also hinders the concentration of reaction products in the vicinity of the disc, thereby lessening the tendency of formation of precipitates on the metal's surface. The formation of precipitates may unfavorably affect the reduction rate of hexavalent chromium to the trivalent state. In addition, the rotating disc has the advantage of providing an easily controllable and accessible surface area, an important parameter for scale up and design purposes. Moreover, with a properly designed continuous stirred reactor, the novel technique may be applied in a continuous treatment mode; making it adequate to industries with high discharges of Cr⁶⁺. Finally, iron is an inexpensive and widely available material.

As is known, the position of iron and its ferrous ions in the electrochemical series is higher than that of hexavalent chromium, which implies that both types are capable of reducing Cr(VI) ions and displacing them from solution in a redox manner as follows (Patterson, 1985):

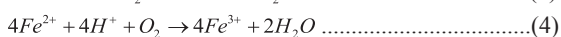
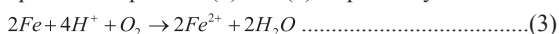
Reaction of dichromate with iron



Reaction of ferrous ions with dichromate



Dissolved oxygen also reacts with iron and its ferrous ions as depicted in Equations (3) and (4) respectively.



Eqs. (1) and (2) clearly imply that the reduction reactions of dichromate require acid and are thus pH dependent. As manifested by Eqs. (3) and (4), dissolved oxygen oxidizes the iron metal to the ferrous state, which is oxidized further to ferric ions. Consequently, well-aerated solutions are expected to consume more iron.

In this research paper, the reduction of Cr(VI) using an iron metal as a rotating disc was investigated. The studied parameters include the initial pH of a wastewater sample, the initial Cr(VI) concentration, the retention time, the rotation rate and the surface area of the rotating disc as well as its shape.

2. Materials and Methods

2.1. Materials

The polluted water sample studied was taken from a dichromate bright dip tank. In such a case, the dichromate solution is expected to contain, in addition to the sodium ions, ferrous and cadmium ions as a result of the bright dipping of cadmium-plated screws and nuts. The concentrations of cadmium and ferrous ions tend to increase with time due to the successive dichromate treatments of the cadmium

plated items. As indicated by Eq. (2), the presence of high concentrations of Fe²⁺ can seriously interfere with the assessment of using the rotating disc as a means for the hexavalent chromium reduction. On the other hand, cadmium ions are expected to have an insignificant influence on the subsequent immobilization of the trivalent chromium ions resulting from the reduction process. Both cadmium and chromium hydroxides are precipitated upon the addition of sodium hydroxide to the solution. While pH at pH 1.5, the solubility of Cr(OH)₃ is minimal; cadmium hydroxide is relatively soluble (Patterson, 1985). The wastewater sample investigated was, therefore, taken from a freshly prepared dichromate bath so that high concentrations of Fe²⁺ and Cd²⁺ were avoided. The analysis of the studied sample is shown in Table 1.

Table 1. Analysis of the investigated wastewater sample.

Constituent	Concentration, mg/l
Cr(VI)	3000
Cd ²⁺	N.D.
Fe ²⁺	19
pH	11

2.1. Experimental set up and procedure

The bench-scale experimental setup used in the current study is shown in Fig. (1). It consisted of a 2000 ml beaker and a rotating disc made of mild steel (S.T37) fitted with a ¼ hp-variable speed motor via a rotating shaft made of stainless steel to avoid the interference of the shaft material in the reduction process. The variable speed motor was capable of providing rotation rates ranging from 0-1800 rpm (revolution per minute). The motor's speed was adjusted via a calibrated control knob incorporated in the motor assembly. Each time the motor's speed was adjusted, a tacho meter was used for the verification of the rotation rate reading.

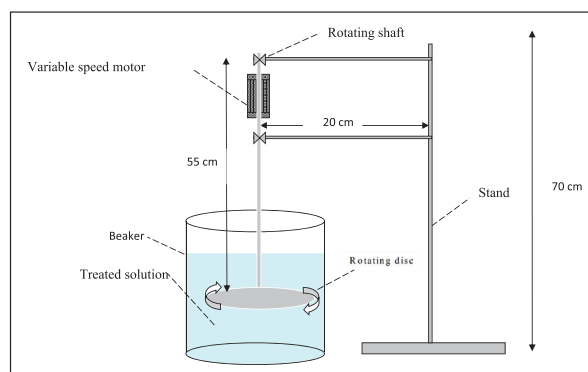


Figure 1. Schematic diagram of the experimental setup.

A horizontal arrangement of the rotating disc was selected to ensure axial symmetry and hence avoid the non-uniformity of the flow regime, generated by the rotating disc that might arise by the action of gravity. Such non-uniformity may interfere with the reduction process through affecting the mass transfer rates of the reacting species from the bulk of solution to the iron metal as well as the diffusion of the dissolved ferrous ions away from the metal's surface. The rotating shaft was therefore kept in an upright position by being clamped to a vertical stand.

At the beginning of each experiment, the iron disc was washed with distilled water and dried with air and degreased with benzene, then acetone to make sure neither fingerprints

nor traces of grease were left on the metal surface. Such traces of dirt act as a barrier preventing contact between the metal's surface and the solution interfering with the redox reactions, which are responsible for the treatment.

A forty-litre solution of hexavalent chromium was taken from the dichromate dip tank and was used as a stock solution. Different solutions of hexavalent chromium were prepared by diluting samples from the stock solution to the required initial concentrations. Solutions of concentrations of 1000, 750, 500, 300, 100 and 50 ppm of hexavalent chromium were made up.

A set of batch treatments on the sample solutions were conducted to investigate the effects of the different parameters on the removal efficiency of Cr(VI). The studied parameters included the initial pH of sample, the retention time, Cr(VI) initial concentration, the surface area of the disc, its shape, and the rotation rate. The initial pH of the samples was adjusted by using either 1 N NaOH or 1 N H₂SO₄. All experiments were conducted at room temperature. Also, the reproducibility of the results was tested by conducting a set of triplicated runs under the same experimental conditions.

Prior to chemical analysis, the treated samples were filtered through a 0.45 µm membrane filter and their pH was adjusted to a value of 8.5, so that trivalent chromium would form an insoluble precipitate (i.e., chromium hydroxide, Cr(OH)₃), which could then be easily removed, and thus the solution arrives at the lowest total chromium concentration; the optimum pH value at which the solubility of chromium hydroxide is minimal is 8.5. The filtrate was then analyzed for the determination of the remaining concentrations of Cr(VI) according to the Standard Methods for the Examination of Water and Wastewater, (21st edition) using a HACH Direct Reading Spectrophotometer (model DR2000). All the reagents used were of AR grade (HACH, USA). A microprocessor pH meter (model pH3000.WTW) was used for the measurement of pH.

2.3. Data Treatment

The removal efficiency of Cr(VI) was calculated according to the following equation,

$$\text{Removal efficiency(\%)} = \frac{\text{Initial concentration of Cr(VI)} - \text{remaining concentration of Cr(VI)}}{\text{initial concentration of Cr(VI)}} \times 100 \dots (5)$$

3. Results and Discussion

3.1. Effect of Retention Time

Figs.2 and 3 illustrate the variation of Cr(VI) removal with the retention (i.e., contact) time. At the beginning of the reduction process, the removal of Cr(VI) significantly increased and as time elapsed, a stage with almost constant removal efficiency was reached. As the reaction time proceeded further, anions were, increasingly, consumed in the reaction till they were totally removed or an equilibrium phase was reached. It is also apparent from Figs.2 and 3 that almost complete removal of Cr(VI) was almost achievable in about fifteen-minute time for the wastewater samples of low starting pH. Moreover, both figures indicate that the starting pH was a key factor in influencing the retention time required for attaining complete removal and/or reaching equilibrium stage; lower pH favored shorter times for attaining equilibrium conditions.

The initially observed sharp rise in the removal efficiency

of Cr(VI) can be attributed to the intense evolution of hydrogen gas observed at the surface of the rotating disc at the onset of the reduction process as a result of the reaction of hydrogen ions with iron. The liberated hydrogen gas bubbles may have resulted in the development of local turbulent eddies, which in turn disturbed the diffusion boundary layer adjacent to the disc's surface and hence enhanced the mass transfer of fresh reactants from the solution bulk to the reductant metal surface. As the dichromate concentration decreased with time, the driving force for the diffusion from the solution bulk to the surface of the rotating disc progressively diminished, the reduction rate of Cr(VI) was retarded as demonstrated by the plateau part of the curves of Figs. 2 and 3.

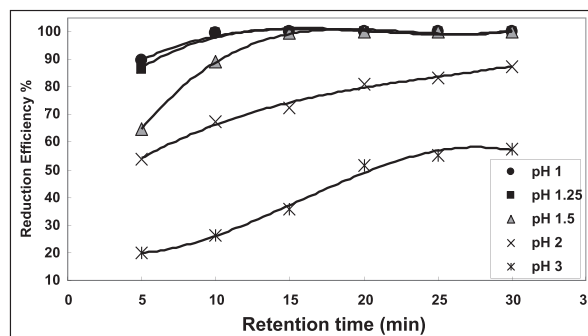


Figure 2. Effect of retention time on removal efficiency of Cr(VI) (initial concentration 50 mg/l, radius of RD 4.75 cm and rotation rate 600rpm).

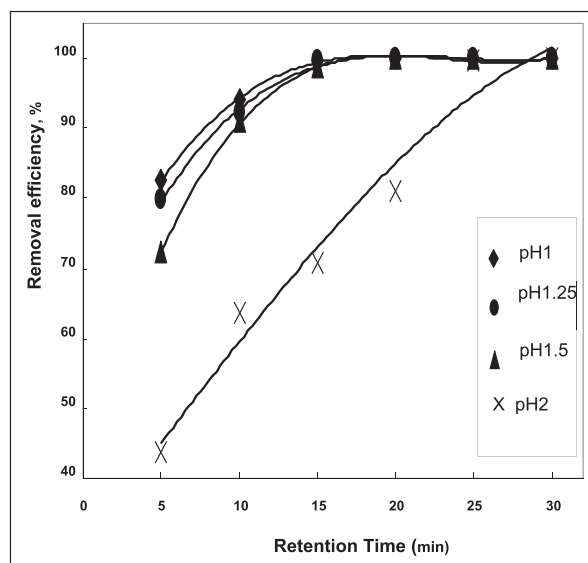


Figure 3. Effect of retention time on removal efficiency of Cr(VI) (initial concentration 50 mg/l, radius of RD 4.75 cm and rotation rate 600rpm).

3.2. Effect of Initial Concentration

As shown by Fig. 4, when the initial concentration of Cr(VI) increased, the removal efficiency was relatively reduced, and the time required for attaining high removals and/or approaching equilibrium state was, significantly, increased. This rise in the equilibrium retention time may be attributed to the growing deficiency in the excess hydrogen ions. As the redox reactions advance; the availability of excess hydrogen ions becomes vital for the occurrence of the reduction process. This was clearly supported by the significant increase in the pH of the treated samples with increasing retention time due to the progressive acid consumption by the redox reactions, as revealed by Fig. 5.

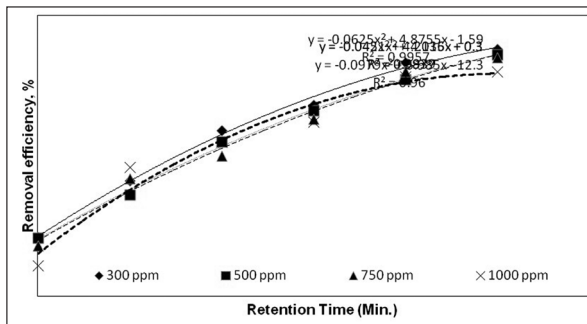


Figure 4. Effect of retention time on removal efficiency of Cr(VI) at different initial concentrations (initial pH 1.5, radius of RD 4.75 cm, rotation rate 600rpm).

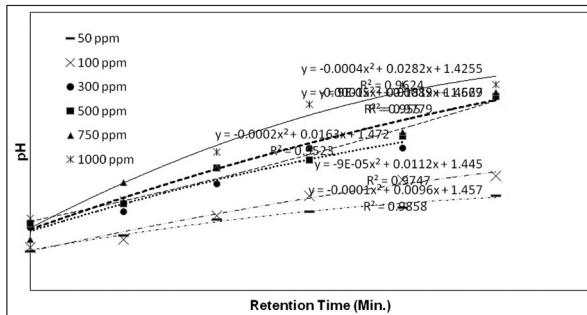


Figure 5. Variation of solution pH with time (initial pH 1.5, radius of RD 4.75 cm, rotation rate 600rpm).

In the current study, the minimum retention time to achieve approximate complete removal of Cr(VI) was much shorter than that reported in the literature. For example, Junyapoon and Weerapong (2006), who used scrap iron filings as the reductant metal, obtained a complete reduction of Cr(VI) in a retention time of 180 minutes. These results may, therefore, confirm the advantages of the rotating disc over other forms of iron used for the reduction of Cr(VI). As mentioned earlier, the rotating disc may have caused some sort of mixing due to the laminar flow developed by its rotation, which may have enhanced the diffusion of fresh reactants to the iron surface. The streamlines generated under laminar flow conditions may also have resulted in unfavorable conditions for the precipitation of the reaction products on the metal surface. Accordingly, better accessibility of the reactants to the iron metal surface was warranted.

3.3. Effect of Initial pH

Generally speaking, the pH of the treated solution may affect the reduction of Cr(VI) via influencing what follows,

- Availability of excess H^+ necessary for the reduction-oxidation reaction to occur;
- Cr(VI) anions adsorption on the metal surface;
- The passivity of the rotating disc surface.

To investigate the effect of the initial pH of the treated solution on the elimination of Cr(VI), the variation of the removal efficiency over a range of initial pH was, therefore, examined. As shown in Fig. 6, for the same retention time, the removal efficiency rapidly and progressively improved with decreasing the initial pH until an equilibrium phase and/or a complete removal was reached. This behavior was more noticeable at higher retention times, thus, indicating that an optimum combination of initial pH and retention time could be sought out in order to maximize the removal efficiency of Cr(VI). Moreover, the reduction reaction represented by

Eq. (1), which is believed to be the most significant reaction in the process, requires acid and is thus pH dependent. In other words, the removal of Cr(VI) was favored by low pH as has also been confirmed recently by Chen et al (2015) and Zhu et al. (2016). In addition, the low initial pH values may have encouraged the adsorption of dichromate ion on the metal surface, hence, facilitating the occurrence of the redox reaction. As the pH of the solution increases, the metal surface tends to become negatively charged and the adsorption of similar ions (e.g., the dichromate ions) is, therefore, expected to be retarded due to electrostatic repulsion (Tokunaga et al., 2001). It is also strongly believed that the heterogeneous process (solid-liquid reaction) of dichromate sorption on the metal surface is an essential step to the commencement of the reduction reaction, which takes place according to Eq. (1). This is supported by the current findings, which may indicate that sorption of hexavalent chromium (as CrO_4^{2-}) was strongly pH dependent and was less likely to occur at high pH values. Eary and Rai (1998) proposed that chromate was not adsorbed in biotite at high pH. Similarly, Zachara et al. (1987) reported that chromate was not adsorbed onto iron oxides at pH of 11.5 to 12. Later, Swietlik (2002) reported that at pH 6, Cr(VI) was primarily present in an adsorbed form while as pH increased, the concentration of the dissolved chromates rose until it became completely in solution at pH 8.8. Several investigators observed the formation of passive insulating layers of magnetite and green rust on the surface of zero-valent iron (Brown and Chambers., 2002; White and Paterson, 1994; Williams and Scherer, 2001; Brown and Chambers, 2002). The oxidizing surface was also found to be, increasingly, susceptible to passivation at high pH values as suggested by Lee et al. (2003), and Yongtian (2003). Niu et al. (2005) also reported insignificant Cr(VI) reduction efficiencies due to the formation of magnetite and goethite on the iron surface under alkaline conditions. In the current study, the passivation and shielding of the rotating disc surface were less likely to occur due to the low pH values as well as the short retention times used, which may have played an important role in averting products' precipitation. In addition, practically, the rotating disc creates laminar flow conditions, which swirl the solution in the vicinity of the disc hindering deposit formation on the metal surface. Similar findings were reported by Alowitz and Scherer (2002), who found that the reduction rate of Cr(VI) by the iron metal varied significantly depending on the pH of the solution, being slower at higher pH values.

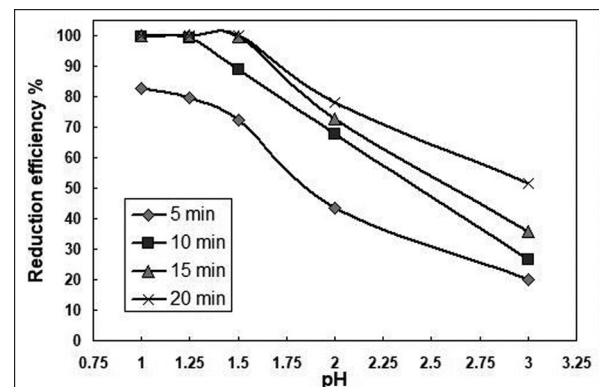


Figure 6. Removal efficiency versus initial pH, (radius of RD 4.75 cm, initial concentration 100 mg/l, rotation rate 600 rpm).

As revealed in the preceding sections, the initial pH of the treated sample highly impacted the time taken to achieve the maximum attainable removal efficiency and/or to reach equilibrium conditions. Fig. 7, which shows the variation of equilibrium time versus the starting pH, clearly indicates that the time taken to reach equilibrium was directly proportional to the initial pH of the sample. For instance, the equilibrium stage (i.e., the maximum attainable removal efficiency of Cr(VI)) for the same treated sample was achieved in a ten-minute time at the starting pH 1 compared to fifteen and forty minutes at an initial pH of 1.5 and 3 respectively. The relatively high removals noted for low initial pH samples could be mainly attributed to the enhanced availability of excess hydrogen ions; H^+ concentration is inversely proportional to pH. Consequently, to comply with regulatory requirements and effluent standards, the use of an optimum combination of pH and retention time is, therefore, vitally important.

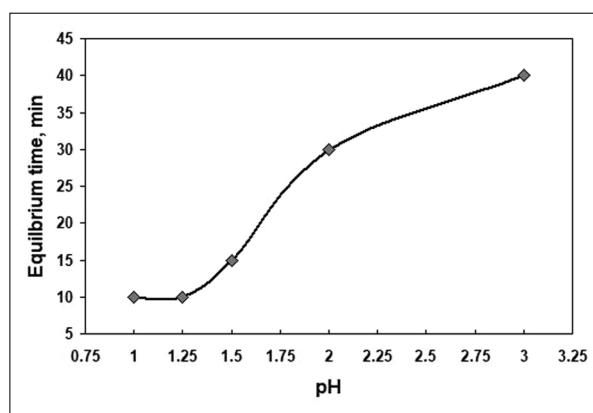


Figure 7. Variation of equilibrium time with initial pH (initial concentration 100 mg/l, radius of RD 4.75 cm, rotation rate 600 rpm).

3.4. The Effect of the Surface Area of the Disc

The effect of the surface area of the rotating disc on the removal efficiency of Cr(VI) was investigated using discs of radii of 3.45 cm, 4.00 cm, and 4.75 cm. The achieved results, displayed in Fig. 8, reveal that the removal efficiency of hexavalent chromium significantly increased as the rotating disc radius increased, but this rise was more pronounced at higher surface areas and longer retention times. Likewise, the utilization of a disc of a relatively higher area resulted in a shorter retention time for the achievement of approximate complete elimination of Cr(VI). For instance, at the retention time of four minutes, increasing the radius of the rotating disc from 3.45 cm to 4.00 cm, improved the removal of Cr(VI) from 31% to 43% in comparison with 42% to 51% when the radius increased from 4.00 cm to 4.75 cm. But at a retention time of fourteen minutes, the removal efficiency improved from 42% to 98% compared to 38% to 75% at a retention time of eight minutes when the radius increased from 3.45 cm to 4.00 cm. The results would have been more revealing if a wider range of surface areas were investigated. The observed sharp increase in the removal efficiency as the disc surface area increased may be attributed to the accompanying augmentation of the disc Re Nos., which increased from 83,704 in case of the 3.45 cm RD to 158,670 for the 4.75 cm RD. The Re No. 158,570 falls within the transitional flow region while the Re No. 83,704 is within the laminar flow regime. Higher Reynolds numbers enhance the transportation

of the reacting species to the disc surface, hence, improving Cr(V) removal. In addition, the greater availability of reactive sites as the radius increased may have contributed into the enhancement of the removal efficiency at the higher surface area of RD. Accessibility and availability of reactive sites allow for continuing the reduction of hexavalent chromium especially at higher retention times. It is believed that $Cr_2O_7^{2-}$ anions were adsorbed onto the surface prior to the commencement of the heterogeneous reduction reaction of Cr(VI) by Fe^0 (El-Shazly et al., 2005). The reduction of Cr(VI) in solution by Fe^{2+} (i.e., Equation (3)) is expected to have a less significant impact on Cr(VI) removal due to the competing spontaneous oxidation of ferrous to ferric ions as in Equation (4).

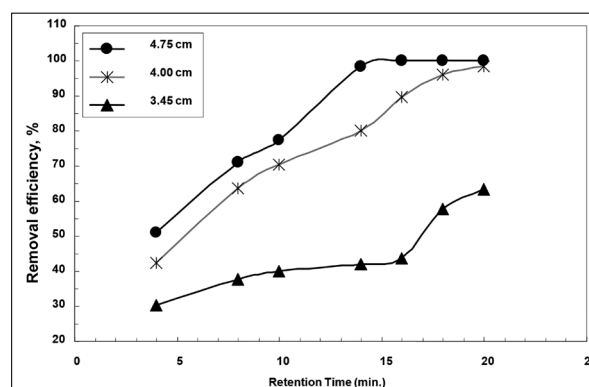


Figure 8. Effect of surface area of RD on the removal efficiency of Cr(VI) (initial concentration 100 mg/l, initial pH 1.5, 600 rpm).

However, other forms of the iron metal used for the reduction of Cr(VI) (e.g., fillings, chips, wool, shots and spheres) may experience some shielding effect and formation of agglomerates as well as the development of channeling especially in the case of fixed beds (Prasad et al., 2011; Lee et al., 2003). This necessarily reduces the effective area available for the reduction reaction. Meanwhile, the rotating disc provides higher percentage of the effective area of the iron, in addition to granting almost equal accessibility of the metal surface by the reactants. Accordingly, the minimum surface area of the rotating disc as well as the optimum retention time required for a complete removal of Cr(VI) may be determined easily.

The findings of the current study are consistent with the results reported by Niu et al. (2005) and Junyapoon and Weerpong (2006), who used nanoparticles and fillings of scrap iron respectively to remove Cr(VI) from aqueous solutions. They found that the removal efficiency was directly proportional to the available iron surface area.

3.5. The Effect of the Rotation Rate

To examine the effect of the rotation rate of the iron disc on the reduction of hexavalent chromium, the variation of the removal efficiency of Cr(VI) with the rotation speed was studied. The investigated speeds were 50, 100, 300, 500 and 600 rpm of Reynolds numbers falling within the transitional and laminar flow regions. Fig. 9 shows that that the removal efficiency increased (e.g., segment AB) with the rotation rate until the equilibrium (i.e., a constant removal) (e.g., segment BC) stage was reached. The initial rapid augmentation in the removal of Cr(VI) with increased rpm may indicate that the reduction reaction of Cr(VI) by iron

metal was diffusion (i.e., mass transfer) controlled, which is in agreement with earlier findings (El-Shazly et al., 2005). The increasing rotation rate expectedly increases the diffusion rate of the dichromate anions from the solution bulk to the disc across the boundary layer adjacent to the solid surface. The thickness of the solid surface is inversely proportional to the angular velocity (Levich, 1962) facilitating the mass transfer of the reacting types. On the other hand, increasing the rotation rate is mutually expected to enhance the diffusion of the reaction products away from the surface due to laminar flow conditions developed by the disc movement, thereby, minimizing the tendency of the formation of precipitates on the disc surface, which may inhibit electron transfer resulting in retardation of the reduction reaction. The equilibrium phase (e.g., BC segment) may imply that the removal efficiency of Cr(VI) became less dependent on the rotation rate, therefore, suggesting that at higher speeds the rate-determining step of the reduction process was the reaction kinetics rather than the diffusion of the reacting species through the bulk solution and the boundary layer. Junyapoon and Weerapong (2006) found that the reduction of Cr(VI) was directly proportional to the agitating rate and they similarly attributed this relationship to the enhancement of the diffusion rate of Cr(VI) from the solution bulk to the iron surface as the agitation rate increased; no constant removal efficiency zone was observed. In their study, the maximum rate investigated was 250 rpm due to limitations in agitator's capacity compared to the maximum rotation rate of 600 rpm of the current study, which may explain the inconsistency of the present results with theirs at rotation rates above 400 rpm. Earlier, it was found that the mass transfer coefficient rate and the rate of reduction of hexavalent chromium, using a fixed bed of scrap iron spheres, increased upon increasing the solution velocity (El-Shazly et al., 2005).

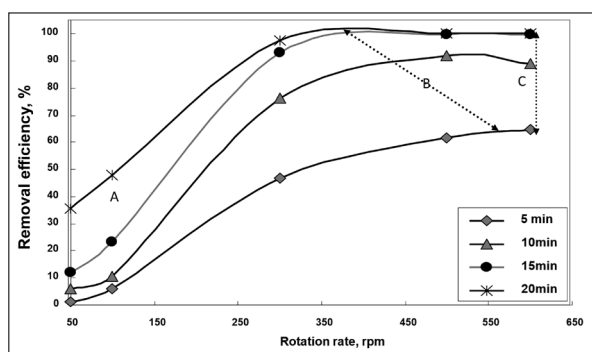


Figure 9. Effect of rotation rate on the removal efficiency of Cr(VI) (initial concentration 100 mg/l, initial pH 1.5, radius of RD 4.75 cm).

3.6. The Effect of the Shape of the Iron Piece

An attempt was made to enhance the removal efficiency of Cr(VI) by employing a fan-shaped rotating iron piece instead of the regular rotating disc as the reductant metal. Fig. 10 shows the variation of the removal efficiency with the retention time for both shapes of the same surface area. As shown, in the first eight minutes of the treatment, the fan-shaped piece resulted in a significant improvement in the removal of Cr(VI) over the regular disc. This advantage was diminished with increasing the retention time, until a stage, at which the performance of both shapes was nearly equal, was reached. It was also important to note that complete reduction

could be achieved at a retention time of about fifteen minutes by the rotating disc compared to nearly eighteen minutes in case of the fan-shaped piece. The experimental setup used in the present study can be considered as a stirred or a mechanically agitated tank, which is characterized by a very large spatial variation in the local energy dissipation rates. Two regions of low and high-energy dissipation rates, therefore, coexisted, which in turn resulted in two regions in relation to the flow. In the vicinity of the impeller (i.e., the rotating iron) fluid circulates (i.e., flows); whereas in the rest of the tank, or in the low energy prevailing region, the fluid relatively remains stagnant. The features of these two regions may substantially change depending upon the shape of the impeller used. On the other hand, fan-shaped impellers lead to higher energy dissipation rates in the close zone, so better mixing may be initiated due to the resultant vigorous fluid circulation (El-Ali, 2001). Accordingly, the higher removal efficiency of Cr(VI), initially observed by using the fan-shaped piece may be attributed to local turbulence created via the obstruction of solution circulation by the fan blades and thus positively influencing the mass transfer of the reactants from the solution bulk to the iron surface, which may lead to higher reductions of Cr(VI). As time elapsed, the fluid movement within the inclinations of the fan may have been hindered and hence adversely affected the diffusion of reaction products away from the reductant metal that tended to concentrate with time forming some sort of precipitates on metal surface. This situation may have led to the progressive decline in the performance of the fan compared to the rotating disc at longer retention times. Furthermore, the fan-shaped piece may have hampered the accessibility of the reactants to the iron surface unlike the rotating disc which offered easier access to the reducing metal.

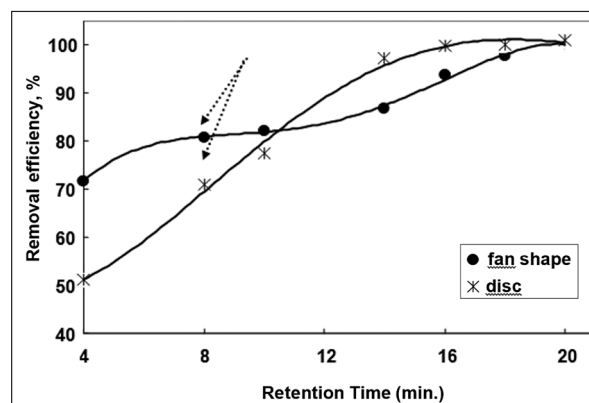


Figure 10. Effect of the shape of the rotating iron piece on the removal efficiency of Cr(VI) (initial concentration 100 mg/l, initial pH 1.5, radius of RD 4.75 cm, 600 rpm).

Conclusion

A complete reduction of Cr(VI) was achievable in a relatively short time by using an iron rotating disc.

The reduction rate of Cr(VI) increased with decreasing the initial pH. The optimum pH value (for removing Cr(VI) effectively from wastewaters having initial Cr(VI) concentration of less than 100 mg/l) was 1.5 at which almost a 100% efficiency was achieved in about fifteen minutes. For higher initial concentrations of Cr(VI) more time was required.

The removal of Cr(VI) increased with the increase in the

surface area of the rotating disc.

The removal efficiency of Cr(VI) was found to be, initially, directly proportional to the rotation rate of the rotating disc; the maximum removal was attained at about 600 rpm.

In practice, an optimum combination of the different parameters affecting the elimination of Cr(VI) should be sought out in order to achieve the minimum concentration of remaining Cr(VI).

The use of an iron rotating disc as a reductant metal for Cr(VI) may constitute a viable, easy, and potentially a cost-effective option to small industrial firms experiencing difficulties in the disposal of Cr(VI) –containing liquid effluents.

Abstract

A novel technique for the reduction of hexavalent chromium to trivalent chromium in acidic medium was studied. This technique is a batch treatment utilizing an iron rotating disc as the reductant metal. The elimination of Cr(VI) under different conditions of retention time, rotation rate, ion initial concentration and initial pH of the solution was investigated. The effect of the shape of the rotating iron piece on the Cr(VI) reduction was also examined. It was found that the removal efficiency of Cr(VI), initially, increases with increasing the rotation rate, retention time and the surface area of the disc until the dichromate ions are totally consumed or a state of equilibrium is reached. Conversely, the removal efficiency of Cr(VI) was found to decrease with increasing the solution pH and the initial concentration of Cr(VI). Almost complete removal of Cr(VI) was achievable in a retention time of about fifteen minutes at pH values less than 1.5 and an initial concentration of 100 ppm. The removal of Cr(VI) practically becomes independent of rotation rates above 400 rpm and with the retention time being higher than fifteen minutes. The use of fan-shaped iron piece, unexpectedly, showed insignificant advantages over the rotating disc as the retention time increased.

References

- [1] Abdo, M. S. and Sedahmed, G. H., 1998. A New Technique for Removing Hexavalent Chromium from Wastewater and Energy Generation via Galvanic Reduction with Scrap Iron, *Energy Convers. Mgmt.*, 39: 943-951.
- [2] Alowitz, M. J., and Scherer, M. M., 2002. Kinetics of Nitrate, Nitrite, and Cr(VI) Reduction by Iron Metal, *Environ. Sci. and Technol.*, 36: 299–306.
- [3] Beukes, J. P., Pienaar, J. J., Lachman, N. G., and Giesekke, E. W., 1999. The Reduction of Hexavalent Chromium by Sulphite in wastewater, *Water SA* 25: 363-370.
- [4] Blowes, D. W., Ptacek, C. J., and Jambor, J. L., 1997. In-situ Remediation of Chromate Contaminated Groundwater Using Permeable Reactive Walls, *Environ. Sci. Technol.*, 31: 3348-3357.
- [5] Brown, G. E. and Chambers, S. A., 2002. Molecular Level Processes Governing the Interaction of Contaminants with Iron and Manganese Oxides, Government reports announcements and index, Pacific Northwest National Laboratory, Richland, WA, 1999.
- [6] Buerge, I. J. and Hug, S. J., 1997 a. Kinetics and pH Dependence of Chromium(VI) Reduction by Iron(II), *Environ. Sci. Technol.*, 31: 1426-1432.
- [7] Buerge, I. J. and Hug, S. J., 1999 b. Influence of Mineral Surfaces on Chromium Reduction by Iron(II), *Environ. Sci. Technol.*, 33(23): 4285-4291.
- [8] Cantrell, K. J., Kaplan, D. I., and Wietzma, T. W., 1995. Zero-Valent Iron for the in Situ Remediation of Selected Metals in Groundwater, *J. Haz. Mat.*, 42: 201-212.
- [9] Chen, J., Chen, R., and Hong, M., 2015. Influence of pH on Hexavalent Chromium Reduction by Fe(II) and Sulfide Compounds, *Water Sci. Technol.*, 72 (11): 22-28.
- [10] Demirbas, E., Kobya, M., Senturk, E., and Ozkan, T., 2004. Adsorption Kinetics for the Removal of Chromium(VI) from Aqueous Solutions on the Activated Carbons Prepared from Agricultural Wastes, *Water SA* 30 (4): 533-539.
- [11] Eary, L. E. and Rai, D., 1988. Kinetics of Chromium(III) Oxidation to Chromium(VI) by Reaction with Manganese dioxide, *Environ. Sci. Technol.*, 21: 1187-1193.
- [12] El-Ali, M. S., 2001. Performance Characteristics of a Novel Liquid-Liquid Contactor, Ph.D. Thesis, Dalhousie University, Halifax, Canada.
- [13] El-Shazly, A. H., Mubarak, A. A., and Konsowa, A. H., 2005. Hexavalent Chromium Reduction Using a Fixed Bed of Scrap Bearing Iron Spheres, *Desalination*, 185: 307-316.
- [14] Gilmore, T. J., Holdren, G. R., and Kaplan, D. I., 1998. Groundwater Well with Reactive Filter Pack, U.S. Patent 5,803,174, U.S. Patent Office, Washington, D.C.
- [15] Gould, J. P., 1982. The Kinetics of Hexavalent Chromium Reduction by Metallic Iron, *Water Res.*, 16: 871-877.
- [16] Huang, Y., Chen, T., Huang, J., and Chen, Y., 2008. Effects of Size and Surface Area of Iron on Reduction of Hexavalent Chromium, *Journal of University of Science and Technology, Beijing*, 30:53-57.
- [17] Junyapoon, S. and Weerapong, S., 2006. Removal of Hexavalent Chromium from Aqueous Solutions by Scrap Fillings, *KMITL Sci. Tech. J.*, 6 (1): 1-12.
- [18] Igalinos, J. D. and Besagas, R. L., 2016. Electrochemical Reduction of Hexavalent Chromium from Chemical Oxygen Demand Hazardous Waste Chemicals using Graphite Electrode, 6 (4): 1356-1362.
- [19] Kendelewicz, T., Liu, P., Doyle, C. S., and Brown, G. E., 2000. Spectroscopic Study of the Reaction of Aqueous Cr(VI) with Fe₃O₄(III) Surfaces, *Surface Sci.*, 469: 144-163.
- [20] Lee, T., Lim, H., Lee, Y., and Park, J. W., 2003. Use of Waste Iron Metal for Removal of Cr (VI) from Water, *Chemosphere*, 53:479-485.
- [21] Levich, V. G., 1962. *Physicochemical Hydrodynamics*, 2nd Ed., Prentice Hall, New Jersey, U.S.A.
- [22] Mackenzie, P. D., Horney, D. P., and Sivavec, T. M., 1999. Mineral Precipitation and Porosity Losses in Granular Iron Columns, *J. Hazard. Mater.*, 68: 1-17.
- [23] Moore, J. W., and Ramamoorthy, S., 1984. *Heavy Metals in Natural Waters*, Springer Series on Environmental Management, Springer New York.
- [24] Niu, S., Liu, Y., Xu, X., and Lou, Z., 2005. Removal of Hexavalent Chromium from Aqueous Solution by Iron Nanoparticles, *Journal of Zhejiang Univ. Sci.*, 6B(10): 1022-1027.
- [25] Patterson, J. W., 1985. *Industrial Wastewater Treatment Technology*, 2nd Edition, Butterworth, Boston, USA.
- [26] Ponder, S. M., Darab, J. G. and Mallouk, T. E., 2000. Remediation of Cr(VI) and Pb(II) Aqueous Solutions Using Supported Nanoscale Iron, *Environ. Sci. Technol.*, 34(12): 2564-2569.
- [27] Powell, R. M., Puls, R. W., 1995. Hightower, S. K. and Sabatini, D. A., Coupled Iron Corrosion and Chromate Reduction: Mechanisms for Subsurface Remediation, *Environ. Sci. Technol.*, 29: 1913-1922.
- [28] Prasad, P. V., Chandan, D., and Golder, A. K., 2011. Reduction of Cr(VI) to Cr(III) and Removal of Total Chromium from Wastewater Using Scrap Iron in the Form of Zerovalent Iron (ZVI): Batch and Columns Studies, *The Canadian Journal of Chemical Engineering*, 31 (6): 1575-1582.
- [29] Pratt, A. R., Blowes, D. W., and Ptacek, C. J., 1997. Products of Chromate Reduction on Proposed Remediation Materials, *Environ. Sci. Technol.*, 31: 2492-2498.
- [30] Richard, F. C., and M Bourg, A. C., 1991. Aqueous Geochemistry: A Review, *Water Res.*, 25(7): 807-816.

- [31] Scherer, M. M., Balko, B. A., and Tratnyek, P. G., 1998. The Role of Oxides in Reduction Reactions at the Metal-Water Interface, Mineral water interfacial reactions: kinetics and mechanisms, ACS Symposium Series 715, Sparks D. and Grundl T. (Eds.), American Chemical Society, Washington, D.C., pp. 301-322.
- [32] Sedlak, D. L. and Chan, P. G., 1997. Reduction of Hexavalent Chromium by Ferrous Iron, *Geochim. Cosmochim. Acta* 61: 2185-2192.
- [33] Shamra, Y. C., Singh, B., Agrawal, A., and Weng, C. H., 2008. Chromium Removal of Chromium by Riverbed Sand from Water and Wastewater: Effect of Important Parameters, *J. Hazard. Mater.*, 151: 789-793.
- [34] Swietlik, R., 2002. Kinetic Study of Redox Processes of Chromium in Natural River Water, *Polish Journal of Environmental Studies*, 11 (4): 441-447.
- [35] Tokunaga, T.K., Wan, J., Firestone, M.K., Hazen, T.C., Schwartz, E., Sutton, S.R. and Newville, M., 2001. Chromium Diffusion and Reduction in Soil Aggregates, *Environ. Sci. Technol.*, 35: 3169-3174.
- [36] White, A. F. and Paterson, M. L., Electrochemistry and Dissolution Kinetics of Magnetite and Ilmenite, *Geochim. Cosmochim. Acta*, 58 (8) (1994) 1859-1875.
- [37] Williams, A. G. B., and Scherer, M. M., 2001. Kinetics of Cr(VI) Reduction by Carbonate Green Rust, *Environ. Sci. Technol.*, 35: 3488-3494.
- [38] Yang, H. F., Fu, P. F. and Zhou, F., 2008. Adsorption and Reduction of Cr(VI) in Aqueous Solution Using Steel Slag Particles, *The Chinese Journal of Process Engineering*, 8 (3): 499-503.
- [39] Yongtian, H., 2003. Chromate Reduction and Immobilization Under High pH and High Ionic Strength Conditions, Ph.D. Dissertation, School of the Ohio State University, U.S.A.
- [40] Zachara, J.M., Girvin, D.C., Schmidt, R.L., and Resch, C.T., 1987. Chromate Adsorption on Amorphous Iron Oxyhydroxide in the Presence of Major groundwater Ions, *Environ. Sci. Technol.*, 21(6): 589-594.
- [41] Zhu, Y., Wei, L., Xu, J., and Shi, W., 2016. Study on the Effect on the Reduction of Hexavalent Chromium in Soil, International Conference on Environment, Climate Change and Sustainable Development (ECCSD 2016), Beijing, China.