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Poly o-phenylenediamine–MgAl@$CaFe_2O_4$ nanohybrid for effective removing of lead(II), chromium(III) and anionic azo dye

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ABSTRACT

In this work magnetic MgAl@$CaFe_2O_4$–poly o-phenylenediamine nanohybrid have been synthesized and was characterized with TEM, SEM, FT-IR, VSM, UV–vis and XRD techniques. Prepared nanocomposite showed excellent adsorption properties respect to lead and chromium ions as well as Congo red (CR). Equilibrium times were 5 and 10 min for metal ions and dye, respectively. Moreover, removal percentages were about 90%, 75% and 96% for lead, chromium and CR. Furthermore, kinetic study revealed that adsorption followed second order mechanism. Maximum adsorption capacity of 500, 1000 and 500 mg g^{-1} was obtained for chromium, lead and CR as adsorption curves well fitted with Langmuir isotherm model.

1. Introduction

The industrial growth has resulted in the release of elevated levels of heavy metals and toxic azo dyes in the environment which can be harmful to both humans and wildlife. Wastewater from the food industries, fertilizer, mining, paper, textile and pharmaceutical, contains soluble organic substances and heavy metals hence, treatment of effluents has become a challenging topic in environmental sciences (Goh et al., 2008; Fan et al., 2014; Li et al., 2015; Reddy et al., 2012; Ihsanullah et al., 2016). A large number of approaches, such as precipitation, ion exchange, solvent extraction, and adsorption have been implemented for removing dye and heavy metal contaminants from wastewater. Owing to its simplicity, effectiveness, low cost, and easy to operation adsorption has become the central research focus. As a result, various adsorbents such as activated carbon, graphene, biomaterials, clay minerals and polymer were used for environmental remediation purpose (Cheng et al., 2012; Lugo-Lugo et al., 2012; Lesniewska et al., 2012; Pavlovic et al., 2009; Zhao et al., 2011; Su et al., 2015; Ahmad et al., 2015; Ansari et al., 2012; Dawood and Sen, 2012; Ghaedia et al., 2012a; Ghaedia et al., 2012b; Pavan et al., 2008; Yu et al., 2014; Hokkanen et al., 2016; Yu et al., 2015). Among the mentioned sorbents, polymer–inorganic nanocomposite has been attracted more interest due to their enhanced physical and chemical properties (Leroux and Besse, 2001; Matusinovic et al., 2009). The inorganic materials mainly include clays and layered silicates such as montmorillonite and layered double hydroxides (LDHs) (Yang et al., 2011; Yang et al., 2013; Larraza et al., 2012). Owing to the tunable charge density

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and more flexible polyhedral structure, the LDHs crystalline have found a wide variety of practical applications in the field of heterogeneous catalysis, as heat stabilizer, ion exchange, in biomedical applications and synthesis of clay–polymer nanocomposite (Costa et al., 2008; Yang et al., 2003; Tichit and Coq, 2003). The LDHs or polymer–LDHs composite has been applied in multidiscipline interests, especially for water treatment purposes such as removal of phosphate, fluoride, heavy metals and anionic dyes (Badreddine et al., 1999; Jiao et al., 2014; Anirudhan et al., 2012). Despite the efficiency of polymer nanocomposite in water treatment, separation and collection of them from reaction media by conventional filtration or centrifugation is a challenge. The use of magnetic nanoparticles can overcome this limitation. In other word, magnetic nanoparticles provide faster, simpler and more precise methodology for separation than traditional methods (Giraldo et al., 2013).

Ceramic ferrites are main groups of magnetic nanoparticles with high chemical and corrosive stability. Among the ferrite nanoparticles, $CaFe_2O_4$ shows remarkable characteristics, such as high thermal stability, superparamagnetic properties as well as biocompatible and eco-friendly characteristics due to the presence of Ca^{2+} instead of heavy metals (Jafari Pirouz et al., 2015; Ding et al., 2015; Liu et al., 2015; Rahimi et al., 2011).

Based on the above viewpoints magnetic clay–polymer nanocomposite was prepared for adsorption of heavy metals and hazardous azo dye from aqueous solutions. For this purpose, magnetic calcium ferrite was synthesized and employed for preparing magnetic Mg–Al mixed metal oxide then; it was used for fabrication of magnetic poly o-phenylenediamine nanocomposite. Prepared material was employed as an excellent adsorbent for removal of Cr^{3+}, Pb^{2+} and Congo red from water solution. Kinetic and isotherm studies were investigated, and effective parameters on the adsorption process were optimized.

2. Experimental

2.1. Materials and instrumentation

$Fe(NO_3)_3{\cdot}9H_2O$, $CaCl_2$, aluminum nitrate, $Mg(NO_3)_2{\cdot}6H_2O$, NaOH and Na_2CO_3 (Merck, Darmstadt, Germany) were applied to preparing $CaFe_2O_4$ and the magnetic metal oxide. 1,2-Phenylenediamine, sodium dodecyl sulfate (SDS), $CHCl_3$, HCl (37%) and $K_2S_2O_8$ employed for polymer synthesis. The stock metal solutions were prepared by dissolving an appropriate amount of the salts in distilled water. The CR which was used as a model dye was supplied from chemistry and chemical engineering research center of Iran. The pH was adjusted using 0.1 M of HCl or NH_3. The prepared particles were characterized by powder X-ray diffraction analysis using a Phillips powder diffractometer, X' Pert MPD, with Cu-Ka ($\lambda = 1.540589$ Å) radiation in 2θ range of 2–100°. SEM analysis and VSM were done using an HITACHI S 4160 and vibration sample magnetometer (Lake Shore Model 7400, Japan). Energy dispersive X-ray spectrometry (EDX) is recorded with an Oxford ED-2000 (England) respectively. The pH-Meter model 781 from Metrohm (Herisau, Switzerland) equipped with glass combination electrode was used for pH measurements. The adsorption studies of the test solutions were carried out using a Varian model AA-400 flame atomic absorption (FAAS) spectrometer (Varian Australia Pty Ltd., Musgrave). Dye adsorption studies of the test solutions were carried out using a UV–vis spectrophotometer (Lambda 25, Perkin Elmer).

2.2. Preparation of $CaFe_2O_4$ and magnetic mixed oxide

Magnetic $CaFe_2O_4$ was prepared by precipitation of Fe^{3+} and Ca^{2+} using NaOH as precipitant. In a typical route, 4.0 g of $Fe(NO_3)_3{\cdot}9H_2O$ and 0.5 $CaCl_2$ was dissolved in 40 mL distilled water followed by addition of 4.0 g of sodium hydroxide. After stirring for 5 min the product was filtered and washed with distilled water and dried at 100 °C for 1 h then, further heated at 700 °C for 4 h. To prepare magnetic Mg–Al@$CaFe_2O_4$, 1.0 g of prepared ferrite, 11.0 g of magnesium nitrate and 8.0 g of aluminum nitrate were sonicated in 100 mL of distilled water then, 5.0 g of NaOH and 4.0 g of Na_2CO_3 in 40 mL distilled water dropped to metal mixture. After stir for 12 h under refluxing, the resultant magnetic material were collected by filtration, rinsed with distilled water and dried at 80 °C for 3 h. Calcined mixed oxide was obtained by heating of the product in a furnace at 450 °C for 3 h.

2.3. Polymer nanocomposite synthesis

To prepare polymer nanocomposite, 1.0 g of metal oxide, 2.0 g SDS, 1.0 g of o-phenylenediamine in 20 mL $CHCl_3$, were stirred for 3 h at room temperature. Afterward, 20 mL of HCl solution (1.0 mol L^{-1}) was added to the mixture followed by dropwise addition of $K_2S_2O_8$ (1.0 g in 20 mL water) to it within 30 min. The reaction was completed after stirring for 12 h at room temperature. Obtained black precipitate was washed several time with distilled water to neutral pH and dried at 60 °C for 6 h.

2.4. Adsorption experiment

The adsorption experiments were performed for 50 mL of Cr^{3+} and Pb^{2+} ions with the concentrations of 0.05–50 mg L^{-1} as well as 50 mL of CR with concentrations of 10–50 mg L^{-1}. The pH of the solutions was adjusted in the optimum value then; appropriate amount of magnetic polymer was added to them and shacked for it was shaken for adequate time to reach the equilibrium. At the end of adsorption period, the adsorbent was separated from the solutions and concentration of heavy metals in supernatant was determined by FAAS. Moreover, concentration of residual CR was determined by measuring the absorbance at 568 nm using a UV–vis spectrophotometer.

3. Results and discussion

3.1. Characterization of magnetic nanocomposite

The EDX analysis (Fig. 1a) confirmed the presence of C, O, Fe, Mg, Ca, and Al as the main component of the prepared mixed oxide. The X-ray powder diffraction analysis (Fig. 1b) was used to verify the Mg–Al@$CaFe_2O_4$ and polymer nanocomposite. The pattern of mixed oxide exhibited typical peaks that appeared at 2θ range of 13–70°. Diffraction peaks are well assigned to the typical crystal plane of Mg–Al LDHs and $CaFe_2O_4$ (Nakayama et al., 2004; Samariya et al., 2013), and indicated that the mixed ferrite has been successfully prepared. Moreover, nanocomposite pattern showed new peaks at 2θ range of 10–20°, which are ascribed to periodicity perpendicular to the polymer chain as well as the distance between the benzene rings in adjacent chains or the close contact interchain distance (Pougeta et al., 1995).