Hydrometallurgy 164 (2016) 208–218

Contents lists available at ScienceDirect

Hydrometallurgy

journal homepage: www.elsevier.com/locate/hydromet

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

R. Hans [a], G. Senanayake [a,*], L.C.S. Dharmasiri [a], J.A.P. Mathes [b], D.J. Kim [c]

[a] Chemical & Metallurgical Engineering & Chemistry, School of Engineering and Information Technology, Murdoch University, 90 South Street, Murdoch, Perth, WA 6150, Australia
[b] Research & Development, Steamatic, 10-11 Walker Street, Braeside, Melbourne, VIC 3195, Australia
[c] Korea Institute of Geoscience and Mineral Resources (KIGAM), Daejeon 305-350, Republic of Korea

ARTICLE INFO

Article history:
Received 18 March 2015
Received in revised form 29 May 2016
Accepted 5 June 2016
Available online 08 June 2016

Keywords:
MIEX resin
Chromium(VI)
Sorption
Isotherms
Film/pore diffusion
Kinetics

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 min. 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 $D_f = 1 \times 10^{-9}$ m^2 s^{-1} and a pore diffusivity of $D_p = 8 \times 10^{-13}$ m^2 s^{-1}.

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 (Zydorczak 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 Cr_2O_3 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 CrO_4^{2-} (Zydorczak 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'Connell 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) (Badruddoza 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-functionalized titanate nanotubes (Wang et al., 2013).

Magnetic ion exchange (MIEX) resin (http://www.miexresin.com) 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

* Corresponding author.
E-mail address: G.Senanayake@murdoch.edu.au (G. Senanayake).

http://dx.doi.org/10.1016/j.hydromet.2016.06.007

Table 1
Comparison of monolayer maximum adsorption capacities and equilibrium time of Cr(VI).

Adsorbent	Q ($mg\ g^{-1}$)	Equilibrium time (min)	References
Amino starch	12.12	120	Dong et al. (2010)
Hexadecylpyridinium bromide modified natural zeolites	14.31	240	Zeng et al. (2010)
Wheat-residue derived black carbon	21.34	240	Wang et al. (2010)
Chitosan-coated fly ash	33.27	50	Wen et al. (2011)
Ionically modified Fe_3O_4 magnetic nanoparticles	35.20	120	Badruddoza et al. (2013)
Eichhornia crassipes root biomass-derived activated carbon	36.34	30	Giri et al. (2012)
Sawdust	41.50	1050	Gupta and Babu (2009)
Modified magnetic chitosan chelating resin	58.48	120	El-Reash et al. (2011)
b-CD and quaternary ammonium groups modified cellulose	61.05	15	Zhou et al. (2011)
Ethylenediamine-functionalized Fe_3O_4 magnetic polymers	61.35	60	Zhao et al. (2010)
Amino functionalized titanate nanotubes	153.8	15	Wang et al., 2013
MIEX resin	92.59	60	This work

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., 2008a, b). 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 ammonium 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 (Atiya, 2006). These results are consistent with the affinity order of some common anions towards the MIEX resin reported as : $ClO_4^- > CrO_4^{2-} > DOC > SO_4^{2-} > NO_3^- > CO_3^{2-} > OH^- > PO_4^{3-} > AsO_4^{3-} > BrO_3^- > NO_2^- > Br^- > Cl^- > HCO_3^- > F^-$ (http://www.miexresin.com). 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). Sodium

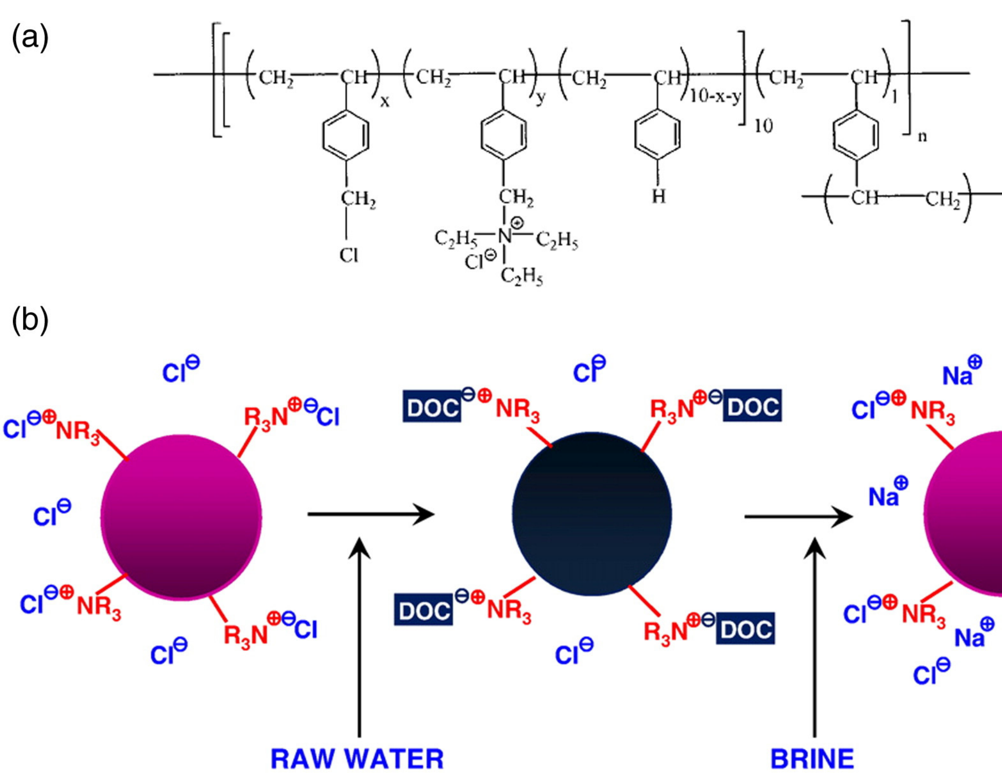

Fig. 1. (a) Segment unit model of MIEX resin, (b) MIEX sorption chemistry and regeneration (Reference: Lee et al., 2003; Nguyen et al., 2011 and http://www.miexresin.com/files/publishedPapers/AquatechNL2000.pdf).