A preliminary batch study of sorption kinetics of Cr(VI) ions from aqueous solutions by a Magnetic Ion Exchange (MIEX®) resin and determination of film/pore diffusivity

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Abstract
A magnetic ion exchange resin was tested for the removal of Cr(VI) ions from aqueous solutions in a batch reactor at different resin dosages (0.5-1.5 g L⁻¹), pH values (2-10), temperatures (25 °C-55 °C) and initial concentrations of Cr(VI) (0.11 -2.12 mmol L⁻¹ or 5.7-110 mg L⁻¹). The experimental data were evaluated using kinetic models based on the rate controlling steps relevant to pseudo-first order or pseudo-second order reactions or diffusion through fluid film or pores of the MIEX resin beads. Fast uptake of Cr(VI) ions by MIEX resin facilitates the attainment of equilibrium within 60 minutes. The sorption process is strongly dependent on the initial pH of the solution with maximum occurring at pH 4-6. The sorption of Cr(VI) at equilibrium increases with the increase in initial concentration according to the Langmuir isotherm, with a maximum sorption capacity of 93 mg g⁻¹ on MIEX resin. Relatively low activation energy of 43 kJ mol⁻¹ at a high initial concentration of 1 mmol L⁻¹ Cr(VI) suggests a mixed chemical-diffusion controlled process, supported by the agreement of the sorption results with the homogeneous particle diffusion model with a film diffusivity of $D_f = 1 \times 10^{-9}$ m² s⁻¹ and a pore diffusivity of $D_p = 8 \times 10^{-13}$ m² s⁻¹.

Key words
MIEX resin, Chromium(VI), Sorption, Isotherms, Film/Pore Diffusion, Kinetics

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1. Introduction

Chromium is a common element in Earth’s crust that is being heavily used in many industrial processes like tanning, electroplating, printed circuit boards, metal finishing, steel fabrication, pigments and wood preservatives (Rakhunde et al., 2012; Pehlivan and Cetin, 2009; Rana et al., 2004). Chromium in rock forming minerals in ultrafamic rocks react with high-valent manganese oxides and release water soluble chromium ions to the environment (Rajapaksha et al., 2013). The deportment of hazardous trace elements such as chromium from the bauxite ore will also produce solutions of low concentrations, where the buildup can occur over time due to the cyclical nature of the Bayer process (Zydorczac et al., 2012). Chromium in stainless steel of the plant construction material subjected to the chemical attack of the hot caustic solution can also cause accumulation of chromium in process liquor. The measured solubility of Cr₂O₃ in 1-6 mol/kg NaOH solutions at 25 °C continues to increase with time and reaches a concentration of 0.45-0.68 mmol L⁻¹ chromium, predominantly in the form of CrO₄²⁻ (Zydorczac et al., 2012). Even at low concentrations Cr(VI) compounds are known to have carcinogenic effects (Shi et al., 2009). Some disposal sites are capable of generating leachates containing up to 100 mg L⁻¹ Cr(VI) (Geelhoed et al., 2002; Wang et al., 2010; Zhang et al., 2009; Sahinkaya et al., 2012; O’Conell et al., 2008), compared to the maximum contamination level of 0.1 mg L⁻¹ for chromium set by the US Environmental Protection Agency (EPA) (Badruruddoza et al., 2013). The ion exchange removal of Cr(VI) has received considerable interest (Table 1) and the fastest rate and highest sorption capacity of Cr(VI) have been achieved using amino-functionalised titanate nanotubes (Wang et al., 2013).

Magnetic ion exchange (MIEX) resin (http://www.miexresin.com/index.asp?page=5) is a magnetically enhanced, macroporous, polyacrylic, strong base anion exchange resin used...
in the chloride form (Fig.1a; Lee et al., 2003). Over the years MIEX resin has gained significant popularity for efficient removal of dissolved organic carbon (DOC) from wastewater and groundwater and convenient regeneration (Nguyen et al., 2011). The anion exchange of DOC for chloride proceeds according to the schematic diagram in Fig. 1b. The geometry of MIEX resins depends on the method of preparation from magnetic polymer microspheres (100-400 µm) composed of a polymer core and a magnet shell. The magnetic property of the resin beads is caused by the embedded magnetite particles (Lee et al. 2003; Nguyen et al., 2011). The polymeric structure of MIEX resin contains quaternary ammonium groups (Fig. 1a) and has a water content of 65% (w/w), porosity of 0.77 and an exchange capacity of 0.32 meq mL\(^{-1}\) (Boyer and Singer, 2008; Boyer et al., 2008). The resin has several advantages over conventional ion exchange resins: (i) magnetically enhanced agglomeration of the individual resin beads makes the gravity based settling very efficient, (ii) the macroporous resin has a higher surface area in comparison to the conventional ion exchange resins, (iii) it has been successfully used in full scale operation due to selective and effective recovery from the solution phase, (iv) the sorption process may be applied to solutions containing other solid phases, if the suspended particles are fine and have low settling rates, due to agglomeration and fast settling of MIEX resin having an average bead size of 234 µm.

In general the chromate ion uptake by quaternary amine ion exchange resins, such as MIEX, decreases in the presence of high concentrations of counter ions such as chloride, nitrate and sulfate, indicating their decreasing affinity towards the MIEX resin in the order sulfate>nitrate>>chloride (Atia, 2006). These results are consistent with the affinity order of some common anions towards the MIEX resin reported as: \( \text{ClO}_4^- > \text{CrO}_4^{2-} > \text{DOC} > \text{SO}_4^{2-} > \text{NO}_3^- > \text{CO}_3^{2-} > \text{OH}^- > \text{PO}_4^{3-} > \text{AsO}_4^{3-} > \text{BrO}_3^- > \text{NO}_2^- > \text{Br}^- > \text{Cl}^- > \text{HCO}_3^- > \text{F}^- \) (http://www.miexresin.com/files/Bicarb%20Regeneration%20IXOM%20CG%20edits.pdf).
Therefore, one or more of these anions present with the target anion in the same medium can act as interferent(s), affecting the amount of uptake and the sorption behavior which can be explained according to the selectivity series. Table 2 shows the negative impact of coexisting anions on the removal of different target species by MIEX resin.

On average, a resin bead at the Wanneroo water treatment plant in Western Australia would expect to see around 600 regeneration cycles over its lifetime. The plug flow regeneration of resin is generally conducted using 1.5-2.0 mol L\(^{-1}\) chloride solutions (US patent # US 7763666 B2, WO 96/07615, EP 1776190 A1, WO 2005105677 A1). Sodium bicarbonate can also be used to regenerate the MIEX resin when chloride is considered to be problematic as it may result a high conductivity in waste streams after regeneration. It has been reported that a 50 g/L sodium bicarbonate solution can be used to restore the MIEX resin in the bicarbonate form (http://www.miexresin.com/files/Bicarb%20Regeneration%20IXOM%20CG%20edits.pdf).

Sodium sulphate has also been identified as an alternative regenerant for MIEX resin, however the applicability after the regeneration may have certain limitations as the sulphate anion has shown higher selectivity towards MIEX resin in the selectivity series described above (http://www.miexresin.com/files/Alternative%20Regenerants%20Ixom%20CG%20Edits.pdf) and in results obtained from previous studies in Table 2.

According to Table 3, the sorption mechanism of MIEX resin for the uptake of both organic (DOC and bentazone) and inorganic (\(\text{BrO}_3^-\) and \(\text{HCO}_3^-\)) anions have been confirmed to be an ion-exchange process as it follows a stoichiometric removal of chloride from the resin (i.e. the uptake of the sorbate and the removal of chloride ions from the resin takes place at a 1:1 molar ratio). Moreover, Liu et al. (2011) have studied the use of the strong-base MIEX
resin in the presence of parathon-methyl, which is a non-ionic herbicide. A very poor uptake of the target compound (< 10%) has been observed as a result of low feasibility towards ion exchange due to its non-ionic nature.

Boyer and Singer (2008) have studied the applicability of a weak-acid MIEX resin, which has a similar composition to the strong-base MIEX resin, but has weakly acidic cation exchange functional groups, to remove bicarbonate and DOC (pH ~ 8). A weak-acid MIEX resin with cation exchange sites makes adsorption the only possible way for the uptake of bicarbonate and DOC. However, no removal of bicarbonate or DOC has been observed even after two days of mixing, whereas they follow a stoichiometric exchange with a resin with a similar composition, but with strong base anion exchange sites. Therefore, ion-exchange has been identified as the predominant mechanism for removal of both organic and inorganic anions by MIEX resin as shown in Fig. 1b.

The sorption mechanism generally involves a series of steps and the overall rate is controlled by the slowest step. In general, the intraparticle diffusion can be the rate limiting step in a batch reactor compared to the film diffusion in a continuous flow system (Gupta et al., 2014). Previous studies on the use of MIEX resin have considered the different reactor types for the removal of DOC, As(V) and Cr(VI) (Jha et al., 2006; Nguyen et al., 2011) from aqueous solutions where the sorption of anions is by ion exchange (Fig. 1a,b). However, a detailed kinetic analysis on the basis of rate controlling steps such as film/intraparticle/pore diffusion, as examined by Gupta et al. (2014), has not been conducted in relation to the ion exchange of Cr(VI) by MIEX. This communication reports the sorption capacity of MIEX® resin for Cr(VI) under different conditions such as pH, resin dosage, Cr(IV) concentration and temperature using a batch reactor and investigates the kinetics and the rate controlling step for ion exchange. The results are used to calculate the coefficients for mass transfer and film/pore
diffusion of Cr(VI) ions. Details of the effect of coexisting ions on the removal of Cr(VI) by MIEX resin and a comparison between batch and column loading and stripping will be presented in a future communication.

2. Materials and Methods

The particle size of the MIEX resin resin beads obtained from Waneroo Wastewater Treatment Plant in Western Australia was determined using the Microtrac S3500 particle size analyser. The scanning electron microscopic and energy dispersive X-ray spectroscopic (SEM/EDS) studies were carried out using the JEOL JCM 6000 bench top SEM with EDX analyser. Perkin Elmer Frontier FTIR/NIR spectrometer was used in infrared spectroscopic studies. The Surface Area and porosity analyser (aka SAPA) was used to determine the BET surface area.

The MIEX resin was in its chloride form and was stored in brine (0.4 mol L \(^{-1}\) NaCl) in closed jars to prevent any loss of absorbed water causing the resin to shrink. Before each experiment the resin was thoroughly rinsed with Milli Q water to remove any excess chloride ions. All reagents were of analytical grade and Milli Q water was used throughout the experiments. Stock solution of 1 g L \(^{-1}\) Cr(VI) (2.829 g K\(_2\)Cr\(_2\)O\(_7\) in 1 L of milli Q water) was diluted as required. Experiments were carried out by contacting a 1 g sample of MIEX resin (unless otherwise specified) with 1 L of Cr(VI) solution for 60 minutes in an overhead stirred tank reactor connected to rotation speed and temperature controls described previously (Senanayake et al., 2011). The pH was adjusted to the desired value (2≤pH≤10) using 0.1 mol L \(^{-1}\) HCl or NaOH. The solution was stirred at 1500 rpm and 5 mL samples were removed from the reactor at 0, 3 minutes and then every 5 minutes, with a 10 mL syringe. Chromium uptake per unit mass of MIEX (mg g \(^{-1}\)) was evaluated using Eq. (1), where, \(C_o\) and \(C_e\) (mmol L \(^{-1}\)) are
the initial and equilibrium concentrations of Cr(VI) in solution, respectively, $V$ (mL) is the volume of the chromium solution and $m_r$ (g) is the mass of MIEX resin. A GBC 933 atomic absorption spectrophotometer (AAS) was used for the determination of Cr(VI) concentration in solution.

$$q_r = (C_o - C_e) \frac{V}{m_r}$$

(1)

4. Results and Discussion

4.1 Characterization

Size distribution of the resin measured by laser sizing and wet sieving showed 80% passing size ($P_{80}$) of 200 μm. The surface area and porosity measurements show that the BET surface area is 43.5 m$^2$/g and the average pore diameter is 2.0 nm. Figs. 2a-b show the scanning electron micrographs of the resin beads. The atom percentages on MIEX resin based on Electron Dispersion Spectroscopy (EDS) of fresh and chromium loaded resin beads (Figs. 2c-d) listed in Table 4 shows the exchange of Cr(VI) ions for chloride ions. Fig. 2e shows the linear correlation of atom percentages on the surface of the resin beads before (fresh) and after loading Cr(VI). The deviation of the composition of Cl and Cr from the linear relationship of slope 1 for other atoms in Fig. 2e indicates the anion exchange replacement of chloride by chromate, similar to that by DOC shown in Fig.1b and described in section 1. The characteristic bands from the Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) of the MIEX resin before and after loading Cr(VI) are illustrated in Fig. 2f and the main functional groups with the corresponding IR bands are listed in Table 5. The two spectra look almost the same, indicating that the main functional groups remain unchanged upon the sorption process. However, the peak at 967 cm$^{-1}$ in the spectrum of the
unloaded resin has become stronger and shifted to 937 cm\(^{-1}\) after Cr(VI) loading. Balan et al. (2013) have reported that Cr=O vibrations appear around 948.96 cm\(^{-1}\) and this can result an enhancement in peak intensity in the spectrum of the loaded resin. The new peak at 771 cm\(^{-1}\) with a significant intensity is due to the Cr-O groups (Balan et al., 2013), which again confirms the Cr(VI) loading on MIEX resin.

4.2 Effect of resin dosage

Figs. 3a-b show the concentration of Cr(VI) at pH 4 in the absence or presence of the MIEX resin indicating that the decrease in concentration of Cr(VI) in solution is a result of the ion exchange by the resin particles, rather than by the glass surface of the vessel. Figs. 3c-d show the effect of resin dosage on the uptake of Cr(VI) by MIEX resin at a temperature of 25 °C, pH 4 and two different initial concentrations of 0.96 and 1.92 mmol L\(^{-1}\) Cr(VI). The results listed in Table 6 show that the maximum uptake in Fig. 3c-d depends on the resin dosage as well as the concentration of Cr(VI) in solution indicating the first order dependence of the ion exchange process corresponding to the equation: \(\ln(C_0/C_t) = kt\) where \(C_0\) is the initial concentration and \(C_t\) is the concentration after time \(t\) and \(k\) is the rate constant. However, Figs. 3e-f indicate that the first order dependence is applicable only in some cases highlighting the need for further analysis of data described later.

4.3 Effect of pH

The strong base anion exchange functional sites of the MIEX resin (\(-\text{NR}_3^+\text{Cl}^-\)) are expected to remain unaffected by any changes in the pH of the solution, except for the competition between Cl\(^-\) and OH\(^-\) for the sites at high pH. However, Ding et al. (2015) noted that the MIEX
resin has an isoelectric point of ~6.1 which makes the surface of the resin negatively charged at pH > 6.1. Thus, the electrostatic repulsion between surface of resin and BrO₃⁻ caused a decrease in sorption from 7.81 mg mL⁻¹ at pH 6 to a lower value of 3.83 mg L⁻¹ at pH 9 (Ding et al., 2015). According to the effect of pH observed in this study depicted in Fig. 4, the favorable pH range for the removal of Cr(VI) using MIEX appears to be between 4 and 6, showing the beneficial effect of operating at a pH ≤6.1. However, the lower sorption at pH 2 (Fig. 4) highlights the importance of considering actual Cr(VI) speciation in solution.

Although a change in pH and redox potential of the Cr(VI) solution can affect the sorption process by altering the species of Cr(VI) to Cr(III) in the presence of electron donor groups attached to the resin (Gandhi et al., 2010), the MIEX resin beads do not have such groups which could be oxidized by Cr(VI).

The Pourbaix diagram (Eh-pH diagram) of chromium-water system in Fig. 5a shows that the predominant Cr(VI) species are H₂CrO₄⁰, HCrO₄⁻ and CrO₄²⁻, depending upon pH and agree with the previously reported diagrams (Barrera-Diaza et al., 2012). Likewise, Fig. 5(b) based on the speciation diagram published by Wang et al. (2013) shows that HCrO₄⁻ is the predominant Cr(VI) species at pH 4 while CrO₄²⁻ is predominant at alkaline pH and agrees with previous findings (Pehlivan and Cetin, 2009; Kotaś and Stasicka, 2000). The ion exchange efficiency (E) calculated using \( E = 100(C_o-C_e)/C_o \) at different pH values was used, as illustrated in Fig. 5(c), for the comparison of the performance of MIEX resin in this preliminary study with other sorbents for Cr(VI) reported in the literature which show similar trends (Dubey and Gopal, 2007; Wang et al., 2013). The maximum and minimum ion exchange efficiencies of 76% and 32% by MIEX were achieved at pH 4 and 2, respectively.

The ion exchange process on MIEX resin at low pH and high pH can be represented by Eq. (2a,b) and Eq. (3), respectively. The change in speciation from HCrO₄⁻ to CrO₄²⁻ and the
competition of OH\(^-\) ions for the ion exchange sites (Sheha and El-Zahhar, 2008) can lower the uptake of Cr(VI) at higher pH of 10. The minimum sorption efficiency of Cr(VI) at the lower pH of 2 in Fig. 4 and Fig. 5c supports the reaction in Eq. (2b) indicating that lower pH favors desorption. At an initial Cr(VI) concentration of 1 mmol L\(^{-1}\) the initial molar ratio of [H\(^+\)]/[Cr(VI)] is 10 at pH 2 and this favors the reverse reaction of Eq. (2b). In contrast, the forward reaction of Eq. (2b) is favored in solutions of pH ≥4 where the ratio of [H\(^+\)]/[Cr(VI)] is ≤0.1.

\[
-NR_3^+Cl^- + HCrO_4^- = -NR_3^+HCrO_4^- + Cl^- \quad (2a)
\]

\[
2(-NR_3^+Cl^-) + HCrO_4^- = (-NR_3^+)2CrO_4^{2-} + H^+ + 2Cl^- \quad (2b)
\]

\[
2(-NR_3^+Cl^-) + CrO_4^{2-} = (-NR_3^+)2CrO_4^{2-} + 2Cl^- \quad (3)
\]

### 4.4 Effect of Cr(VI) concentration and isotherms

Fig. 6(a) shows the effect of increase of Cr(VI) concentration on ion exchange by the resin at pH 4 and 25 °C. The concentration of Cr(VI) on resin (q\(_e\), mg g\(^{-1}\)) and in solution (C\(_e\), mg L\(^{-1}\)) at equilibrium are plotted in Fig. 6(b). The value of q\(_e\) increases with the increase in C\(_e\) and reaches a plateau of 91 mg g\(^{-1}\) (1.75 mmol g\(^{-1}\)). The Langmuir isotherm (Langmuir, 1918) described by Eq. (4) is the simplest theoretical model for monolayer sorption onto a surface with finite number of identical sites with no side interactions between the uptake ions:

\[
\frac{C_e}{q_e} = \frac{C_e}{q} + \frac{1}{qb} \quad (4)
\]
where \( Q \) (mg g\(^{-1}\)) is the maximum sorption capacity of the resin and \( b \) (L mg\(^{-1}\)) is the Langmuir constant related to the free energy of sorption. A plot of \( C_e/q_e \) as a function of \( C_e \) based on the equilibrium data resulted in a straight line with a high correlation coefficient (0.99), as shown in Fig. 6(c). The slope and y-intercept of the plot were used to determine the values of \( Q = 92.6 \) mg g\(^{-1}\) and \( b = 3.48 \) L mg\(^{-1}\), respectively. The value of \( Q \) is generally higher than most of the values for similar types of resins reported by previous researchers listed in Table 1.

The plot of \( \log q_e \) as a function of \( \log C_e \) in Fig. 6(d) shows poor linearity with \( R^2=0.88 \), indicating the non-applicability of the Freundlich isotherm, given by Eq. (5) where \( K_F \) is the Freundlich constant related to maximum sorption capacity (mg g\(^{-1}\)) and \( n \) is the heterogeneity factor related to the sorption intensity. Unlike in other studies on the adsorption of methylene blue dye from waste water on polyaniline zirconium(IV) silicophosphate nanocomposite which show reasonably good correlation with both Langmuir and Freundlich isotherms (Gupta et al., 2014) further comparison between the two isotherms was not considered in this study due to poor correlation in Fig. 6d.

\[
\log q_e = \log K_F + \left( \frac{1}{n} \right) \log C_e \tag{5}
\]

4.5 Adsorption kinetics

4.5.1 Initial rates

Fig. 7(a-b) show the effect of pH and initial concentration of Cr(VI) on the initial rates of ion exchange (mmol g\(^{-1}\) min\(^{-1}\)). Although pH has no significant effect on initial rates (Fig. 7(a)), the slope close to unity in Fig. 7(b) indicates that the rate is controlled by a first order
phenomenon and/or mass transfer through fluid film around the resin bead. This warrants further analysis of kinetic data described below.

4.5.2 First order or second order kinetic models

The rate equation for the pseudo-first order kinetic model is expressed by Eq. (6) (Qiu et al., 2009), where \( k_1 \) is the pseudo-first order reaction rate constant \( \text{(min}^{-1} \) ) and \( q_t \) is the sorption \( \text{(mmol g}^{-1} \) ) after time \( t \).

\[
\ln(q_e - q_t) = \ln q_e - k_1 t
\]  

(6)

Typical plots of \( \ln(q_e-q_t) \) as a function of \( t \) for selected concentrations are shown in Fig. 8(a) along with the regression coefficients \( (R^2) \) and the first order rate constants listed in Table 7. The linear plots suggest that the sorption of Cr(VI) on MIEX resin may follow the pseudo first order kinetics and the rate is dependent on the initial concentration. However, considering the \( R^2 \) values, pseudo-first order model does not show a good agreement with linearity.

The linear form of the pseudo-second order kinetic model with a second order rate constant \( k_2 \) expressed by Eq. (7) (Hamadi et al., 2001) could be fitted for the experimental results over the whole range of concentrations as shown in Fig. 8(b).

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t
\]  

(7)

The values of \( R^2 \) close to unity and better agreement between the predicted and measured values of \( q_e \) in comparison to the pseudo-first-order model, support pseudo-second order kinetics. This behavior is consistent with the results for the sorption of Cr(VI) by amino
funtionalized titanate nanotubes (Wang et al., 2013) and by ionically modified magnetic nanoparticles (Badrudoza et al., 2013). Sorption of other species by MIEX resin also obeys second order kinetics (Table 8).

The activation energy $E_a$ (kJ mol$^{-1}$) for the sorption of Cr(VI) ions onto MIEX resin was determined using the Arrhenius equation:

$$lnk = lnA - \frac{E_a}{RT}$$  \hspace{1cm} (8)

Rate constant $k_2$ obtained from pseudo-second order analysis were plotted against the reciprocal of temperature as shown in Fig. 8(c). The activation energy determined from the slopes is $\sim 43$ kJ mol$^{-1}$ and confirms the view that ion exchange of Cr(VI) by MIEX resin follows a mixed chemical-diffusion controlled process (Sheha and El-Khouly, 2013). This value of $E_a$ is also in agreement with the range of 24-40 kJ mol$^{-1}$ for general ion exchange processes (Inglezakis and Zorpas, 2012).

4.5.3 External film diffusion model

The initial period of a sorption process is controlled by diffusion in the liquid film surrounding the particle. Therefore, an external-film diffusion model has been developed for the initial period by writing a mass balance for the sorption in a batch system based on five assumptions (Ponnusami et al., 2010): (i) sorbent particles are spherical, (ii) the solution is thoroughly mixed and the bulk concentration is uniform, (iii) the influence of solid phase diffusion of sorbed species is negligible during the initial period due to insignificant
concentration in the solid phase, (iv) the rate of loss of anions from the bulk solution is equal to the rate of sorption from the liquid phase to the outer surface of the particle, and (v) first order rate equation is applicable. The rate of sorption is written as:

\[
\frac{dC_t}{dt} = -k_{ef} \frac{A_s}{V} (C_t - C_s)
\]  \hspace{1cm} (9)

where, \(C_t\) and \(C_s\) (mmol L\(^{-1}\)) represent the concentration of Cr(VI) at time \(t\) in the bulk solution and at the surface of the solid phase, respectively, \(k_{ef}\) (m s\(^{-1}\)) is the external film transfer coefficient, \(A_s\) (m\(^2\) g\(^{-1}\)) is the total surface area of all particles in 1 g, \(V\) (mL) is the volume of solution. Integral solution of Eq. (9) upon substituting the boundary conditions \(C_t=0\) at \(t=0\) and \(C_s=0\) at time \(t\) is:

\[
-log \left( \frac{C_t}{C_0} \right) = \frac{k_{ef} A_s}{2.303 V} t
\]  \hspace{1cm} (10)

Fig. 9 shows a linear plot of -\(\log(C_t/C_0)\) as a function of \(t\) with zero intercept at a low initial concentration of 0.1 mmol L\(^{-1}\) and suggests the validity of this model. The slope of the linear relationship (0.0025 s\(^{-1}\)) in Fig. 9 for an initial concentration of 0.1 mmol L\(^{-1}\) Cr(VI) along with the values \(A_s = 43.5\) m\(^2\) g\(^{-1}\) for MIEX resin used in this study, 2003) and \(V = 10^3\) cm\(^3\) at the resin loading of 1 g/L resin (section 2) can be used to calculate the value of \(k_{ef} = 1 \times 10^{-5}\) cm s\(^{-1}\). This value is smaller than the predicted value of 5 x 10\(^{-3}\) cm s\(^{-1}\) (McCabe et al., 2005) for the mass-transfer coefficient to a suspended particle of 200 µm diameter in water.

### 4.5.4 Homogeneous particle diffusion model
The homogenous particle diffusion model (HPDM) (El-Kamash et al., 2007) allows the identification of the actual slowest step during the sorption process: (a) film diffusion, during which the ions diffuse through the liquid film surrounding the particle or (b) particle (pore) diffusion that involves the diffusion of ions into the resin beads. These two rate determining steps are represented by Eqs. (11) and (12), respectively, where \( X(t) \) is the fractional attainment of equilibrium at time \( t \) or the extent of sorbent conversion, \( C_s \) (mmol L\(^{-1}\)) is the equilibrium concentration of Cr(VI) in the solid phase, \( D_f \) (or \( D_p \)) is the diffusion coefficient in the liquid phase (or solid phase), \( r_o \) is the radius of MIEX resin particles assumed to be spherical and \( \delta \) is the film thickness, approximately 0.001 cm (Koner et al., 2012; Chabani et al., 2006).

\[
\ln(1 - X(t)) = \frac{3D_f C_e}{r_o \delta C_s} t = k_f t \\
\ln(1 - X^2(t)) = \frac{2D_p \pi^2}{\delta^2} t = k_p t
\]

Fig. 10(a) shows the linear plots for the film diffusion model at low concentrations based on Eq. 11 over the first 10 min. When the data were analyzed with the particle diffusion model based on Eq. 12, linearity was observed over a longer period of time as shown in Fig. 10(b). These results support the view that particle diffusion control is favored at high sorbate concentrations. The slope of the linear relationship in Fig. 10(a) for the initial concentration of 0.79 mmol L\(^{-1}\) Cr(VI) is \( k_f = 0.0033 \) s\(^{-1}\) and the value of \( C_e \) is 0.22 mmol L\(^{-1}\). The calculated value of \( C_s \) based on the value of \( q_e = 0.57 \) mmol g\(^{-1}\) and the wet settled density of 0.35 g cm\(^{-3}\) is \( 1.2 \times 10^3 \) mmol L\(^{-1}\). Substitution of these values along with \( r_o = 1 \times 10^{-4} \) m for a particle diameter of 200 \( \mu m \) and \( \delta = 1 \times 10^{-5} \) m in Eq. 11 gives a value of \( D_f \approx 1 \times 10^{-9} \) m\(^2\) s\(^{-1}\). This value is of the same order as the reported value of \( D_f = 1.13 \times 10^{-9} \) m\(^2\) s\(^{-1}\) for CrO\(_4^{2-}\) (Marcus, 1997).
The slope of the linear relationship in Fig. 10(b) for the initial concentration of 1 mmol L\(^{-1}\) Cr(VI) is \(k_p = 0.0017\) s\(^{-1}\). Substitution of this value along with \(r_o = 1 \times 10^{-4}\) m in Eq. (12) gives a value of \(D_p = 8.6 \times 10^{-13}\) m\(^2\) s\(^{-1}\). Furthermore, the smaller value of \(D_p\) compared to \(D_f\) and the relatively low activation energy of 43 kJ mol\(^{-1}\) suggest that the rate is controlled by ion exchange and diffusion inside the pores of MIEX resin.

5.0 Conclusions

The HCrO\(_4^-\) species of Cr(VI) is predominant at the pH range 4-6 and it is most efficiently uptaken by MIEX resin. The ion exchange equilibrium obeys the Langmuir isotherm. Detailed analysis of rate data reveals pseudo-second order kinetics. The results are consistent with the published test results for the sorption of a range of other species by MIEX resin as summarized in Table 8. The increase in temperature causes an increase in the rate of ion exchange. Rate data at a higher concentration of Cr(VI) (1 mmol L\(^{-1}\)) supports an activation energy 43 kJ mol\(^{-1}\) and a mixed chemical diffusion controlled process as well as the homogeneous particle diffusion model with a film diffusivity of \(D_f = 1 \times 10^{-9}\) m\(^2\) s\(^{-1}\) and a pore diffusivity of \(D_p = 8 \times 10^{-13}\) m\(^2\) s\(^{-1}\).

6.0 Acknowledgements

The authors are grateful to the Water Corporation for providing the MIEX resin samples. Authors acknowledge the financial support from Murdoch University and Leading Foreign Research Institute Recruitment Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT and Future Planning (2013).

References


Jha, A.K., Bose, A., Downey, J.P., 2006. Removal of As(V) and Cr(VI) ions from aqueous solutions using a continuous, hybrid field-gradient magnetic separation device. Separation Science and Technology 41, 3297-3312.


Fig. 1 (a) Segment unit model of MIEX resin, (b) MIEX sorption chemistry and regeneration (Reference: Lee et al., 2003; Nguyen et al., 2011 and http://www.miexresin.com/files/publishedPapers/AquatechNL2000.pdf)
Fig. 2

(a) MIEX resin beads  
(b) MIEX resin beads at 472 magnification

(c) EDS of washed MIEX resin beads  
(d) EDS of Cr(VI) loaded MIEX resin beads

(e) Correlation of atom % from EDS  
(f) FT-IR spectra

Fig. 2. SEM images, EDS spectrum and FT-IR spectra of MIEX resin.
(a) SEM (from http://www.miexresin.com/files/publishedPapers/AquatechNL2000.pdf) (b) SEM at magnification of 472; (c) EDS spectrum of washed fresh resin (d) EDS spectrum of Cr(VI) loaded resin, (e) correlation of atom% from EDS of Cr(VI) loaded resin and fresh resin (Table 4), (f) FT-IR spectra before and after loading Cr(VI) (Table 5) (b, c, d, e, f from this work)
Fig. 3

(a) 25 °C

(b) 55 °C

(c) 25 °C, 0.96 mmol L⁻¹ Cr(VI)

(d) 25 °C, 1.92 mmol L⁻¹ Cr(VI)
Fig. 3. Effect of resin and Cr(VI) dosages on adsorption on MIEX microspheres at pH 4 and applicability of first order kinetics: (a, b) without resin (open circles) and with 0.45 g/L resin (closed circles) in 0.2 mmol L\(^{-1}\) Cr(VI) at 55 °C; (c, d) Cr(VI) adsorption, (e, f) first order dependence.
Fig. 4. Effect of pH on adsorption of Cr(VI) onto 1 g of MIEX microspheres in 1 L of 1.00 mmol L\(^{-1}\) Cr(VI) at 25 °C.
Fig. 5

(a) Effect of Eh-pH on species distribution

(b) Effect of pH on species distribution

(c) Effect of pH on Cr(VI) adsorption

Fig. 5. (a) Eh-pH diagram for Cr/Cr(II)/Cr(III)/Cr(VI)/H$_2$O system (based on HSC 7.1 data base, Roine, 2012) at 25 °C and 0.1 mmol L$^{-1}$ chromium species; (b) Effect of pH on Cr(VI) speciation at 25 °C (Wang et al., 2013); (c) effect of pH on Cr(VI) adsorption by MIEX microspheres (this work, from Fig. 4), amino functionalized titanate nanotubes (from Wang et al., 2013) and activated carbon prepared from groundnut husk (Dubey and Gopal, 2007).
Fig. 6. (a) Effect of concentration of Cr(VI) on adsorption at $T = 25^\circ{C}$, pH = 4, (b) equilibrium data for adsorption, (c) Langmuir isotherm (d) Freundlich isotherm
Fig. 7. Effect of variables on initial rates of Cr(VI) adsorption (a) effect of pH at 1 mmol L$^{-1}$ Cr(VI), (b) effect of Cr(VI) concentration (both at 1 g/ L resin at 25 °C)
Fig. 8

(a) 

(b) 

(c)
Fig. 8. Kinetic plots for adsorption of Cr(VI) on MIEX at different initial concentrations (a) pseudo-first order, (b) pseudo-second order (c) Arrhenius plot for pseudo-second order
Fig. 9

Fig. 9. External film diffusion plots for Cr(VI) adsorption at different initial concentrations
Fig. 10

Fig. 10. Linear relationships of HPDM plots for Cr(VI) adsorption onto MIEX (a) film diffusion model at low concentration, (b) particle diffusion model at high concentrations (all adsorption data from Fig. 7a)
Table 1. Comparison of monolayer maximum adsorption capacities and equilibrium time of Cr(VI)

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Q (mg g⁻¹)</th>
<th>Equilibrium time (min)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amino starch</td>
<td>12.12</td>
<td>120</td>
<td>Dong et al. (2010)</td>
</tr>
<tr>
<td>Hexadecylpyridinium bromide modified natural zeolites</td>
<td>14.31</td>
<td>240</td>
<td>Zeng et al. (2010)</td>
</tr>
<tr>
<td>Wheat-residue derived black carbon</td>
<td>21.34</td>
<td>240</td>
<td>Wang et al. (2010)</td>
</tr>
<tr>
<td>Chitosan-coated fly ash</td>
<td>33.27</td>
<td>50</td>
<td>Wen et al. (2011)</td>
</tr>
<tr>
<td>Ionomically modified Fe₃O₄ magnetic nanoparticles</td>
<td>35.20</td>
<td>120</td>
<td>Badruddoza et al. (2013)</td>
</tr>
<tr>
<td>Eichhorniacrassipes root biomass-derived activated carbon</td>
<td>36.34</td>
<td>30</td>
<td>Giri et al. (2012)</td>
</tr>
<tr>
<td>Sawdust</td>
<td>41.50</td>
<td>1050</td>
<td>Gupta and Babu (2009)</td>
</tr>
<tr>
<td>Modified magnetic chitosan chelating resin</td>
<td>58.48</td>
<td>120</td>
<td>El-Reash et al. (2011)</td>
</tr>
<tr>
<td>b-CD and quaternary ammonium groups modified cellulose</td>
<td>61.05</td>
<td>15</td>
<td>Zhou et al. (2011)</td>
</tr>
<tr>
<td>Ethylenediamine-functionlized Fe₃O₄ magnetic polymers</td>
<td>61.35</td>
<td>60</td>
<td>Zhao et al. (2010)</td>
</tr>
<tr>
<td>Amino functionalized titanate nanotubes</td>
<td>153.8</td>
<td>15</td>
<td>Wang et al., 2013</td>
</tr>
<tr>
<td>MIEX resin</td>
<td>92.59</td>
<td>60</td>
<td>This work</td>
</tr>
</tbody>
</table>

Table 2. The effect of coexisting ions on MIEX adsorption

<table>
<thead>
<tr>
<th>Concentration of target speciesa</th>
<th>Coexisting anionsb</th>
<th>MIEX (mL/L)</th>
<th>T (K)</th>
<th>rpm</th>
<th>Conditions</th>
<th>Negative impactc</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 mg/L ClO₄⁻</td>
<td>NO₃⁻, SO₄²⁻, CO₃²⁻, PO₄³⁻</td>
<td>2</td>
<td>298</td>
<td>120</td>
<td>No pH adjustment; concentration of the other anions varied from 1-20 molar concentration ratios to ClO₄⁻</td>
<td>SO₄²⁻ &gt; CO₃²⁻ ~ PO₄³⁻ &gt; NO₃⁻</td>
<td>Tang et al. (2013)</td>
</tr>
<tr>
<td>1.99 mg/L TBBP A</td>
<td>NO₃⁻, SO₄²⁻, HCO₃⁻, HPO₄²⁻</td>
<td>0.25</td>
<td>298</td>
<td>120</td>
<td>pH=6; concentration of the other anions varied from 1-30 mg/L</td>
<td>HPO₄²⁻ &gt; SO₄²⁻ &gt; HCO₃⁻ &gt; NO₃⁻</td>
<td>Tang et al. (2014)</td>
</tr>
<tr>
<td>5 mg/L BrO₃⁻</td>
<td>SO₄²⁻, HCO₃⁻, Cl⁻</td>
<td>0.4</td>
<td>285</td>
<td>150</td>
<td>Concentration of the other anions varied from 1-30 mg/L</td>
<td>SO₄²⁻ &gt; HCO₃⁻ ~ Cl⁻</td>
<td>Ding et al. (2015)d</td>
</tr>
</tbody>
</table>

a. ClO₄⁻, TBBP A, BrO₃⁻ and coexisting anions were used as their sodium salts, unless stated otherwise.
b. Impact on lowering the uptake of the target species.
c. TBBP A: Tetrabromobisphenol A (pKₐ 7.5 and 8.5). At pH 6, the predominant form is the molecular form. It contains two aromatic rings which are rich in delocalized pi-electrons and form strong cation-pi electron interactions with the quaternary ammonium ions of the MIEX resin (Tang et al., 2014; Boyer et al., 2008; Zhang et al., 2013; Qu et al., 2008).
d. Cations were not specified.
Table 3. Previous sorption studies on different types of MIEX resin

<table>
<thead>
<tr>
<th>Sorbent and properties</th>
<th>Sorbate</th>
<th>Exchange ratio of sorbate: Cl(^-)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>MIEX (Strong base-anion exchange resin)</td>
<td>Bicarbonate or Bicarbonate + DOC Bentazone (^a) Parathion-methyl (non-ionic herbicide)</td>
<td>1:1</td>
<td>Boyer et al. (2008) Liu et al. (2011)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Negligible uptake of sorbate</td>
<td></td>
</tr>
<tr>
<td>WA-MIEX (^b) (Weak acid-cation exchange resin)</td>
<td>Bicarbonate or Bicarbonate + DOC</td>
<td>1:1</td>
<td>Ding et al. (2014)</td>
</tr>
</tbody>
</table>

\(^a\) Bentazone (pK\(_a\) 3.3) is present in its anionic form (enolate) under natural aquatic environments (Liu et al., 2011)

\(^b\) WA-MIEX: Weak acid MIEX

Table 4. Atomic composition of MIEX resin based on EDS

<table>
<thead>
<tr>
<th>Element</th>
<th>Atom % from EDS</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>Fresh resin</td>
</tr>
<tr>
<td></td>
<td>36.9</td>
</tr>
<tr>
<td>Al</td>
<td>3.23</td>
</tr>
<tr>
<td>Si</td>
<td>5.91</td>
</tr>
<tr>
<td>P</td>
<td>0.79</td>
</tr>
<tr>
<td>S</td>
<td>1.29</td>
</tr>
<tr>
<td>Cl</td>
<td>1.91</td>
</tr>
<tr>
<td>Cr</td>
<td>0.12</td>
</tr>
<tr>
<td>Fe</td>
<td>49.9</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
</tr>
</tbody>
</table>

\(^a\) after 1 h in 0.2 mmol L\(^{-1}\) Cr(VI) at 25 °C
Table 5. FT-IR analysis of the MIEX resin

<table>
<thead>
<tr>
<th>Wavenumber (cm⁻¹)</th>
<th>Peak assignment</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh resin</td>
<td>Cr(VI) loaded resin</td>
<td></td>
</tr>
<tr>
<td>3413</td>
<td>O-H stretching</td>
<td>Wen-queing et al. (2012)</td>
</tr>
<tr>
<td>2991</td>
<td>C-H stretching of benzene</td>
<td></td>
</tr>
<tr>
<td>2947</td>
<td>CH₃ symmetric stretching</td>
<td>Nakamoto (2009)</td>
</tr>
<tr>
<td>1722</td>
<td>C=O vibrations (ester groups)</td>
<td>Liang et al. (2015)</td>
</tr>
<tr>
<td>1622</td>
<td>Benzene ring skeleton stretching</td>
<td>Wen-queing et al. (2012)</td>
</tr>
<tr>
<td>1476</td>
<td>C-H symmetric bending (attached to the quaternary ammonium)</td>
<td>Balan et al. (2013)</td>
</tr>
<tr>
<td>1387</td>
<td>CH₃ symmetric bending</td>
<td>Wen-queing et al. (2012)</td>
</tr>
<tr>
<td>1240</td>
<td>C-N stretching</td>
<td>Xiao et al. (2016)</td>
</tr>
<tr>
<td>1148</td>
<td>C-O vibrations (ester groups)</td>
<td>Liang et al. (2015)</td>
</tr>
<tr>
<td>967</td>
<td>CH₂ rocking</td>
<td>Nakamoto (2009)</td>
</tr>
<tr>
<td>917</td>
<td>Deformation vibrations of 1,4-disubstituted benzene rings</td>
<td>Wolowicz and Hubicki (2009)</td>
</tr>
<tr>
<td>771</td>
<td>Cr-O</td>
<td>Balan et al. (2013)</td>
</tr>
</tbody>
</table>

Table 6. Effect of resin dosage on Cr(VI) adsorption

<table>
<thead>
<tr>
<th>Initial dosage of resin and Cr(VI)</th>
<th>Maximum adsorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resin (g/L)</td>
<td>Cr(VI) (mmol L⁻¹)</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>0.96</td>
</tr>
<tr>
<td></td>
<td>1.92</td>
</tr>
<tr>
<td>1.0</td>
<td>0.96</td>
</tr>
<tr>
<td></td>
<td>1.92</td>
</tr>
<tr>
<td>1.5</td>
<td>0.96</td>
</tr>
<tr>
<td></td>
<td>1.92</td>
</tr>
</tbody>
</table>

Solution volume = 1 Temperature 25 °C, Stirring rate 1000 rpm, Data from Fig. 3; average value in the last column is 0.94 mmol/g

Table 7. Pseudo-first order and pseudo-second order kinetic parameters

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Pseudo-first order</th>
<th>Pseudo-second order</th>
<th>qe (mmol g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T (°C)</td>
<td>C₀ (mmol L⁻¹)</td>
<td>pH</td>
<td>k₁ (min⁻¹)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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<table>
<thead>
<tr>
<th>Sorbate</th>
<th>Pseudo second order(^a)</th>
<th>Film diffusion</th>
<th>Langmuir isotherm</th>
<th>E(_a) (kJ \text{ mol}^{-1})</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>BrO(_3^-)</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes(^b)</td>
<td>32</td>
<td>Ding et al. (2015)</td>
</tr>
<tr>
<td>TBBP A</td>
<td>Yes</td>
<td>NR</td>
<td>Yes</td>
<td>NR</td>
<td>Tang et al. (2014)</td>
</tr>
<tr>
<td>ClO(_4^-)</td>
<td>Yes</td>
<td>NR</td>
<td>No(^c)</td>
<td>NR</td>
<td>Tang et al. (2013)</td>
</tr>
<tr>
<td>Bentazone (enolate form in Table 3)</td>
<td>Yes</td>
<td>No(^d)</td>
<td>Yes</td>
<td>NR</td>
<td>Liu et al. (2011)</td>
</tr>
<tr>
<td>CrO(_4^{2-})</td>
<td>Yes</td>
<td>Yes(^e)</td>
<td>Yes</td>
<td>43</td>
<td>This work</td>
</tr>
</tbody>
</table>

\(^a\) See Eq. (7).  
\(^b\) Well fitted into both Langmuir and Redlich-Peterson isotherms.  
\(^c\) Well described by the Freundlich isotherm.  
\(^d\) Intra-particle diffusion is the rate controlling step.  
\(^e\) Film diffusion is followed by pore-diffusion.

Table 8: Kinetic models, isotherms and activation energy of the sorption process by MIEX resin

Resin dosage = 1 g/L, Solution volume = 1 L, Stirring rate = 1000 rpm
Highlights

The sorption kinetics of Cr(VI) on the characterized MIEX resin was tested in a batch reactor

Most efficient sorption as HCrO$_4^-$ takes place at pH 4-6 with an activation energy of 43 kJ mol$^{-1}$

Sorption obeys Langmuir isotherm and pseudo-second order kinetics

Coefficients of film/pore diffusion of Cr(VI) were calculated