

## A Novel Rotating Fixed Bed Batch Reactor for Hexavalent Chromium Reduction

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### ABSTRACT

Hexavalent chromium reduction using iron powder has the advantages of being efficient and capable of degrading pollutants, as well as inexpensive and simple to procure. The performance of a new rotating fixed-bed batch reactor in treating aqueous solutions containing chromium hexavalent ions with iron powder was investigated. Two magnets were covered with iron powder and coupled with an isolated stainless-steel shaft in a new agitator design. Variables such as time, initial hexavalent chromium content, iron powder dose, rotational speed, and pH were investigated in order to discover the optimum chromium removal approach. The analysis of variance (ANOVA) was used to determine the experimental kinetics. Contact time of 21 minutes, initial Cr(VI) concentration of 30 ppm, iron powder dosage of 10 g, rpm of 276 and pH of 3 were determined to be the optimal conditions for removing hexavalent chromium.

**Keywords:** hexavalent chromium; reduction efficiency; fixed bed; iron powder; kinetics.

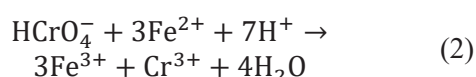
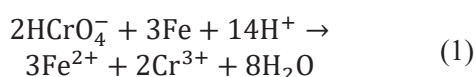
### INTRODUCTION

Environmental pollution of heavy metals has become a major area of concern, because they can produce cumulative harmful effects on a wide variety of aquatic species, even at low doses [Gheju, 2018]. Chromium (Cr) is one of the most popular heavy metals [Qasem et al. 2021]. Chromium is released into the environment as a result of the discharge of various effluents produced by a wide range of industries, including electroplating, animal skin tanning, paints, pigment production, pulp processing, wood preservation, metal corrosion inhibition, and steel manufacturing. All of these industries result in the release of massive amounts of hexavalent chromium-containing waste into the environment [El-Ashtouky et al. 2018]. Chromium has two stable oxidation states in aqueous solutions: hexavalent [Cr(VI)] and trivalent [Cr(III)] [Kang et al. 2017]. Cr(III) is less

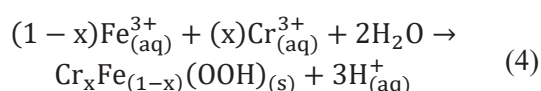
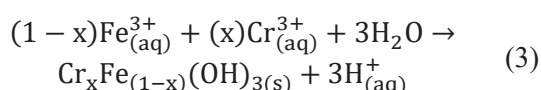
poisonous, insoluble, and essential for human health [Venkatesan & Subramani, 2019]. The Cr(VI) compounds, such as hydrogen chromate ( $\text{HCrO}_4^-$ ), chromate ( $\text{CrO}_4^{2-}$ ) and dichromate ( $\text{Cr}_2\text{O}_7^{2-}$ ), are toxic due to their high solubility and diffusivity, which allow them to easily cross biological membrane tissues [Pakade et al. 2019]. For a more sustainable environment, industrial effluents must be treated in an environmentally friendly manner to remove hexavalent chromium ions prior to release into waterbodies. To remove Cr(VI) from industrial wastes, various physico-chemical approaches such as precipitation, ion exchange, membrane-based procedures, and adsorption utilizing activated carbon are routinely utilized [Kumar & Saini, 2019]. These methods frequently have drawbacks, such as high energy demands, large capital investments, and often limited selectivity [Abdel-Aziz et al., 2020; Verma & Balomajumder, 2020]. Chemical reduction

is a good way to treat chromium-containing effluents because it can convert highly soluble and poisonous Cr(VI) to less soluble and innocuous Cr(III) [Zaib et al. 2021]. Ferrous sulfate and elemental sulfur are two common chemical reductants. However, these chemical reductants may result in high chemical consumption costs and low efficiencies. As a result, finding a new way to reduce Cr(VI) is important [Wang & Cui, 2019; Lv et al. 2018]. One of the most plentiful metals on the earth is zero-valent iron metal ( $\text{Fe}^0$ ), which is a powerful reducing agent. Due to its low cost, simplicity of procurement, efficacy, and capacity to breakdown pollutants,  $\text{Fe}^0$  is a very essential reactive medium [Fu et al., 2014]. The use of zero-valent iron for groundwater remediation and wastewater treatment: a review. *Journal of Hazardous Materials*, 267, 194–205].

Many reactor designs, such as fixed bed of scrap bearing iron spheres reactors, have been examined for their potential to remove Cr(VI) from wastewater using zero-valent iron [El-Shazly, 2005], reciprocating perforated disc [Elshazly, 2010], iron spheres in a spinning perforated basket [Abdel-Aziz et al., 2018] and fluidized bed [Chen et al., 2007]. As it is well known, iron and its ferrous ions have a higher position in the electrochemical series than chromium, indicating that both types are capable of reducing Cr(VI) ions and displacing them from solution in a redox manner, as shown below [Gheju & Balcu, 2010]:



Chromium can be removed by co-precipitation of mixed Fe(III)–Cr(III) hydroxide solid solution  $\text{Cr}_x\text{Fe}_{1-x}(\text{OH})_{3(s)}$  (or mixed Fe(III)–Cr(III) oxyhydroxide solid solution  $\text{Cr}_x\text{Fe}_{1-x}(\text{OOH})_{(s)}$ ), according to:



where:  $x$  vary from 0 to 1 [Gheju & Iovi, 2006].

Despite the progress made in the reduction of Cr(VI) by metallic iron, there is still opportunity for new, more efficient reactors to be developed. The current study focuses on removing Cr(VI)

from dilute solutions using a novel magnetic rotating fixed bed reactor that consists of two magnets, isolated with epoxy, covered with iron powder and attached to an isolated stainless steel shaft. The studied parameters include the reaction time, initial Cr(VI) concentration, iron dose, rpm, and pH.

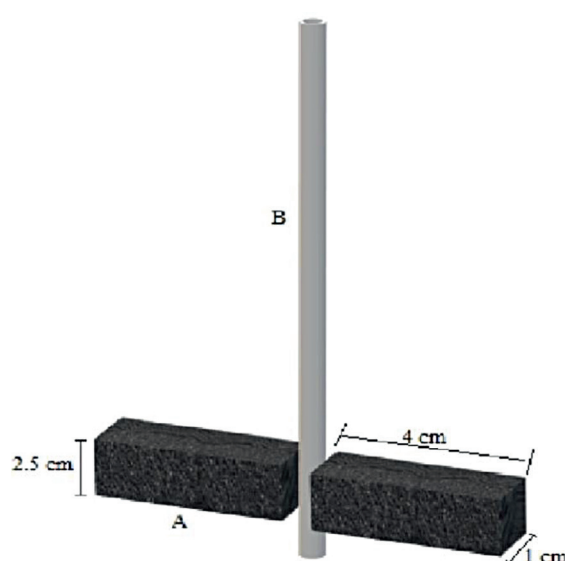
## MATERIALS AND METHODS

### Materials

All chemical reagents were analytical reagent quality, including  $\text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{Fe}^0$  powder (250–300 mesh),  $\text{H}_2\text{SO}_4$ ,  $\text{H}_3\text{PO}_4$ , NaOH, and acetone. A known weight of  $\text{K}_2\text{Cr}_2\text{O}_7$  was dried in an oven for 30 minutes to remove any moisture before being stored in a desiccator. Then, 2.83 g of dry potassium dichromate analytical reagent was dissolved in distilled water and diluted to 1 L to make a stock Cr(VI) solution (1000 mg/l).

### Methods

Figure 1 schematically depicts the rotating fixed bed reactor employed in this study. The reactor is made out of a plexiglass cylindrical container with a diameter of 11.4 cm and a height of 20 cm. The rotating fixed bed blades consists of two isolated magnets that were covered with plastic bag, covered with  $\text{Fe}^0$  powder (250–300 mesh) of different doses. The plastic bag was used



**Figure 1.** Rotating fixed bed reactor: (a) magnet covered with iron powder and (b) insulated stainless steel shaft

to facilitate the removal of Fe<sup>0</sup> powder particles at the end of experiments. The size of magnets was 4 × 2.5 × 1 cm and the weight of every magnet was 46.4 g. Each isolated magnet was attached to a 0.5 cm diameter isolated stainless-steel shaft that was 1.5 cm above the tank bottom and connected to a variable speed motor. The necessary concentrations in the experiment were produced by diluting the stock solution with distilled water several times. The pH of the samples was adjusted using diluted NaOH or H<sub>2</sub>SO<sub>4</sub> as a starting point.

All of the experiments were carried out at room temperature. Each run utilized one liter of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution. The operation started when the rotational speed of the fixed two magnets was adjusted to the desired value. A typical experiment lasted 21 minutes, with 10 mL samples obtained from the reaction solution every 3 minutes. After centrifuging the treated solutions to remove colloidal particles generated by the precipitation of mixed Cr(III)–Fe(III) oxyhydroxides (Eqs. 3 & 4), the percent removal of Cr(VI) ions was determined. The diphenylcarbazide colorimetric method [Baird et al., 2012] was used to analyze Cr(VI) using a U.V. spectrophotometer (UNICO, Model 1200) at 560 nm, in which 1,5-diphenyl carbazide interacted with Cr(VI) to create a red violet color complex after 10 minutes in a highly acidic solution of pH ≈ 1. Using the following equation [Peng et al., 2021], the removal efficiency of Cr(VI) was estimated:

$$\% \text{ RE} = \frac{\text{Cr(VI)}_{\text{IC}} - \text{Cr(VI)}_{\text{RC}}}{\text{Cr(VI)}_{\text{IC}}} \times 100 \quad (5)$$

where: RE – removal efficiency, IC – initial concentration, RC – remaining concentration.

## RESULTS AND DISCUSSION

### Analysis of variance

ANOVA was applied for Cr(VI) removal performance experiments, using general linear model approach in Minitab. The *R*<sup>2</sup> value is 98.49%, indicating that the model is extremely well fitted to the data. Table 1 shows ANOVA for the response of chromium removal at the selected experimental parameters. The *P* value determines whether or not a given factor is significant. A parameter with a *P* value < 0.05 is considered significant. The initial Cr(VI) concentration, iron dose, rpm, and pH are all significant influences with the *P* values of less than 0.05.

**Table 1.** ANOVA analysis for Cr(VI) removal

Source	P-Value	Significance
Concentration (ppm)	0.000	significant
Iron dose (gm)	0.012	significant
Rotation speed (rpm)	0.008	significant
pH	0.000	significant

### Kinetic study

The reduction of Cr(VI) on Fe metal in acidic environments obviously follows first-order kinetics, as represented by the equation below [Abdel-Aziz et al, 2018]:

$$\ln\left(\frac{C_0}{C}\right) = kt \quad (6)$$

where: *C*<sub>0</sub> and *C* – represent the starting Cr(VI) concentration and the Cr(VI) concentration at any time (*t*), respectively; *k* – represents the mass transfer coefficient (min<sup>-1</sup>).

A linear plot of  $\ln\left(\frac{C_0}{C}\right)$  vs. *t*, as shown in Figure 2, indicates that the Cr(VI) reduction rate is a first-order kinetics with regard to Cr(VI) ions under various working circumstances.

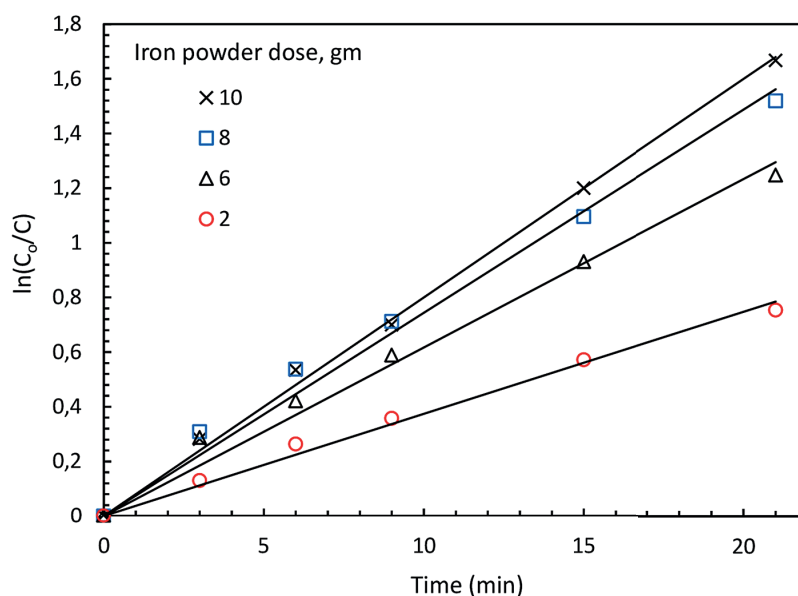
The influence of iron powder dose on the rate of Cr(VI) reduction is shown in Table 2. The data shows that mass transfer coefficient values decreased from 0.08 min<sup>-1</sup> to 0.04 min<sup>-1</sup> by decreasing iron powder dose from 10 gm to 2 gm.

### Effect of time

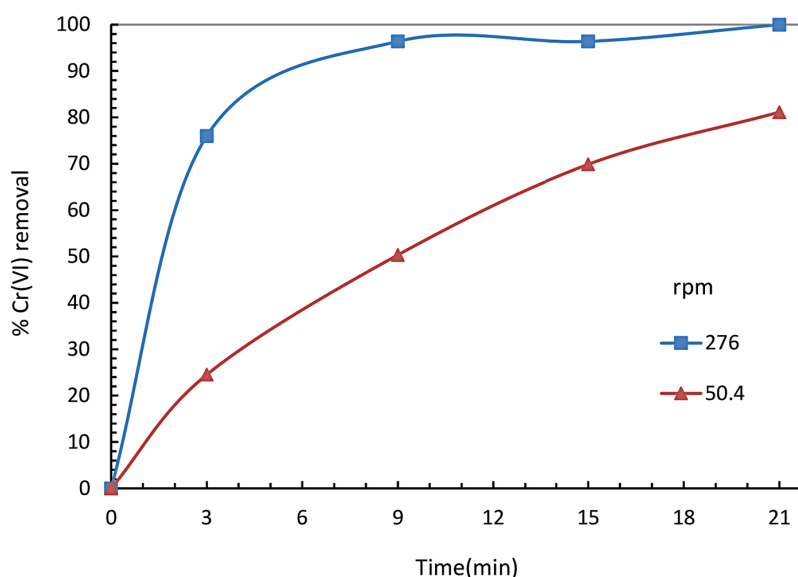
The reaction time has an effect on the elimination of Cr(VI) from water [Amin et al., 2022]. A series of tests were carried out to see how time affected the % elimination of hexavalent chromium ions using two different rpm, 276 and 50.4, at constant iron powder dose, pH and initial Cr(VI) concentration and subjected to different time (Fig. 3). It can be noted that when rotational speed was 276 rpm, almost Cr(VI) were removed within 21 min. In addition, in the case of 50.4 rotational

**Table 2.** Values of *k* and *R*<sup>2</sup> for the experimental data

Iron dose (g)	<i>k</i> (min <sup>-1</sup> )	<i>R</i> <sup>2</sup>
10	0.08	0.9972
8	0.07	0.9869
6	0.06	0.9840
2	0.04	0.9912



**Figure 2.** Typical plot of  $\ln(C_0/C)$  vs. time at different iron dose (rpm = 50.4, pH = 3, and initial Cr(VI) concentration = 30 ppm)



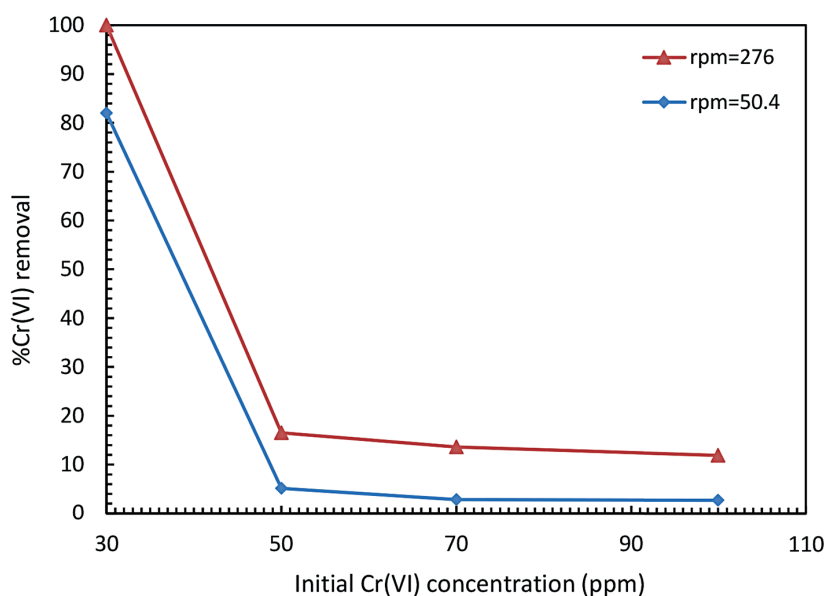
**Figure 3.** Effect of time on % Cr(VI) removal at different rpm (iron powder dose = 10 g, pH = 3 and initial Cr(VI) concentration = 30 ppm)

speed, it was observed that by increasing time to 21 min the percent removal of Cr(VI) increased from 0 to 82. The data in Figure 3 show that a greater reduction of Cr(VI) concentration can be obtained by increasing contact time and rotation speed. These results are consistent with the results of Li et al. [Li et al., 2009].

#### Effect of initial Cr(VI) concentration

The starting Cr(VI) concentration values were set to be 30, 50, 70 and 100. The pH was 3 and the

reaction time was 21 min. The solution containing Cr(VI) was treated with 10 g iron powder. Figure 4 shows that high reduction extent is observed when initial Cr(VI) concentration was 30 ppm, whereas a strong decline in the Cr(VI) reduction takes place for 50, 70 and 100 ppm. This trend appears at agitation rate of 276 and 50.4. For the highest rpm, as the initial Cr(VI) concentration increased from 30 to 100 ppm, the removal efficiencies of Cr(VI) were decreased from 100% to 11.9%. The removal efficiencies of Cr(VI) were reduced from 82 percent to 2.7 percent at the lowest rpm. This is most



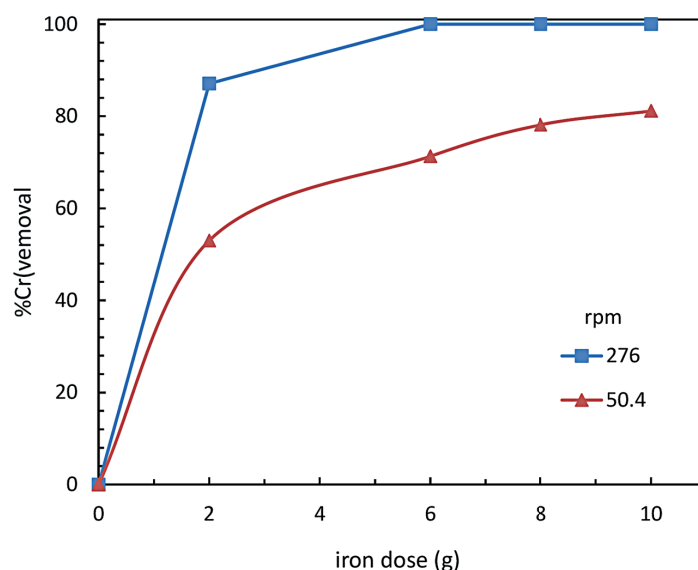
**Figure 4.** Effect of initial Cr(VI) concentration on % Cr(VI) removal at different rpm (iron powder dose = 10 gm, pH = 3 and time = 21 min)

likely owing to increased iron surface passivation and a lower accessible surface area of iron to chromium ratio at higher Cr(VI) concentrations, resulting in less iron reactivity [Gheju & Iovi, 2006].

#### Effect of iron powder dose

From Figure 5 the effect of iron powder mass on the Cr(VI) reduction was investigated under these conditions: initial Cr(VI) concentration of 30 ppm, pH of 3, rpm of 276 and 50.4. The variation of iron powder mass ranged from 2 to 10

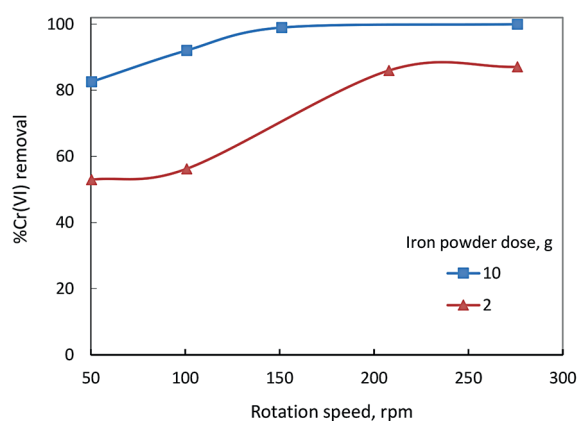
gm. The reduction reaction completely ended at 21 min. It is clear that on increasing rpm, % removal of Cr(VI) increased. On the other hand, at rotational speed of 276, that there was a sharp increase in Cr(VI) percent removal, it gave 100% Cr(VI) removal. Meanwhile, at rotational speed of 50.4, it can be seen that as the iron powder dosage increases from 2 to 10 g the percent removal of hexavalent chromium increases from 53 to 82. This is due to larger surface area of contact or reactive sites for higher iron dosage [Prasad et al., 2011].



**Figure 5.** Effect of iron powder dose on % Cr(VI) removal at different rpm (initial Cr(VI) concentration = 30 ppm, pH = 3 and time = 21 min)

### Effect of rotation speed

The trend of the rpm effect was observed from Figure 6. As it can be seen, the % removal of Cr(VI) increased as the value of iron dose increased and the reaction remained stable when it reached equilibrium at higher rpm. There was a complete removal of hexavalent chromium ions at the highest rpm and iron dose of 10 g after 21 min. Moreover, minimum % removal of Cr(VI) (87.1) was achieved at the highest rpm and iron dose of 2 g after 21 min. On the other hand, when using 10 g of iron powder at the lowest rpm, 82% removal of Cr(VI) achieved. However, only 53% of the Cr(VI) removed at the lowest rpm and on using 2 g of iron powder.

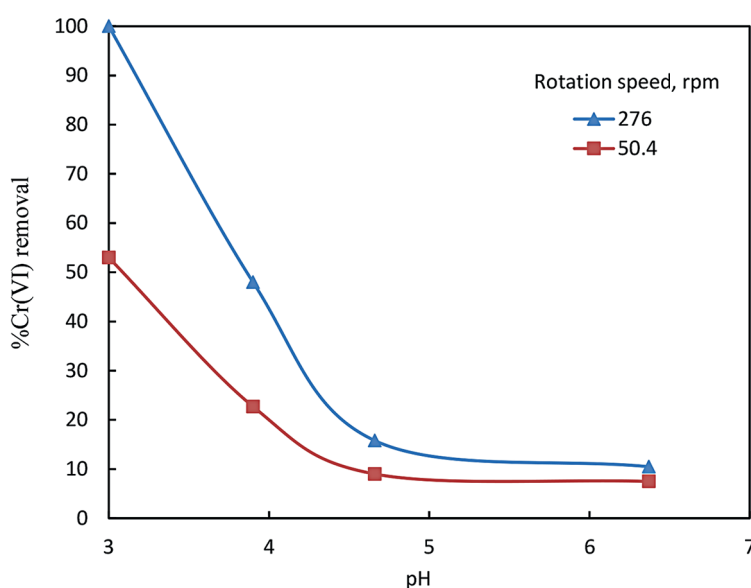


**Figure 6.** Effect of rotation speed on % Cr(VI) removal at different iron powder doses (initial Cr(VI) concentration = 30 ppm, pH = 3 and time = 21 min)

This trend is attributed to an increase in the diffusion rate of Cr(VI) solution, as rpm increases, which decreases the diffusion layer thickness on iron powder and increases iron reactivity [Abdel-Aziz et al., 2018].

### Effect of pH

The solution pH is a vital characteristic that can determine how efficient a process is. The percent elimination of hexavalent chromium ions was examined as a function of pH at varied rpm, constant initial Cr(VI) concentration, and constant iron dose. The pH of the solution was set between 3 and 6.4. At pH 3 and 276 rpm, the Cr(VI) reduction was quite high, as illustrated in Figure 7. This is because the stoichiometry of the reaction (Eq. (1)) requires 7 mol of  $H^+$  for each mol of Cr(VI), implying that Cr(VI) reduction is substantially dependent on the  $H^+$  concentration, i.e. low pH [Baird et al., 2012]. Furthermore, at rpm = 276 and 50.4, operating at the pH values greater than 3 results in a substantial fall in Cr(VI) reduction, with the influence of pH on percent Cr(VI) reduction being much less pronounced. This is most likely due to elemental Fe dissolution causing the co-precipitation of insoluble mixed Fe(III)–Cr(III) (oxy)hydroxides. Cr(VI) access to the iron surface may be obstructed by this Cr–Fe (oxy)hydroxide phase, causing Cr(VI) reduction to lower [Prasad et al., 2011; Gheju et al., 2008].



**Figure 7.** Effect of pH on % Cr(VI) removal at different rpm (iron powder dose = 10 g, initial Cr(VI) concentration = 30 ppm and time = 21 min)

## CONCLUSIONS

Industrial activities release a substantial amount of Cr(VI)-containing waste into the environment, posing a health risk. Iron powder reduction of Cr(VI) to Cr(III) from aqueous solution has been proven to be an effective Cr(VI) removal procedure. As a result, various reactor layouts have been examined for their capacity to reduce Cr(VI). A new reactor shape was tested to see how well it performed. On the basis of the findings of this study, the following conclusions can be drawn. The effects of Cr(VI) concentration at start-up, pH, iron powder loading, and rpm are statistically significant. The first-order process represents the researched reduction reaction, according to experimental kinetic results. The percent of Cr(VI) reduction using iron powder is greatly affected by pH, with higher reduction at lower pH levels. Lower initial Cr(VI) concentrations, lower pH, higher iron powder loading, and higher rpm all resulted in higher percent Cr(VI) reduction.

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