Batch reactor performance improvement for hexavalent chromium reduction by scrap iron using reciprocating perforated disc

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The aim of the present work is to improve the performance of a batch reactor used for the reduction of hexavalent chromium ions to trivalent ions by scrap iron shreds using reciprocating perforated disc. Many variables were investigated for its effect on the rate of reduction reaction such as frequency and amplitude of oscillation (vibration velocity), initial concentration of hexavalent chromium ions, phase ratio between the mass of solid scrap iron shreds and the volume of hexavalent chromium solution (m/v), and disc diameter. The results showed that the rate of hexavalent chromium ions reduction was increased by increasing the frequency and amplitude of oscillation (vibration velocity), increasing the phase ratio and increasing the disc diameter. On the other hand, the rate of reduction decreased by increasing the initial concentration of hexavalent chromium ions. It was found that the rate of mass transfer has increased by a factor ranging from 5 to 10 than the reduction without disc oscillation depending on vibration intensity of the disc oscillation. In addition mass transfer study of the process has revealed that the data fit the dimensionless equation $Sh_m = 0.032 \, Re^{1.12} \, Sc^{0.33}$. The importance of using the above equation in the design and operation of high productivity reactor was pointed out.

**Key words:** hexavalent chromium reduction, scrap iron, reciprocation, vibration, wastewater.

INTRODUCTION

Chromium is a common pollutant in the environment resulting from widespread industrial use such as, textile dying, tanneries, metallurgy, metal electroplating, cooling towers and wood preserving. The toxicity of chromium depends on its oxidation state. Chromium(VI) such as $\text{CrO}_4^{2-}$ and $\text{Cr}_2\text{O}_7^{2-}$ is known to be toxic to humans, animals, plants and microorganisms whereas trivalent chromium is essential for humans and less toxic than hexavalent chromium and easily removed by simple precipitation by lime as $\text{Cr(OH)}_3$ [1, 2]. Many techniques have been considered to reduce the content of chromium ion in waste water streams such as ion exchange and activated carbon adsorption [3–5], electrochemical techniques [6, 7] and chemical reduction using reducing agents such as $\text{SO}_2$, $\text{FeSO}_4$, etc. and precipitation method [8, 9]. Although ion exchange and activated carbon adsorption have been successfully demonstrated on the laboratory scale, they have not been employed to any significant degree in full-scale operation and are only suitable for low concentrations of chromium ion (less than 100 ppm) [3–5]. On the other hand hand reduction of $\text{Cr(VI)}$ to $\text{Cr(III)}$ by different reducing agents such as $\text{NaHSO}_3$, $\text{FeS}$, $\text{FeSO}_4$, $\text{SO}_2$, etc., followed by chemical precipitation of $\text{Cr(III)}$ by lime as $\text{Cr(OH)}_3$ has received a great attention [10–13], and was found to operate effectively with higher rate and higher % recovery at pH values 2–3. These methods are controlled by the cost of the chemicals used and the dosage required of each one. Typically it was found that, the chemical dosage required for $\text{Cr(VI)}$ reduction is twice the stoichiometric required [13, 14]. With regard to cost considerations metallic Iron has received a great attention as a reducing agent for $\text{Cr(VI)}$. In recent years, zerovalent iron was used for the in situ reduction of redox active metals from contaminated groundwater [15–18]. Previous investigators [19] have shown that $\text{Cr(VI)}$ may be removed from solution via reduction to $\text{Cr(III)}$ according to the following equations:

$$2\text{Cr}_2\text{O}_7^{2-} (aq) + 6\text{Fe}^0(s) + 28\text{H}^+ (aq) \rightarrow 4\text{Cr}^{3+} (aq) + 6\text{Fe}^{2+} (aq) + 14\text{H}_2\text{O}$$  \hspace{1cm} (1)

$$\text{Cr}_2\text{O}_7^{2-} (aq) + 6\text{Fe}^{2+} (aq) + 14\text{H}^+ (aq) \rightarrow 2\text{Cr}^{3+} (aq) + 6\text{Fe}^{3+} (aq) + 7\text{H}_2\text{O}$$  \hspace{1cm} (2)

The net reaction for the reduction process can be written as:

$$\text{Cr}_2\text{O}_7^{2-} (aq) + 2\text{Fe}^0(s) + 14\text{H}^+ (aq) \rightarrow 2\text{Cr}^{3+} (aq) + 2\text{Fe}^{3+} (aq) + 7\text{H}_2\text{O}$$  \hspace{1cm} (3)

The reduction of $\text{Cr} (VI)$ to $\text{Cr (III)}$ using a relatively pure iron wire was investigated by Gould [20], who concluded that iron surface is effective in
reducing Cr (VI) to Cr (III) under pH conditions of 2–3. Bowers et al. [21], have examined the use of scrap iron filings to treat Cr(VI) containing metal plating wastewaters and came to the conclusion that using iron filings to treat Cr(VI) containing solutions have the advantages that the chemical costs using scrap iron filings are substantially lower than conventional reducing agents such as SO$_2$, NaHSO$_3$, FeS, FeSO$_4$, etc. also the dissolved iron provide a well conditioned sludge product. The indirect reduction of hexavalent chromium to trivalent chromium with scrap iron and simultaneous generation of electrical energy using a divided parallel plate cell and fixed bed electrodes was investigated by Abdo et al. [22], who came to the conclusion that this technique can reduce Cr(VI) to the permissible limit value effectively while it neither consumes energy nor expensive chemicals. Hou et al. [23], studied the effect of presence of different divalent cations on the reduction of hexavalent chromium by zerovalent iron and came to the conclusion that presence of copper ions and iron ions could improve the reduction process while calcium ions might inhibit the process.

Previous investigations for the reduction of Cr(VI) to Cr(III) on iron surface proved that the reduction reaction is a diffusion controlled one [19, 24]. From this point of view the rate of reaction can be increased using different techniques such solution circulation or agitation using mechanical tools. The aim of the present work is to implement mechanical vibration or reciprocation for enhancing the rate of reduction reaction. The application of vibrations, pulsation and or reciprocation has been recognized as effective process intensification techniques that enhances mass and heat transfer rates, and improves both process productivity and product quality [25–30]. Zaki et al. [31] suggested the possibility of using oscillating screen array as a catalytic reactor suitable for conducting liquid–solid diffusion controlled catalytic reactions such as removal of organic pollutants from industrial effluents by wet oxidation. In addition application of oscillatory motion in electrochemical processing has been of particular interest due to its ability to enhance mass transfer rate, current density and system energy utilization. Recently, it was shown that more than 20-fold increase in the mass transfer rate could be achieved by vibrating vertical electrodes along their length [32]. Among its applications in that field are electrochemical processing, electroplating, metal recovery from bio-leaching solutions, and more recently manufacture of Printed Wiring Board [33–38]. In all of the above mentioned applications, generating of an oscillatory field at the solid–liquid interface is achieved by vibrating either the solid surface or the fluid surrounding it. Although both approaches achieve the same objective, the former is more energy efficient since the energy dissipation there is mainly focused in the boundary layer adjacent to the solid–liquid interface rather than in the bulk of the fluid medium. When the power needed to vibrate the electrode was taken into consideration, Al Taweel et al. [38] found that both amplitude and frequency have almost equal effect on the enhancement obtained per unit power consumed.

From the above it is clear that pulsation or vibration is a good tool for enhancing the rate of hexavalent reduction using scrap iron shreds. In addition scrap iron shreds will improve the economy of the process.

EXPERIMENTAL

Fig. 1 shows the experimental setup used in the present study. It consisted of the vibrating system and the reactor. The vibrating system consisted of a reciprocating perforated plastic disc with different diameters ranging from 6 to 12 cm, with constant perforations fixed at 0.25 cm in diameter and arranged in lines with constant spacing of 1 cm. The perforated disc was placed in a Plexiglas column of 15 cm diameter and 30 cm height. The disc was held inside the column by insulated stainless steel stem of 3 mm diameter which penetrated the disc at its centre by means of epoxy coated steel nuts. The upper end of the stem was connected to the vibrator through a Teflon sleeve. Vertical oscillation was induced to the perforated disc by means of a mechanical vibrator connected to the upper end of the stem. The mechanical vibrator consisted of a disc rotated by means of an electrical motor. The rotating motion of the disc was transferred into a reciprocating motion by means of a crank shaft connected to the disc at a distance from its centre. The frequency of vibration was measured by means of a portable digital tachometer and changed by means of a set of pulleys and gear box connected to the electrical motor. The amplitude was adjusted by adjusting the distance between the rotating disc centre and the point of its connection with the crank shaft. The rate of hexavalent chromium reduction on scrap iron shaving surface was followed by measuring the change in concentration of hexavalent chromium ions solution with time. Before each run, scrap iron shavings were prepared with different mesh ranged from 10 to 50 and soaked in 0.1 N HCl for about 2 minutes to remove any rust or coats, then washed with distilled water, dried and placed in...
two litres of freshly prepared acidified potassium dichromate solution were placed in the column that have iron shavings. In the meantime the solution was subjected to oscillation at the required vibration intensity. Samples of the solution (5 ml) were withdrawn at regular time intervals ranged from 1.5 to 3 min at high and low vibration intensities respectively. These samples were titrated against standard 0.1 N ferrous ammonium sulphate using diphenylamine barium salt as indicator [39]. Different initial concentrations of potassium dichromate solution were used in the present study namely, 0.025, 0.05, 0.075 and 0.1 M, all solutions contained 0.5 M H₂SO₄, and prepared using A.R. chemicals and distilled water. Experiments were carried out at room temperature which ranged from 21–22°C, while the pH of the solutions was adjusted at 2.5 in all experiments using a portable digital pH meter and 0.1 N NaOH solutions. The solution viscosity and solution density used in data correlation were measured by an Ostwald viscometer and density bottle respectively. While diffusivity at different temperatures were calculated using Stokes-Einstein equation (\( D \mu / T \) = constant), and the literature [40, 41].

The area of iron shavings is not defined and can not be easily determined so the volumetric mass transfer coefficient (\( k' = K \alpha A \)) will be used for data analysis. \( K' \) was obtained under different conditions by plotting \( \ln((C_0 - C_e)/(C - C_e)) \) vs. \( t \) as shown in Fig. 2 and then calculating the volumetric mass transfer coefficient from the slope of the resulting plot.

![Fig. 2. Ln((C₀ - Cₑ)/(C - Cₑ)) vs time at different vibration velocity.](image_url)

**RESULTS AND DISCUSSION**

For the simple batch reactor used in the present work the mass transfer coefficient (\( K \)) can be calculated using the equation [42]

\[
 V_s \log((C_0 - C_e)/(C - C_e)) = K.A.t
\]

Where \( V_s \) is the solution volume; \( C_0 \), \( C_e \) and \( C \) are initial, equilibrium and concentration at any time \( t \) of dichromate solution, respectively; \( A \) is the active area of the scrap iron shreds; \( t \) is the time of reaction. The above equation is the integrated form of the material balance equation of the batch reactor, namely

\[
 -V_s \cdot d(C - C_e)/dt = K.A.(C - C_e)
\]

As the area of iron shavings is not defined and can not be easily determined so the volumetric mass transfer coefficient (\( k' = K \alpha A \)) will be used for data analysis. \( K' \) was obtained under different conditions by plotting \( \ln((C_0 - C_e)/(C - C_e)) \) vs. \( t \) as shown in Fig. 2 and then calculating the volumetric mass transfer coefficient from the slope of the resulting plot.

**Effect of amplitude and frequency of oscillation**

Figures 2, 3 and 4 show the effect of amplitude (\( A_m \)), frequency (\( f \)) and vibration velocity \( V_1 \) (\( V_1 = 4A_m.f \)) on the rate of reduction reaction and rate of mass transfer. The volumetric mass transfer coefficient increased by increasing both amplitude and frequency or vibration intensity. The increase in the reduction rate may be attributed to the fact that increasing vibration intensity will increase turbulences especially those of the small scale high frequency eddies, these eddies will reduce the thickness of the diffusion layer and hence increase the rate of mass transfer (\( K = D/\delta \)) where \( D \) is the ions diffusivity and \( \delta \) is the diffusion layer thickness. In addition increasing vibration velocity increases fluid circulations inside the column which fluidizes iron shreds and increases the contact area between the two phases and hence increases the rate of mass transfer.

Figure 4, shows that the volumetric mass transfer coefficient can be related to the vibration intensity by the relation that: \( k' = aV_1 + b \). The value of \( a \) can be approximated to the value 0.033 with an average deviation of about 2%, while that of \( b \) its value ranges from 0.0658 to 0.6897 at amplitudes of 1cm and 4 cm respectively, which indicates that the volumetric mass transfer coefficient has been increased by a factor of 10.48 by increasing the amplitude from 1cm to 4cm.
Effect of initial dichromate concentration

Figure 5 shows that, the volumetric mass transfer coefficient decreased by increasing the initial concentration of dichromate solution [Cr(VI) concentration]. This can be attributed to the passivation of iron surface and reduction in iron corrosion that stops the main reactions of the reduction process (reactions 1 and 2) [43]. In addition, the diffusivity of dichromate ions decreases with increasing its concentration thus decreasing the rate of reduction reaction \( (K = D/\delta) \). From figure 5, it is obvious that the % increase in the rate of reduction for higher vibration velocity (58.2 cm/s) is approximately 8 times the rate at the lower velocity (13 cm/s) both at the same amplitude, which confirm the enhancement effect of pulsation for improving the rate of reduction reaction to a good extent.

Effect of phase ratio (solid/liquid)

Figure 6, shows that the volumetric mass transfer coefficient increased by increasing phase ratio, which can be ascribed to the increased surface area available for the reduction reaction. In addition, passivation of iron surface decreases by increasing surface area of iron, thus the rate of reduction reaction increase.
Overall correlation using dimensional analysis

For the purpose of design consideration dimensional analysis was used for correlating the main variables affecting the reduction operation. It was found that the data fits the general mass transfer equation that

\[ \text{Sh} = a \text{Re}_v^{\alpha} \text{Sc}^{0.33} \]  
(6)

The exponent of Sc was proved by other investigators to be 0.33 [44], where \(a\) and \(\alpha\) are constants. As mentioned before the true area of mass transfer is not easy to be determined so the modified Sherwood number (Shm) will be used instead of Sh, where \(\text{Sh}_m = 4 K/\pi d D\), where \(d\) is the column diameter and \(D\) is the ions diffusivity. The exponent of vibrational Reynolds (constants \(\alpha\)) was obtained by plotting \(\log \text{Sh}_m\) vs. \(\log \text{Re}_v\) for different Sc as shown in Figure 8 and it was found to be about 1.12.

The higher value of exponent \(\alpha\) (1.12) confirms that the reaction is diffusion controlled one. In addition, this higher value compared to the theoretical value 0.5–0.57 [44] may be attributed to the enhancing effects of \(\text{H}_2\) evolution, which occurs simultaneously with chromate reduction at the shreds surface (observed visually) as a result of the reaction:

\[ \text{Fe} + 2\text{H}^+ = \text{Fe}^{2+} + \text{H}_2 \]  
(7)

The rising \(\text{H}_2\) bubbles collide with the surface of iron shreds and disturb the diffusion layer with a consequent increase in the mass transfer coefficient \(K\) (\(K = D/\delta\)).

As shown in Figure (9), \(\text{Sh}_m\) was drawn versus \(\text{Re}_v^{1.12} \cdot \text{Sc}^{0.33}\), for finding out the value of constant \(a\). The overall correlation was found to fit the equation that:

\[ \text{Sh}_m = 0.032 \text{Re}_v^{1.12} \cdot \text{Sc}^{0.33} \]  
(8)

This equation is valid in the range 1275 > Sc > 1020 and 7900 > Re\(_v\) > 1764.

The deviation of data was found to be high as the value of \(R^2\) was found to be about 0.75 this higher deviation of data may be ascribed to the complex nature of the mass transfer mechanism over the iron shreds surface as a result of simultaneous H\(_2\) evolution with direct chromate reduction on the iron surface [24]. In the design consideration of pulsating or reciprocating system using iron shreds for the reduction of hexavalent chromium, experimental investigations, with the given correlation will be more reliable with the aid of the obtained results for each variable studied.

CONCLUSION

The reduction kinetics of hexavalent chromium to trivalent chromium using a fixed bed of scrap iron shreds subjected to pulsation using reciprocating perforated disc was investigated under different conditions of amplitude and frequency (vibration intensity) of vibration, initial concentration of a synthetic solution of acidified potassium dichromate, phase ratio(solid/liquid), and disc diameter. It was found that the mass transfer coefficient and the rate of reduction reaction increased by increasing frequency and amplitude of vibration (vibration intensity), disc diameter and phase ratio (solid/liquid) and decreasing by increasing the initial concentration of the acidified potassium dichromate solution. The results show that the volumetric mass transfer coefficient has increased by a factor ranging from 5 to 10 depending on vibration intensity. For the rational design and operation of batch reactor using scrap iron shreds subjected to reciprocation and used for the reduction of hexavalent chromium from waste solutions the following mass transfer correlation was obtained \(\text{Sh}_m = 0.032 \text{Re}_v^{1.12} \cdot \text{Sc}^{0.33}\).

This equation is valid in the range 1275 > Sc > 1020 and 7900 > Re\(_v\) > 1764. The deviation of data was found to be high as the value of \(R^2\) was found to be about 0.75 this higher deviation of data may be ascribed to the complex nature of the mass transfer mechanism over the iron shreds surface as a
result of simultaneous H₂ evolution with direct chromate reduction on the iron surface.

This system is suitable for treating higher discharge rates of industrial wastewater polluted with the toxic hexavalent chromium ions with lower cost.

List of symbols and nomenclatures

\( A \)  active area of iron shreds (cm²);
\( A_m \)  the amplitude of oscillation (cm);
\( C_0, C_c, \) and \( C \)  are initial, equilibrium and concentration at any time of dichromate solution (M);
\( d \)  disc diameter (cm);
\( D \)  diffusivity of dichromate ions (cm²/s);
\( F \)  frequency of oscillation (s⁻¹);
\( K \)  mass transfer coefficient (cm/s);
\( K' \)  volumetric mass transfer coefficient (cm³/s);
\( t \)  time (s);
\( V_s \)  solution volume (cm³);
\( \text{Sc} \)  Schmidt number (μD/P);
\( \text{Sh} \)  Sherwood number (Kd/D);
\( \text{Sh}_m \)  modified Sherwood number (4K/πDd);
\( \text{Re}_v \)  vibrational Reynolds number (pV₁ d/μ);
\( \mu \)  solution viscosity (g/cm.s);
\( \rho \)  solution density (g/cm³);
\( \delta \)  diffusion layer thickness (cm).

REFERENCES

Целта на настоящата работа е подобряване на действието на реактор с периодично действие за редукция на шествалентни хромни йони до тривалентни йони чрез късове от железен скрап с използване на възвратно-постъпателен перфориран диск. Изследвани са много променливи за ефекта върху скоростта на реакцията на редукция като: честота и амплитуда на осцилациите, начинна концентрация, на шествалентните хромни йони, фазово съотношение на масата на късовете от железен скрап и обем на разтвора на шествалентните хромни йони (m/v) и диаметъра на диска. Резултатите показват, че скоростта на редукция на шествалентните хромни йони расте с увеличаване на честотата и амплитудата на осцилациите на диска (скоростта на вибриране), увеличаване на фазовото съотношение, и увеличаване на диаметъра на диска. От друга страна, скоростта на редукция намалява с увеличаване на началната концентрация на шествалентните хромни йони. Намерено е, че скоростта на масопренасяне при вибрации на диска се увеличава 5–10 пъти в сравнение с редукция с без осцилации на диска. В допълнение, изследването на процеса на масопренасяне показва, че данните съответстват на безизмерно уравнение $Sh_m = 0.032 \ Re^{1.12} \ Sc^{0.33}$. Показано е значението на посоченото уравнение за проектирането и действието на реактор с висока производителност.