Rapid small-scale column tests for Cr(VI) removal by granular magnetite
Efthimia Kaprara, Konstantinos Simeonidis, Anastasios Zouboulis and Manassis Mitrakas

ABSTRACT
This study evaluates the possibility of using magnetite as an adsorbent for the removal of Cr(VI) in a bed column setup under continuous flow conditions. For this purpose, granular magnetite was synthesized on a large scale and tested in both batch and rapid small-scale column experiments using reliable conditions of drinking water treatment. Column tests, which were designed to scale-down larger adsorption systems in terms of size, time and water flow, indicate a higher removal capacity compared to that observed during batch experiments with magnetite powder, reaching 9.2 mg/g at pH 6.4 before residual Cr(VI) exceeds 10 μg/L. The main parameters of this process, including pH, contact time and granular size, were also examined under similar column tests suggesting the improvement of the overall effectiveness and operation time at lower water pH, higher empty bed contact times and larger particle dimensions.

Key words | column tests, granular magnetite, hexavalent chromium

INTRODUCTION
The release of the movie ‘Erin Brockovich’ in 2000 has raised public awareness regarding Cr(VI) presence in drinking water. Until that time, most people were ignorant of its severe toxicity and carcinogenicity. Nowadays, Cr(VI) is considered as a priority pollutant, and it is a challenge to effectively remove it from water supplies. Cr(VI) can enter groundwater from both anthropogenic and natural sources. Anthropogenic sources may include industrial by-products from the manufacturing processes of stainless steel, chrome plating, etc. The natural origin of Cr(VI) is typically associated with the contact of water with ultramafic rocks and soils, such as serpentinite, dunites, and ophiolites (Cooper 2002; Kazakis et al. 2015). In recent years, an increasing number of references have identified the natural formation as a major origin of significant Cr(VI) levels (>50 μg/L) appearing in groundwater sources all over the world (Bourette et al. 2009; Kaprara et al. 2015).

Although the World Health Organization considers Cr(VI) as a priority pollutant, US EPA and the European Community have set Maximum Concentration Limits (MCLs) of total chromium at 100 μg/L and 50 μg/L, respectively. The lack of specialized regulation for Cr(VI) and the fact that the current total Cr limit underestimates the risks associated with this element, gave rise to an intense debate worldwide for establishing a new lower MCL for Cr(VI) in drinking water. In this direction, on 1 July 2014, the US State of California adopted the new MCL of 10 μg Cr(VI)/L, setting an example for other countries to follow. Therefore, it becomes necessary to develop new technologies that can reliably remove Cr(VI) from water to concentrations of these lower ppb levels.

Up to the present time, a significant number of remediation methods have been developed to remove chromium from aquatic systems, including chemical reduction
followed by precipitation (Melitas et al. 2001; Mitrakas et al. 2011), adsorption (Mohan & Pittman 2006), ion exchange (Dabrowski et al. 2004), membrane separation (Korus & Loska 2009), electro-dialysis (Nataraj et al. 2007), phyto-remediation (Cervantes et al. 2001), flotation (Matis & Mavros 1991) and solvent extraction (Vincent & Gaïl 2001). But in spite of the extensive scientific literature, most of the aforementioned methods refer to remediation of high Cr(VI) concentrations (ppm levels) in acidic environments, while the number of processes related to drinking water treatment is rather limited. In addition, taking into account that potable water treatment focuses on Cr(VI) removal at a low-ppb level, while preserving the pristine quality of water, it becomes even more difficult to establish an effective large-scale process. Adsorption on inorganic media meets most of these criteria and offers flexibility in design and operation (Kaprara et al. 2013). The use of inorganic adsorbents in the removal of chromium has been studied by several researchers, mostly for high Cr(VI) concentrations commonly found in wastewaters. Lehmann and co-workers have investigated the adsorption capacity of seven inorganic sorbents (GAC, β-Fe(OH)₃, MgCO₃, TiO₂, LDH, α-FeOOH, Cr.-G.), some in powdered and some in granulated form (Lehmann et al. 1999). Other researchers have examined the use of iron oxides such as goethite (Deliyanni et al. 2004) and akaganeite (Lazaridis et al. 2005), crystalline hydrous titanium oxide (Debnath & Ghosh 2008) and magnesium hydroxide (Liu et al. 2011). More recent studies have focused on the ability of magnetic nanoparticles to adsorb chromium (Hu et al. 2005; Chowdhury & Yanful 2010; Asuha et al. 2011). In this case, after the completion of adsorption, the adsorbent media (magnetic nanoparticles) can be separated from the aqueous solution by a magnetic field (Simeonidis et al. 2015a). Despite their interesting results, most of the aforementioned publications refer to significantly higher initial Cr(VI) concentrations commonly encountered in wastewaters. Furthermore, the adsorbent materials studied so far have demonstrated a moderate capacity for chromium removal and their maximum uptake capacity is achieved in acidic conditions, which are incompatible with drinking water treatment.

Among inorganic adsorbents that have been tested for the remediation of Cr(VI), magnetite (Fe₃O₄) presents a promising solution as it combines sufficient reductive and adsorption capacity (Simeonidis et al. 2015b). Particularly, the presence of Fe(II) ions on the structure of magnetite creates a surface reductive environment able to reduce Cr(VI) from the aqueous phase to insoluble Cr(III) forms which remain attached to the surface (Galilios & Vaclavikova 2008). Evidence of the reduction of Cr(VI) and the simultaneous oxidation of Fe(II) to Fe(III) on the magnetite’s surface were obtained by extended X-ray photoemission and absorption studies (Kendelewicz et al. 2000; Jung et al. 2007). However, the gradual consumption of Fe(II) sites located at the surface creates a passivation layer which prevents the reducing ability of magnetite after a relatively short period of use (Villacís-García et al. 2015). Passivation is also assisted by the oxidative activity of dissolved oxygen as well as the occupation of the magnetite’s surface by precipitating Cr(III) hydroxides (Peterson et al. 1997). The competition of Cr(VI) and oxygen for Fe(II) strongly depends on the pH. For instance, the reaction of Fe(II) with oxygen at pH 8 is more than 10 times faster than that between Fe(II) and Cr(VI) whereas the rate of Fe(II) oxidation by oxygen is decreased by more than 10 times at pH 7 (He & Traina 2005).

Although many researchers have examined magnetite’s effectiveness for adsorption of Cr(VI), there is a gap in reports on its removal capacity under continuous flow conditions. The aim of this study was to evaluate magnetite’s effectiveness for Cr(VI) removal when using a continuous flow process, and to identify the major factors affecting its performance. For this research, granular magnetite was synthesised and applied in both batch and column experiments (Rapid Small-Scale Column Tests, RSSCT), under conditions simulating the operation of a full-scale relevant system.

**EXPERIMENTAL**

**Synthesis-characterization**

Magnetite was prepared at kilogram-scale by aqueous co-precipitation of FeSO₄·H₂O and Fe₂(SO₄)₃·xH₂O, with a Fe(II)/Fe(III) ratio equal to 1:2, in an alkaline environment, in a two-stage continuous flow reactor, similar to that described by Tresintsi and co-workers (Tresintsi et al. 2012) (Figure 1).
Preliminary experiments showed that the second reactor stage was critical to control accurately and tune the key parameters of the process, such as pH ($12.3 \pm 0.2$) and redox potential ($\left[\frac{E}{C}0\right]_{1,000} \pm 50$ mV).

Solutions of iron salts in distilled water ($33$ g/L FeSO$_4 \cdot$H$_2$O and $72.7$ g/L Fe$_2$(SO$_4$)$_3 \cdot x$H$_2$O) were continuously pumped in the first stage of the reactor ($10$ L/h), and in the second stage precipitation took place at room temperature and at the pH value of $12.3 \pm 0.2$, controlled by the addition of a NaOH solution. The collected outflowing solid suspension was thickened for $24$ h in an Imhoff tank and then the obtained sludge was washed, centrifuged, dried at $30^\circ$C, ground and sieved to obtain either a fine powder form ($<45$ μm), used for batch adsorption experiments, or the respective granules (sizes $0.25$–$0.50$ and $0.50$–$1.0$ mm) for column tests.

Regarding the chemical characterization of magnetite, total iron content was determined by atomic absorption spectroscopy (Perkin-Elmer AAnalyst 800), after acid dissolution, while the Fe(II) presence was quantified by titration with KMnO$_4$ $0.05$ N. The structural and surface characteristics were identified by X-ray diffraction (XRD), thermogravimetric analysis (TG-DTA) and BET specific surface area determination. X-ray diffraction (XRD) was carried out using a water-cooled Rigaku Ultima + diffractometer with CuK$_x$ radiation, a step size of $0.05^\circ$ and a step time of $3$ s, operating at $40$ kV and $30$ mA. Thermogravimetric data (TG-DTA) were collected by a water-cooled Perkin-Elmer STA 6000 instrument in the temperature range $30$–$900$ °C, at a heating rate of $20$ °C/min and nitrogen flow. The surface area of magnetite was estimated by nitrogen gas adsorption at liquid N$_2$ temperature (77 K) using a micropore surface area analyzer according to the Brunauer-Emmett-Teller (BET) model. The electric surface properties of the material were examined through the measurement of the isoelectric point (IEP) which describes the effective charge at the surface double layer, the point of zero charge (PZC) which indicates the actual charge at the material’s surface and the surface charge density. In particular, IEP was determined by the curve of zeta-potential at $20 \pm 1$ °C of magnetite dispersion in $0.01$ M NaNO$_3$ versus pH solution, using a Rank Brothers Micro-electrophoresis Apparatus Mk II device, while PZC and surface charge density were defined by acid/base potentiometric mass titration in suspensions of the adsorbent at various ionic strengths (Kosmulski 2009).

**Cr(VI) removal**

The Cr(VI) removal capacity of produced magnetite was studied by using both batch and RSSCT experiments. The evaluation of magnetite as a Cr(VI) adsorbent was focused on its ability to decrease the residual Cr(VI) concentration below $10$ μg/L. For the batch mode experiments, a quantity of adsorbent ($5$–$150$ mg) was added to a volume of Cr(VI)-containing distilled or test water ($50$–$1,000$ μg Cr(VI)/L) in a $300$ mL conical flask and shaken for a sufficient period of time ($24$ h). Target pH values were adjusted by the addition of drops of either NaOH or HNO$_3$ during the first $2$ h. The solid was separated after the experiment by filtering through a $0.2\mu$m membrane filter and the filtrate was analyzed for residual chromium concentration. The test Cr(VI) solutions were prepared in natural-like water (according to the National Sanitation Foundation, NSF standard) in...
order to investigate the collective effect of commonly co-existing and possibly interfering ions and to compare the removal capacity with the corresponding one obtained by using distilled water. For the preparation of 10 L of NSF water, 2.520 g NaHCO₃, 1.470 g CaCl₂·2H₂O, 1.283 g MgSO₄·7H₂O, 0.706 g NaSiO₃·5H₂O, 0.1214 g NaNO₃, 0.0221 g NaF and 0.0018 g NaH₂PO₄·H₂O were dissolved in distilled water.

RSSCTs were designed to simulate the performance of full-scale adsorption columns, based upon the respective proportional diffusivity relationships. Laboratory glass columns with a diameter of 1.1 cm and a height of 40 cm with PTFE valves and caps and a glass frit in the bottom were used. Columns were filled with magnetite granules at a bed height of around 15 cm. Columns were fed with 100 μg/L Cr(VI) solution in NSF water via a dosing pump and samples were periodically collected from the effluent and analyzed for residual Cr(VI) concentration (Figure 2). Several column experiments were conducted in order to evaluate the influence of the main process parameters, such as pH value, empty bed contact time (EBCT) and granule size. All experimental runs were carried out at 20 °C. Initial and residual Cr(VI) concentrations were determined by the diphenyl-carbazide spectrophotometric method.

RESULTS AND DISCUSSION

Material characterization

The obtained results for the characterization of produced material are summarized in Table 1 and Figure 3.

<table>
<thead>
<tr>
<th>Synthesis reagents</th>
<th>FeSO₄·H₂O/Fe₂(SO₄)₃·xH₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthesis pH</td>
<td>12.3 ± 0.2</td>
</tr>
<tr>
<td>Alkaline reagent</td>
<td>NaOH 30%, w/w</td>
</tr>
<tr>
<td>Redox</td>
<td>−1,000 ± 50 mV</td>
</tr>
<tr>
<td>Fe</td>
<td>55.0%, w/w</td>
</tr>
<tr>
<td>Fe(II)</td>
<td>13.3%, w/w</td>
</tr>
<tr>
<td>IEP</td>
<td>6.6</td>
</tr>
<tr>
<td>PZC</td>
<td>9.2</td>
</tr>
<tr>
<td>Surface charge density</td>
<td>0.86 mmol [OH⁻]/g</td>
</tr>
<tr>
<td>Specific surface area</td>
<td>69 m²/g</td>
</tr>
</tbody>
</table>

Figure 2 | Experimental set-up for RSSCTs.

Figure 3 | XRD (a) and TG-DTA (b) diagrams of the produced material.
The comparison of the XRD diagram (Figure 3(a)) with the relative ICDD/JCPDS PDF database files for magnetite (#19-0629) indicates the domination of this phase. However, due to its structural similarity with other iron oxide structures (γ-Fe₂O₃, #39-1346), XRD cannot be used as a proof for the exclusive presence of magnetite. But after consideration of results from the valent state determination of iron (Table 1), it can be concluded that the produced material mainly consists of magnetite since a high ratio of Fe(II)/Fe(III) is evidenced. Nevertheless, an extent of oxidation to maghemite is also evident. The TGA curve (Figure 3(b)) suggests a low percentage of natural adsorbed humidity on the produced material, which is around 2%. A weak peak in the heat flow curve indicates the γ-Fe₂O₃ transition to α-Fe₂O₃ at 620 °C that signifies the low percentage of maghemite in the initial structure.

The significant difference between IEP and PZC (6.6 and 9.2) can be explained by the formation of a negatively charged magnetite’s surface during the synthesis in an alkaline environment which is counterbalanced by other ions in the double layer to provide an almost neutral apparent behavior to the adsorbent grains.

Cr(VI) removal evaluation by batch experiments

In order to compare the Cr(VI) uptake capacity of magnetite in the RSSCTs configuration with the corresponding set-up generally implemented in laboratories, batch-type experiments were performed at pH values of 6, 7 and 8, using either distilled (Figure 4(a)) or NSF water matrix (Figure 4(b)). It is clear that Cr(VI) removal is favoured in an acidic environment, while magnetite’s performance is inhibited at pH values higher than 7. This stands for both distilled and NSF water experiments. Such an observation can be attributed to (i) the increase of negative surface charge of magnetite when pH rises above the IEP value of 6.6 and (ii) the competition of dissolved oxygen for Fe(II) oxidation (Equation (1)), which becomes determinative at a pH value greater than 7 (Stumm & Lee 1961).

\[-\frac{d[Fe(II)]}{dt} = k_{Fe}[Fe(II)][OH^{-}]^2pO_2\quad (1)\]

It is also important to note that the process is significantly affected by the presence of the other co-existing interfering constituents of NSF water. In particular, magnetite’s removal capacity at 10 μg Cr(VI)/L (q10) for distilled water experiments at pH 7 is 3.3 mg/g, while the corresponding value for NSF water experiments falls to 1.5 mg/g (Figure 4).

Cr(VI) removal evaluation by column experiments

In order to assess magnetite’s capacity for Cr(VI) removal by applying a continuous flow process and identifying the critical factors that determine its performance, RSSCTs were carried out using granular magnetite to treat a 100 μg/L solution of Cr(VI) in NSF water. The removal capacity breakthrough curves of magnetite for Cr(VI) removal for different pH values are presented in Figure 5. These experimental results showed that magnetite holds the ability to decrease residual Cr(VI) concentration below the analytical detection limit for a significant period of the process. Furthermore, Cr(VI) removal is favoured in an acidic environment which is
consistent with the observations from the batch mode experiments. Namely, the $q_{10}$ value for the process at pH 6.4, is found to be 9.2 mg/g, while at pH 7.2 and 7.8 this value falls to 3.9 mg/g and 1.8 mg/g, respectively. Such a decrease in the effectiveness of magnetite as the process pH increases, is probably attributed to the dissolved oxygen competition for the Fe(II) oxidation and the increase of magnetite’s surface negative charge when pH values rise above the IEP.

The EBCT appears to show a small inverse effect in magnetite’s removal capacity for residual Cr(VI) concentrations above 10 $\mu$g/L in the range of 1–2 min (Figure 6). However, the significant variation of Cr(VI) breakthrough concentration at an EBCT of 1 min indicates that a higher contact time should be implemented. Moreover, an EBCT of 2 min can ensure the elimination of Cr(VI) below the detection limit for a longer period of operational time (Figure 6).

An increase of magnetite’s granule size was found to improve significantly its removal capacity. More specifically, RSSCT experiments indicate a $q_{10}$ value of 3.9 and 4.5 mg/g for the particle size ranges of 0.25–0.50 mm (mean particle diameter 0.35 mm) and 0.50–1.0 mm (mean particle diameter 0.71 mm), respectively (Figure 7). An even lower value was obtained from the batch experiments (1.5 mg/g at pH 7) where the grain size was below 45 $\mu$m (Figure 4(b)). According to this trend, one should expect an improvement of removal capacity for the higher particle sizes usually implemented in full-scale configurations (mean particle diameter 1 mm).

**CONCLUSIONS**

This work was focused on the evaluation of the effectiveness of magnetite for Cr(VI) removal in a continuous flow.
process and the investigation of the main parameters that influence its performance. Rapid small-scale column tests proved the effectiveness of magnetite to decrease Cr(VI) concentration at the sub-ppb level (<1 μg/L) for the pH range 6.4–7.8 with the maximum removal capacity to be observed at 9.2 mg/g for pH 6.4. The removal capacity of magnetite is strongly diminished at equilibrium pH values above 7 and in the presence of common ions encountered in natural waters. Comparative experiments showed that the variation of EBCT does not significantly modify the breakthrough concentration, although a time of at least 2 min should be implemented. On the other hand, the effect of the granule size of magnetite was found to be more significant, considering an improvement of removal capacity by 15% when the mean particle diameter increased from 0.35 to 0.71 mm.

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