

An iron rotating disk for the elimination of hexavalent chromium ion from industrial wastewaters: putting it to work

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ABSTRACT

This work aimed to predict the optimal operational limits for reducing Cr(VI) to Cr(III) ions using an iron rotating disk. Therefore, the kinetics of Cr(VI) reduction utilizing an iron rotating disk were studied under various experimental conditions of contact time, rotation rate, Cr(VI) initial concentration, and disk surface area. All the experiments were conducted at room temperature with a starting pH of 1.5. It was revealed that the reduction of Cr(VI) to Cr(III) could be modeled with a first-order reaction rate. It was found that the reduction rate constant first increased steadily (i.e., mass transfer-controlled) with the square root of the disk's rotation speed but then fell as the flow transitioned to turbulence until it became relatively unchanged (i.e., kinetics-controlled). Furthermore, the rate constant inversely varied with initial concentration up to 300 mg/L, but then remained unaffected as the concentration increased. The disk radius also influenced the time required to completely remove Cr(VI). It decreased as the radius of the disk increased. As a result, achieving high removals of Cr(VI) in a short contact time requires operating the disk in laminar and transitional flows (Re no. maximum 150,000), as well as optimum Cr(VI) initial concentration, rotation speed, and disk area. Because it can be used in batch or integrated into a continuous treatment system, the rotating disk may offer a potentially practical and unique technique for treating wastewaters with high and low concentrations of Cr(VI) ions.

Keywords: Industrial wastewater treatment; Cr(VI) reduction; Rotating disk; Chromium removal

1. Introduction

Humans, animals, and biological life can be poisoned by compounds containing Cr(VI) ions. Cr(VI) can enter the human body through inhalation, ingestion, or skin absorption. Because they are usually present as a dissolved ions in aqueous solutions, Cr(VI) ions are easily mobilized in both marine and terrestrial environments. The trivalent form of chromium, on the other hand, has a limited solubility and can be precipitated as hydroxide [1].

Cr(VI) ions are common in wastewaters and originate from a variety of sources, including metal finishing, tannery, corrosion inhibitors, stainless steel, inks, dyes. The international environmental standards and guidelines are getting increasingly stringent in order to protect drinking water supplies as well as water bodies from pollution with Cr(VI) ions. Therefore, the maximum permissible levels of total chromium (mainly Cr(VI) plus Cr(III)) are 0.05 ppm for drinking water, 0.10 ppm for treated effluents released to water bodies and the environment, and 3.00 ppm for wastewater discharged into sewer systems.

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Cr(VI) ions are usually reduced to Cr(III) using meta bisulfites and ferrous ions, followed by chromium hydroxide precipitation [2–4]. In the case of concentrated Cr(VI) effluents, evaporation has proven to be a technically and economically viable method for recovering of Cr(VI) ions [4,5]. Conventional Fenton and heterogeneous Fenton oxidation processes were found to be effective for treating tannery wastewater (i.e., containing Cr(VI) ions). Lab-prepared nano zero-valent iron particles were used as a solid catalyst in the heterogeneous Fenton process [6].

Researchers have recently paid more attention to the reduction of Cr(VI) in wastewaters by iron metal (i.e., zero-valent iron). Hexavalent chromium ions are mostly transformed to Cr(III) ions by reacting with iron metal and its aqueous ferrous ions [7–26]. Metal wool, chips, shots, and other forms of iron metal have been used as reductants in packed columns, rotating chambers, or tumble barrels. All of these technologies have a major drawback in common; shielding of the iron surface as well as susceptibility to clogging due to accumulation of reaction products and suspended materials present in the wastewater. 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 ($\text{Fe}(\text{OH})_3$) have all been found on the metal surface [16–26]. This significantly reduces the rate of Cr(VI) reduction. Moreover, these treatment units require frequent maintenance. On the other hand, using an iron rotating disk may prevent reaction products and suspended materials from precipitating on the iron surface. It improves multi-phase interaction by creating streamlines, which may enhance mass transfer of reactants and products to and from the disk surface [27,28]. However, in real applications, the passivation of the metal surface is a significant element to consider. Furthermore, using a rotating disk allows for easier access to the metal surface and greater control of the surface area, both of which are important parameters for the treatment reactor's sizing and design. Finally, the associated cost of this novel technique is expected to be significantly lower than those of existing technologies.

In a previous study, Al-Waqfi and Telfah [29] used iron metal as a rotating disk to remove Cr(VI) from acidic liquid effluents. Batch treatment was used. They investigated Cr(VI) reduction under various experimental conditions of rotation rate, retention time, initial concentration, and starting pH. When the initial concentration of Cr(VI) was 100 mg/L, complete elimination was achievable in 15 min at a pH of 1.5. At the same retention time, it was revealed that Cr(VI) elimination became independent of rotation rates greater than 600 rpm. The current study, on the other hand, sought to explore deeper into the kinetics of Cr(VI) reduction under a variety of experimental conditions.

2. Materials and method

2.1. Materials

A low carbon steel sheet (carbon 0.17%) was purchased on the local market. The sheet was cut into several circular shapes with radii of 4.75, 4.00, and 3.5 cm. These samples were used as rotating disks.

To avoid the presence of ferrous and cadmium ions, which could interfere with the reduction process, the wastewater

sample was taken from a freshly prepared dichromate dip tank. The dichromate dip tank was part of a cadmium plating shop where screws and nuts dipped after they had been cadmium plated. Table 1 shows the composition of the investigated sample.

Because of the low concentration of ferrous ions in the original wastewater sample, the existing Fe^{2+} ions had no effect on the reduction process. High Fe^{2+} concentrations may have a negative impact on the rotating disk's effectiveness as a Cr(VI) reduction method.

A stock solution of Cr(VI) was prepared from the dichromate dip tank. Then several samples of different concentrations of Cr(VI) were prepared from the stock solution.

2.2. Experimental

Fig. 1 depicts the schematic diagram of the bench-scale experimental setup of the batch treatment used to treat Cr(VI)-containing samples.

As shown, a stainless-steel shaft was attached to the rotating disk to prevent interference with reduction reactions. This rotating shaft was part of a 1/4 horse power-variable speed motor assembly. The calibrated nob of the motor was used to adjust the disk's rotation rate. In all experiments, the motor rotation rate was verified using a tacometer. The rotating disk was immersed in a 2,000 mL beaker containing the sample to be treated.

A horizontal alignment of the rotating disk was maintained to ensure axial symmetry and to prevent the rise of non-uniformity of the flow around the disk caused by gravity. Non-uniform flow regimes may influence the diffusion of reactants and products of the reduction process from the bulk solution to the disk surface and vice versa. This could eventually have an impact on Cr(VI) removal efficiency. By clamping the rotating shaft to a vertical stand, it was kept perpendicular to the rotating disk. The rotating disk was used for only one experiment; it was cleaned with excess distilled water, air dried, degreased with benzene, and then washed with acetone before conducting all experiments. These cleaning steps to ensure clean surface with no fingerprints or grease. Any impurities present may prevent contact between the disk's surface and the Cr(VI) ions, thereby impeding the reduction reactions.

Several batch treatment experiments were carried out at room temperature with varying conditions (rotation speed, initial concentration, and disk radius) and starting pH of 1.5. The pH of the samples was adjusted with 1 N NaOH and 1 N H_2SO_4 . The treated samples were filtered through a membrane filter of 0.45 μm , then their pH was adjusted to 8.5; the optimum value for trivalent chromium precipitation as hydroxide, which can be easily filtered. The filtrate was then analyzed using a HACH Direct Reading Spectrophotometer (model DR2800), which displayed the residual Cr(VI) concentration in the treated sample, in accordance with the Standard Methods for the Examination of Water and Wastewater, 22nd ed. (approved by the USEPA). All laboratory chemicals used in the study were of AR grade (HACH, USA). For pH measurement, a microprocessor pH meter (model pH3000.WTW) was used.

A series of triplicate experiments were carried out to ensure the reproducibility of the results.

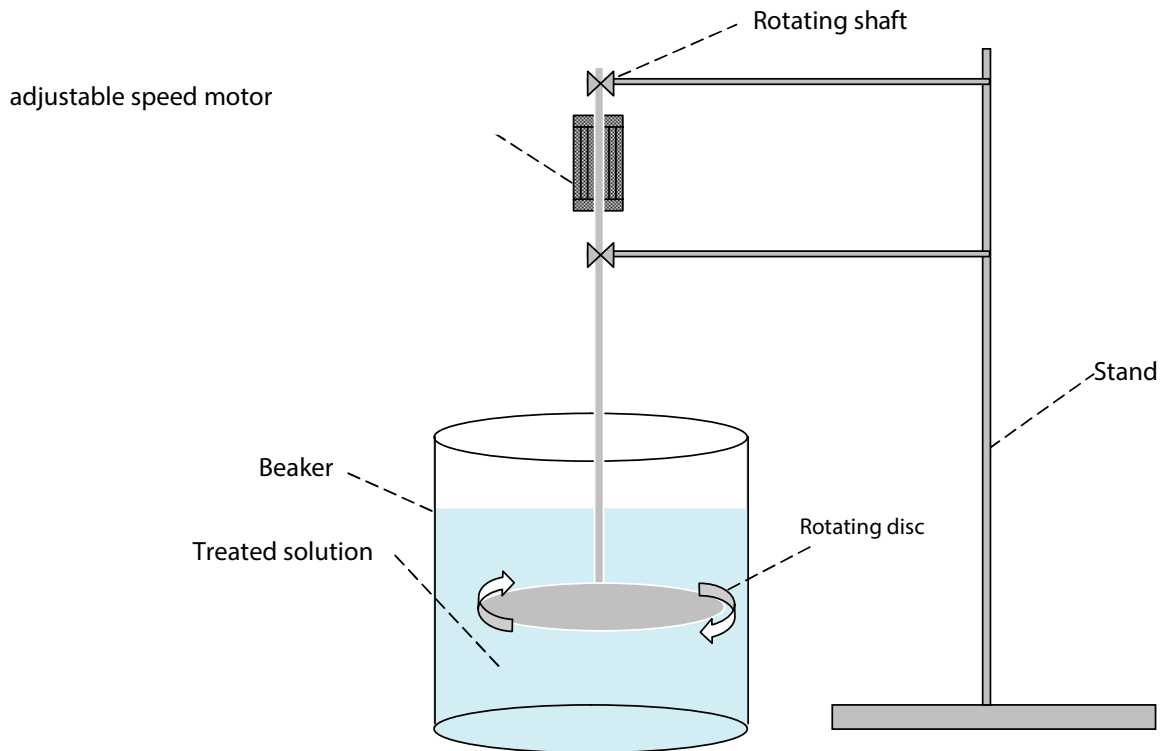
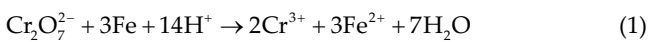


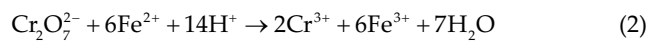
Fig. 1. Schematic diagram of the experimental arrangement.

3. Results and discussions

In the current research, Cr(VI) is reduced to Cr(III) through an oxidation–reduction reaction between the dichromate ion and the iron metal as illustrated by Eq. (1)



Then, the produced ferrous ions react with the dichromate ions as per Eq. (2)



The reduction process is heterogeneous (i.e., solid–aqueous phases). The first reaction occurs at the disk surface, which requires dichromate ions to diffuse from the solution’s bulk to metal’s surface caused by the streamlines created by the disk movement. The produced ferrous and Cr(III) ions, on the other hand, diffuse away to the solution bulk, where ferrous ions further reduce the dichromate ions according to Eq. (2).

Since the concentrations of Fe⁰, Fe²⁺, and hydrogen ion are essentially constant compared to the concentration of dichromate, the rate equation for Cr(VI) reduction can, therefore, be written as follows:

$$\frac{d(\text{Cr(VI)})}{dt} = -K[\text{Cr}^{6+}] \quad (3)$$

Or

$$\frac{dC}{dt} = -KC \quad (4)$$

where *K* is the rate constant (s⁻¹) and *C* is the concentration of Cr(VI) at time *t* (mg/L). Integrating the above equation gives the following linear relationship:

$$-\ln \frac{C}{C_0} = Kt \quad (5)$$

where *C*₀ is the initial concentration (mg/L), to test the order of reaction rate, ln(*C*₀/*C*) was plotted vs. *t* at various rotation rates and an initial concentration of 100 mg/L.

As shown in Fig. 2, ln(*C*₀/*C*) varied linearly with time at all rotation rates, but with significant deviations from linearity at low speeds (e.g., 50 and 100 rpm), indicating that the Cr(VI) reduction can be described by a first-order reaction rate equation this conclusion is consistent with the reviewed literature [12–16]. Increasing the rotation speed also increased the removal of Cr(VI) until it reached a point (700 rpm and above) where it remained nearly constant, implying that Cr(VI) reduction shifted from mass transfer to kinetic control (Fig. 2). For example, after 10 min of treatment, the removal of Cr(VI) was approximately 10%, 22%, 70%, 78%, 84%, 90%, 91%, and 91% for 50, 100, 300, 500, 600, 700, 800, and 1,500 rpm respectively. This result

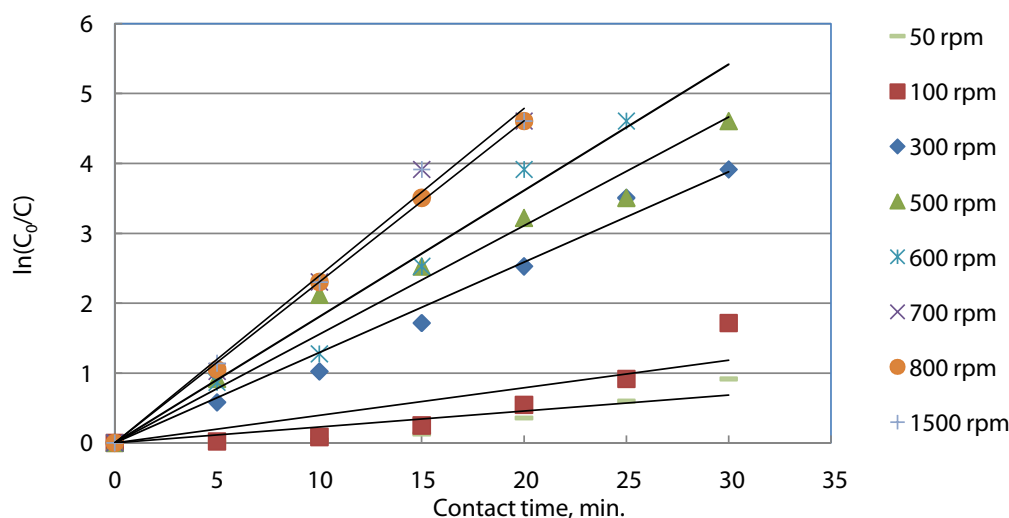


Fig. 2. Reduction kinetics ($C_0 = 100$ ppm; pH 1.5; radius 4.75 cm).

is crucial in determining the optimal design and process scaling rotation speed. Junyapoon and Weerapong [13] discovered that Cr(VI) reduction rate constantly increased as the agitation rate increased. This disparity could be explained by the fact that a narrower range of rotational speeds (i.e., agitation rates) was used in their study. The maximum rate investigated was 250 rpm due to limitations in the agitator's capacity compared to 1,500 rpm in the current work.

Table 2 shows the fitting results of the experimental data to a first-order reaction rate equation at various rotation speeds (rpm). The observed deviations from linearity at low rotation speeds could be attributed to changes in metal surface reactivity due to increased passivation tendency caused by products and precipitates forming on the disk's surface. Several studies have identified the secondary products; magnetite, green rust, rust, goethite, and ferric hydroxide on the surface of other forms of iron metal used for Cr(VI) reduction [16–26].

According to Levich [27], a disk rotating with a Reynolds number less than 100,000 develops a laminar flow regime, and the diffusional solute rate constant from the bulk of solution to the disk's surface can thus be modeled using the Eq. (6).

$$k = 0.62 D^{2/3} v^{-1/6} \omega^{1/2} \quad (6)$$

where D is the solute diffusion coefficient ($\text{m}^2 \text{s}^{-1}$), v is the fluid kinematic viscosity ($\text{m}^2 \text{s}^{-1}$) and ω is angular velocity (s^{-1}).

The rate constant was plotted against $(\text{rpm})^{1/2}$ as exhibited in Fig. 3. As shown, it increased steadily at first (i.e., mass transfer controlled, part A), and then asymptotically behaved as the flow transitioned to turbulence (above 600 rpm), becoming essentially independent of the rotation speed (i.e., kinetics-controlled, part B), which is consistent with earlier findings [30–32]. According to Gould [30], the reaction rate constant increased with the mixing rate until it reached a maximum, after which

Table 1
Composition of the wastewater sample

Ion	Concentration, mg/L
Cr(VI)	3,000
Cd ²⁺	Not detected
Fe ²⁺	19
pH	11

Table 2
First-order kinetics fitting results

Rotation rate, rpm	Re	R ²	K, s ⁻¹
50	13,203	0.7894	0.023
100	26,432	0.7497	0.04
300	79,320	0.9842	0.129
500	132,183	0.9750	0.156
600	158,537	0.9744	0.181
700	185,115	0.98882	0.239
800	211,560	0.9990	0.231
1,500	396,676	0.9898	0.239
Standard deviation			0.086

it remained constant. Also, it was found that the mass transfer coefficient increased with agitation speed, but with a noticeable decrease in the coefficient's rise rate as the rpm exceeded 500 [31]. This therefore may confirm that the reduction process is diffusion-controlled. But in the latter two studies, Vilardi et al. [31] and Semary et al. [32], the transition from mass transfer to kinetics control was not as clear. Both studies, covered a narrower range of rpms, suggesting that the process was diffusion-controlled throughout. It was discovered that increasing the solution velocity increased the mass transfer coefficient and thus the rate of Cr(VI) reduction when a fixed

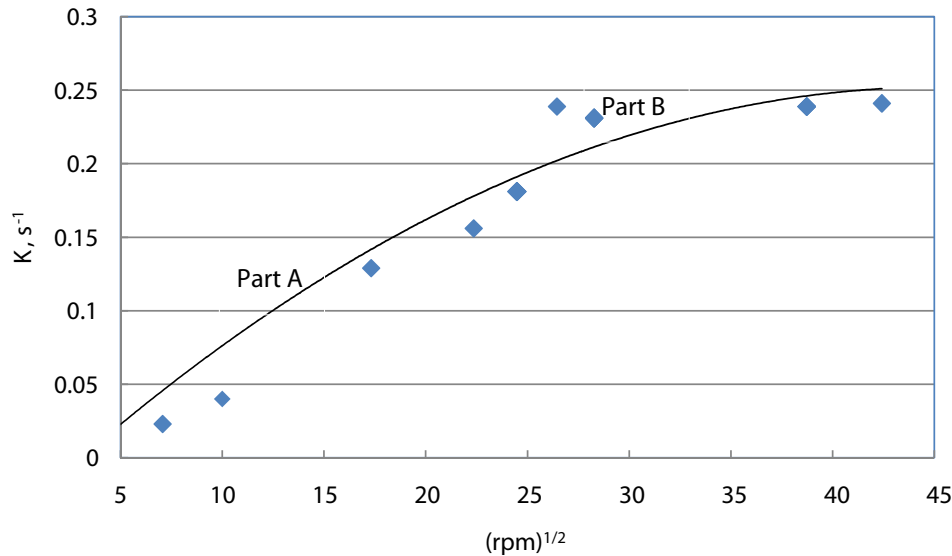


Fig. 3. Change of the rate constant of the reaction with angular velocity.

bed of scrap iron spheres was used, implying that the reduction reaction was diffusion controlled. The velocities tested ranged from 6 to 12 m/s; a broader range of velocities would be more accurate in determining the factor that controls the reduction reaction [12].

The non-linear variation of Cr(VI) removal with contact time was investigated at various rotational rates. As shown in Fig. 4, the variation trend indicates that the removal efficiency became independent of rotation rates above 500 rpm, emphasizing the current study's earlier findings. As previously stated, this could imply that as the rotation speed increases, the mass transfer controlling effects fade in favor of the reaction kinetics, which tends to become the dominant controlling factor. Furthermore, at rotation speeds of 300 rpm and higher, the variation trend of removal efficiency with contact time remained unchanged, but the time required to achieve maximum removal of Cr(VI) decreased as the rpm increased. These results are consistent with the findings reported by Vilardi et al. [31], who used nanohematite particles in an agitated tank with a Rushton-type impeller to eliminate Cr(VI) ions. Similarly, several researchers [33–37] observed a decrease in the reduction rate with time, which they attributed to the redox reaction controlling mechanism and iron surface passivation.

Fig. 5 depicts the plot of equation 5 at various initial Cr(VI) concentrations. As shown, $\ln(C_0/C)$ linearly varied with contact time at all investigated concentrations, supporting the hypothesis that Cr(VI) reduction can be modeled using a first-order reaction rate equation. Semary et al. [32] obtained similar results.

Moreover, the variation of the rate constant with initial concentration was examined. As shown in Fig. 6, the rate constant decreased steadily as the initial concentration increased up to about 250 mg/L, after which it appeared to be independent of the Cr(VI) concentration. These findings could imply that Cr(VI) reduction is diffusion-controlled (i.e., mass transfer-controlled) at low concentrations, and the kinetics controlling effects become more

significant as the initial concentration increases. At a concentration of about 400 mg/L, it becomes fully kinetically controlled. Several workers reported that Cr(VI) reduction rate using different forms of iron metal decreased with initial concentration [23,30,33,39]. For ionic strengths less than 0.1 M, increasing ionic strength led to a fast decline of the rate constant, but for ionic strengths greater than 0.1 M, the rate constant became independent of ionic strength [30] which is consistent with the current work.

Cr(VI) removal was plotted against contact time at different initial concentrations. As shown in Fig. 7, for initial concentrations less than 100 mg/L, complete Cr(VI) removal could be accomplished in about 20 min. At initial concentrations of 300 mg/L or higher, total elimination of Cr(VI) was not possible. Fewer Cr(VI) ions are available at low concentrations compared to the number of reactive sites, which may maintain iron reactivity and thus increase Cr(VI) removal. However, at higher initial concentrations, the available reactive sites decrease over time due to reaction with Cr(VI) ions, potentially leading to an accumulation of unreacted Cr(VI) ions at the metal surface, which may also inhibit ferrous ion release [39]. This will most likely impede the further transfer of Cr(VI) ions from the bulk, resulting in the evolution of the removal-time curves shown in Fig. 7. These findings suggest that continuous stirred tanks with rotating iron disks can be employed to treat wastewaters with high Cr(VI) concentrations. Iron rotating disks can thus be integrated into continuous treatment systems.

The same trends have been reported previously but with much longer contact times for complete removal [40–43]. Iron nanoparticles and plates were used in these studies. Niu et al. [43] used Fe⁰ nanoparticles as the reductant metal and achieved 100% removal of Cr(VI) in about 15 min when the initial concentration was 10 mg/L compared to 50 and 100 mg/L in the current study. The lower removal efficiencies reported by Niu et al. [43] could be attributed, mainly, to the agglomeration of Fe⁰ nanoparticles as well as

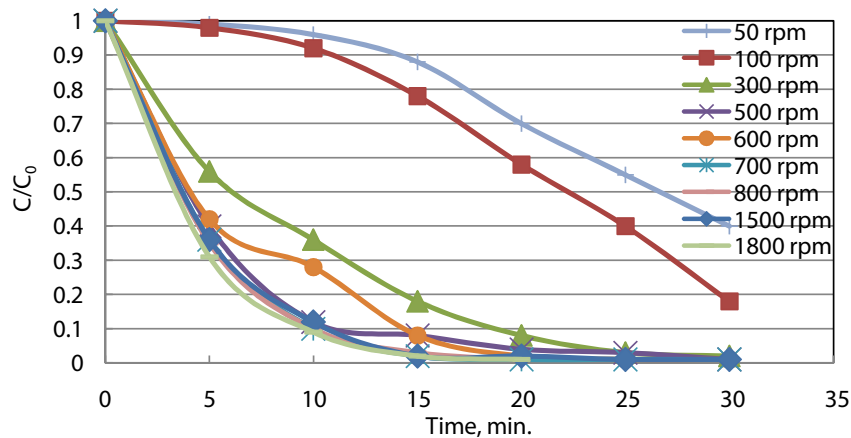


Fig. 4. Influence of reaction time on the removal efficiency ($C_0 = 100$ ppm; pH 1.5; radius 4.75 cm).

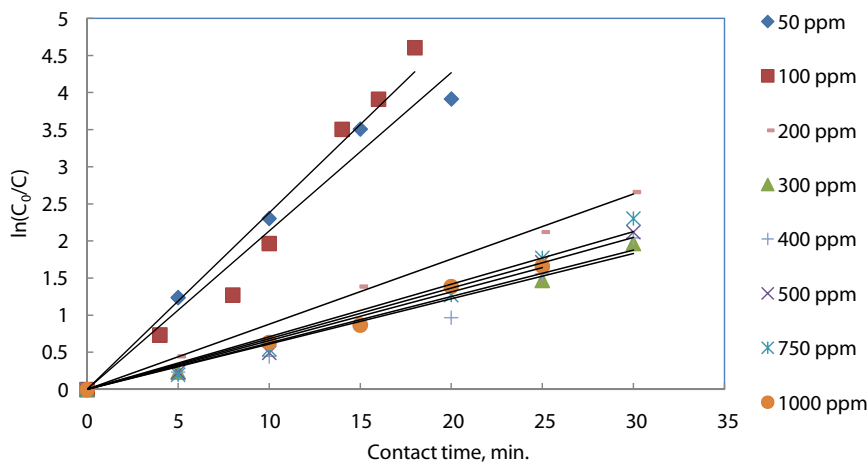


Fig. 5. Reduction kinetics (pH 1.5; 600 rpm; radius 4.75 cm).

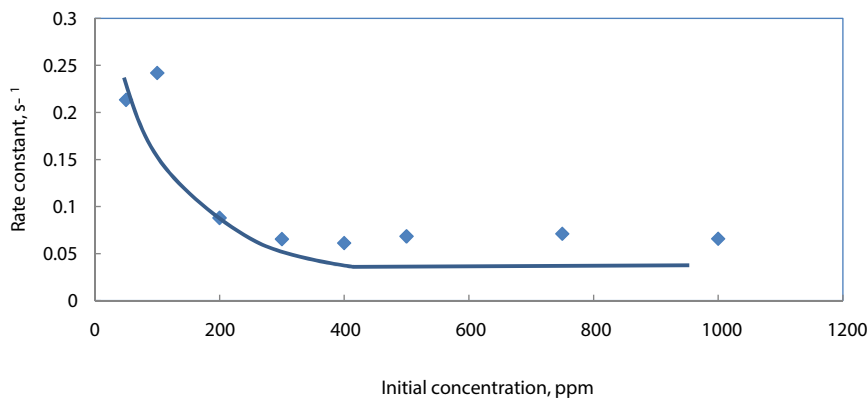


Fig. 6. Variation of rate constant with starting concentration of Cr(VI) (pH 1.5; 600 rpm; radius 4.75 cm).

the higher initial pH used. This finding may confirm the superior performance of the iron rotating disk as a reductant metal compared to other iron forms.

The effect of disk radius on Cr(VI) removal is depicted in Fig. 8. The time required for complete removal of Cr(VI) was shown to be dependent on the disk radius. It decreased as the disk radius increased. In a larger disk area, there may

have been more reactive sites for Cr(VI) reduction, which may have improved the removal efficiency. These findings are in agreement with those of Huang et al. [44] and Niu et al. [43], who used Fe^0 nanoparticles to reduce Cr(VI). They discovered that increasing the Fe^0 concentration or dose, similar to increasing the disk area, improved removal efficiency. However, expanding the disk area may not always result in

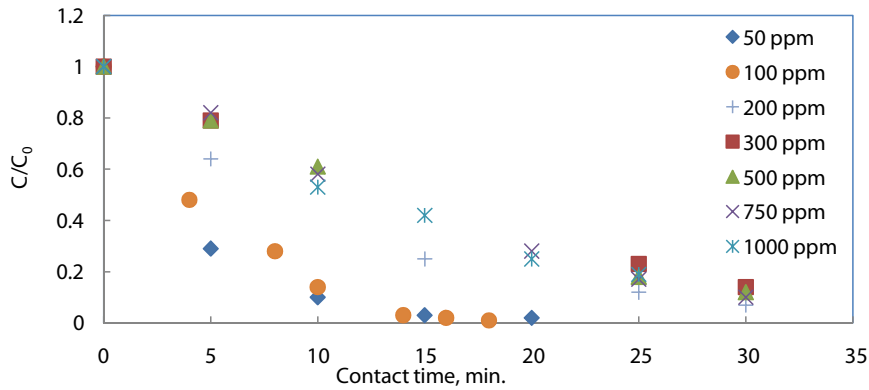


Fig. 7. Elimination of Cr(VI) using iron metal at varying starting concentration (pH 1.5; 600 rpm; radius 4.75 cm).

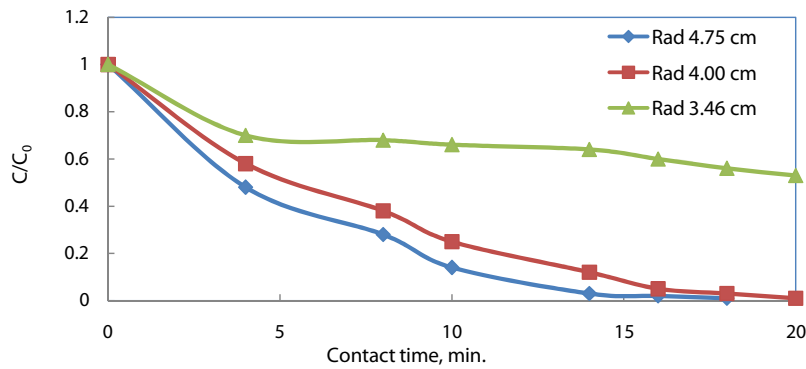


Fig. 8. Cr(VI) reduction by iron rotating disk of different surface areas ($C_0 = 100$ ppm; pH 1.5; 600 rpm).

a significant decrease in the removal time. When the disk area increases, some reactive sites may become redundant as their number exceeds the reaction requirement. When the initial Cr(VI) concentration was 100 mg/L or less, the optimal disk radius for complete removal was around 4.00 cm, rather than 4.75 cm.

4. Conclusions

Based on the results of this experimental study, the following concluding remarks are presented. In addition, some recommendations for future work are accompanied by these conclusions:

- It was revealed that Cr(VI) reduction follows first-order reaction kinetics.
- Given that the temperature and starting pH were constant, the key factors influencing the removal efficiency and reduction rate of Cr(VI) to Cr(III) ions, using the rotating disk, included:
 - Rotation speed
The removal efficiency was found to be directly proportional to the rotation speed up to about 600 rpm. It becomes independent of rotation rate at rpms higher than 600.
 - Initial Cr(VI) concentration
For initial concentrations (less than 100 mg/L), complete Cr(VI) removal was possible in 20 min. Fewer ions are

available at low concentrations compared to the reactive sites, which may maintain iron reactivity and thus increase Cr(VI) removal. For solutions of 300 mg/L and above, complete elimination of Cr(VI) is not likely. Under these conditions, the number of available reactive sites decreases over time due to reaction with Cr(VI) ions, potentially leading to an accumulation of unreacted Cr(VI) ions at the metal surface and preventing ferrous ions release.

- Disk surface area

It was discovered that the disk radius influences Cr(VI) removal. A larger disk area with more reactive sites may improve the reduction rate. Because many reactive sites become redundant, increasing surface area excessively may result in an insignificant improvement in Cr(VI) removal. As a result, the optimal disk surface area should be sought.

- The reduction rate constant was found to be dependent on
 - Flow pattern
The rate constant steadily increases up to a Reynolds number of about 150,000, which indicates laminar flow conditions, and then remains nearly unchanged as the flow transitions to turbulent conditions with a Reynolds number greater than 150,000. This could imply that the reduction of Cr(VI) in laminar flow is diffusion controlled while it is kinetic controlled in turbulent flow.
 - Initial concentration

The rate constant was found to be inversely proportional to the initial concentrations up to approximately 250 mg/L, after which it appeared to be independent of the Cr(VI) concentration, implying that Cr(VI) reduction is diffusion-controlled. As the concentration rises, the kinetics controlling effects become more pronounced. It became fully kinetically controlled at a concentration of about 400 mg/L.

- The iron rotating disk was effective in removing Cr(VI) from industrial wastewater. For example, 100 mg/L of Cr(VI) were completely removed in about 20 min. As a result, an iron rotating disk can be a practical and viable alternative to other forms of iron metal (e.g., wool, chips, shots, and nanoparticles packed in columns, fluidized beds, and tumble barrels) for Cr(VI) removal.
- A batch treatment system based on an iron rotating disk may be adequate for small industrial applications, particularly those with intermittent and low volumes of Cr(VI)-containing effluents. Iron rotating disk batch treatment systems are simple to size, build, control, operate, and maintain. In addition, its associated costs may be significantly lower than those of fluidized beds, packed beds, and tumble barrels.
- In order to achieve complete or high removal efficiencies, the rotating disk must operate in the transitional flow regime (Re Nos. 130,000–150,000), where the reaction is essentially diffusion-controlled (i.e., mass transfer controlled) and has relatively a high-rate constant. Operating the disk in turbulent conditions, where the reduction process is kinetically controlled (i.e., at high rotation rates), may lead to increased energy consumption with no significant improvement in Cr(VI) removal. It is, therefore, critical to avoid such scenarios in practice.
- The iron rotating disk can be practical for treating industrial effluents with high Cr(VI) concentrations. It is possible to outfit a continuous stirred-tank arrangement with iron rotating disks for treating high Cr(VI) concentrations. Thus, iron rotating disk can be integrated into continuous treatment systems.
- Pilot studies are required to determine the optimal design and operational limits of the iron rotating disk as a novel technique for removing Cr(VI) ions from wastewater.
- For higher concentrations of Cr(VI) ions, a combined treatment system of electrocoagulation with the iron rotating disc or any other combination may reach more removal efficiencies than that of the single treatment process. It will be the subject of our further research [45].

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