Chemosphere 127 (2015) 35–41

Contents lists available at ScienceDirect

Chemosphere

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

Effects of inorganic electrolyte anions on enrichment of Cu(II) ions with aminated Fe_3O_4/graphene oxide: Cu(II) speciation prediction and surface charge measurement

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HIGHLIGHTS

- Divalent anions had bigger effects on Cu(II) adsorption than monovalent anions.
- Both monovalent and divalent anions could alter the zeta potential of AMGO.
- Divalent inorganic electrolyte anions could significantly affect Cu(II) species.
- HPO_4^{2-} had the biggest effect on Cu(II) removal in the multi-ion system.
- Interactions of $Cl^- \times SO_4^{2-}$ and $Cl^- \times SO_4^{2-}$ had big effects on Cu(II) removal.

ARTICLE INFO

Article history:
Received 24 September 2014
Received in revised form 11 December 2014
Accepted 8 January 2015
Available online 2 February 2015

Handling Editor: X. Cao

Keywords:
Inorganic electrolyte anions
Zeta potential
Graphene oxide
Cu(II) speciation prediction
Fractional factorial design
Adsorption

ABSTRACT

The present work evaluated the effects of six inorganic electrolyte anions on Cu(II) removal using aminated Fe_3O_4/graphene oxide (AMGO) in single- and multi-ion systems. A 2^{6-2} fractional factorial design (FFD) was employed for assessing the effects of multiple anions on the adsorption process. The results indicated that the Cu(II) adsorption was strongly dependent on pH and could be significantly affected by inorganic electrolyte anions due to the changes in Cu(II) speciation and surface charge of AMGO. In the single-ion systems, the presence of monovalent anions (Cl^-, ClO_4^-, and NO_3^-) slightly increased the Cu(II) adsorption onto AMGO at low pH, while the Cu(II) adsorption was largely enhanced by the presence of SO_4^{2-}, CO_3^{2-}, and HPO_4^{2-}. Based on the estimates of major effects and interactions from FFD, the factorial effects of the six selected species on Cu(II) adsorption in multi-ion system were in the following sequence: $HPO_4^{2-} > CO_3^{2-} > Cl^- > SO_4^{2-} > NO_3^- = ClO_4^-$, and the combined factors of AD ($Cl^- \times SO_4^{2-}$) and EF ($Cl^- \times SO_4^{2-}$) had significant effects on Cu(II) removal.

1. Introduction

Adsorption is a popular and economical method for treating metal pollutions in natural water and wastewater (Babel and Kurniawan, 2003; Lam et al., 2008). Many studies have shown that heavy metals could be efficiently adsorbed by a wide variety of adsorbents (Babel and Kurniawan, 2003; Lam et al., 2008; Bui and Choi, 2010; Liu et al., 2011; Hu et al., 2013). Graphene oxide (GO) is an ideal material for removing heavy metals from aqueous solution due to its exceptional physicochemical properties. In recent years, magnetic graphene oxide composites (MGO) have been synthesized and shown some good properties for water treatment due to that the integration of magnetic properties into GO combines the advantages of adsorption with the merit of easy separation (Liu et al., 2011; Li et al., 2012; Hu et al., 2013). Diethylenetriamine (DETA), an organic compound, contains three amino groups that are known to form stable complexes with various metals. Therefore, grafting DETA onto MGO surface may increase the adsorption capacity of MGO for metal ions.

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http://dx.doi.org/10.1016/j.chemosphere.2015.01.013
0045-6535/

It is well known that adsorption behavior of heavy metals in water is controlled by adsorbent properties, heavy metal species, and water characteristics (Bui and Choi, 2010). The composition of heavy metal wastewaters from different industries varies widely. Generally, industrial wastewaters contain not only heavy metal ions but also high concentrations of organic and inorganic substances. Inorganic electrolyte anions, such as chloride (Cl^-), nitrate (NO_3^-), sulfate (SO_4^{2-}), phosphate ($H_2PO_4^-/HPO_4^{2-}$), and bicarbonate/carbonate (HCO_3^-/CO_3^{2-}), are commonly present in natural water and wastewater systems (Zhu et al., 2007), and these anions can affect metal cations adsorption directly or indirectly (Doula and Ioannou, 2003). Thus, investigation of the influence of inorganic electrolyte anions on heavy metals adsorption is essential to evaluate the adsorption capacity of an adsorbent and apply the laboratory results to practical projects. Although previous studies have given some insights into the influences of anions on adsorption of heavy metals, more research is still needed to better understand the influence mechanism.

Inorganic electrolyte anions play important roles in the speciation of metal ions due to that the metal ions often exist in bulk aqueous phase as complexes with ligands (Doula and Ioannou, 2003). The metal–ligand complexes may be adsorbed only weakly or not at all by the adsorbent, thereby inhibiting the metal ions removal. If the metal–ligand complexes are precipitates or can be strongly adsorbed by the adsorbent, the adsorption of metal ions may be improved by the presence of the inorganic electrolyte anions (Doula and Ioannou, 2003). Therefore, reliable methods for predicting metal speciation are critically needed as the first step in determining the influence mechanism of anions on adsorption of heavy metals. Besides, the inorganic electrolyte anions may interact with the adsorbent surface, thereby altering the surface electrical properties. Zeta potential is widely used to quantify the magnitude of the electronic charge on adsorbent surfaces. Thus, the observable changes in zeta potential due to the effects of inorganic electrolyte anions can provide valuable insight into the potential changes in metal ions removal during water treatment processes (Pommerenk and Schafran, 2005).

The main objectives of this study were to: (1) prepare AMGO by grafting DETA onto MGO surface and apply it as an adsorbent for decontamination of Cu(II) from aqueous solution; (2) evaluate the influences of inorganic electrolyte anions on the adsorption of Cu(II) onto AMGO; (3) discuss the influence mechanism by analyzing the speciation of metal ions and evaluating the effects of inorganic electrolyte anions on the zeta potential of the adsorbent; (4) determine the important factors and the extent of each individual ion effect on the Cu(II) removal using fractional factorial design (FFD).

2. Materials and methods

2.1. Synthesis of AMGO

Graphene oxide (GO) and magnetic graphene oxide (MGO) were prepared following the methods described in our previous papers (Hu et al., 2013, 2014a). The aminated Fe_3O_4/graphene oxide (AMGO) was prepared by grafting DETA onto the MGO surface (Ma et al., 2012). Briefly, 0.9 mL ammonia solution was added into 100 mL MGO suspension (3 mg mL^{-1}) and the mixture was stirred for 5 min at room temperature. Then 3.6 mL diethylenetriamine was added, and the suspension was stirred for 10 min at room temperature, and then stirred at 95 °C for another 6 h. The obtained AMGO was rinsed with ethanol and Milli-Q water for several times and stored at room temperature.

2.2. Effects of single anions on adsorption process

All adsorption experiments were performed according to the batch method in conical flasks on an orbital shaker with a shaking speed of 150 rpm. The stock solution of Cu(II) and the stock suspension of AMGO were added to achieve the desired concentrations of the different components. To investigate the adsorptive efficiency of AMGO for Cu(II) in the presence of various inorganic electrolyte anions, NaCl, $NaClO_4$, $NaNO_3$, Na_2SO_4, Na_2CO_3 and Na_2HPO_4 were added into the conical flasks, respectively. After mixed for 24 h, the mixture was separated by a magnetic process using a permanent magnet. The Cu(II) concentration in the supernatant was analyzed using flame atomic absorption spectrometry (PerkinElmer AA700, USA). All batch experiments were conducted in triplicates and the data are expressed as mean ± standard deviation. The adsorption capacity (q_e) of Cu(II) adsorbed on AMGO was calculated from the difference between the initial concentration (C_0) and the equilibrium concentration (C_e) (Gong et al., 2011).

2.3. Zeta potential determination

The samples were prepared by ultrasonification of 9.6 mg AMGO with 500 mL of solution in the absence and presence of 10 mM inorganic electrolyte anions (Cl^-, ClO_4^-, NO_3^-, SO_4^{2-}, CO_3^{2-}, and HPO_4^{2-}) and the solution pH was adjusted to different values (2–11). Then, the zeta potentials were measured using a Zetasizer Nano SZ (ZEN3690, Malvern, UK).

2.4. Speciation modeling methods

In order to analyze the effects of inorganic electrolyte anions on copper speciation in aqueous solution under different pH conditions, Visual MINTEQ (ver. 3.1) was used for the chemical speciation calculations. The parameters were set as follows: pH was fixed at different values; temperature was 30 °C; ionic strength was to be calculated depending on components added; different concentrations of $Cu(NO_3)_2$ and inorganic electrolyte anions were added as components (Hu et al., 2014b).

2.5. Fractional factorial design

In order to evaluate the statistical significance of the effects of the six different inorganic electrolyte anions and their interactions on Cu(II) removal, the 2^{6-2} FFD with resolution IV was developed. The confounded (aliased) factors and the interactions for this 2^{6-2} FFD are explained in detail in literature (Tanboonchuy et al., 2012). The design matrix of the 2^{6-2} FFD and the levels of each stated anion are given in Table 1. Statistical analysis of the fractional factorial design was performed using the software Design-Expert 8.0.6 (Stat-Ease Inc., Minneapolis, MN, USA).

3. Results and discussion

3.1. Effects of monovalent anions

The effects of monovalent anions (Cl^-, ClO_4^-, and NO_3^-) on Cu(II) adsorption as a function of pH values were examined and the results are demonstrated in Fig. 1a–c. The adsorption of Cu(II) onto AMGO increased with the increase of pH values from 2 to 11 in the absence and presence of monovalent inorganic electrolyte anions. As well known, solution pH is one of the most important variables affecting the adsorption process because the pH affects not only the adsorbent surface charge and ionization, but also the speciation of adsorbate (Hameed and El-Khaiary, 2008). In order to quantify the magnitude of electronic charge on adsorbent surfaces, the zeta