



# Magnetic cellulose ionomer/layered double hydroxide: An efficient anion exchange platform with enhanced diclofenac adsorption property



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## ABSTRACT

Polymeric ionomers with anion exchange capability are considered to be classes of environmentally friendly compounds as combination of them with anionic layered hydroxides constitute emerging advance materials. Biosorption by polymeric ionomer – layered double hydroxide (LDH) hybrid material exhibits an attractive green, low cost and low toxic – clean way. As a result, a novel anion exchange platform has been developed by the reaction of CaAl – LDH with Fe<sup>2+</sup>, cellulose solution, epichlorohydrin and pyridine. Magnetite cellulose – LDH (MCL) and the ionomer were used for efficient biosorption of diclofenac sodium (DF). Results showed that ionomer has more efficiency for DF adsorption relative to MCL. Magnetite ionomer showed fast equilibrium time (2 min) with maximum uptake of 268 mg g<sup>-1</sup>. Isotherm and Kinetic models were also studied. Regeneration of the sorbent was performed with a mixture of methanol – NaOH (2.0 mol L<sup>-1</sup>) solution.

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## 1. Introduction

Diclofenac (2-[(2, 6-dichlorophenyl) amino] benzene acetic acid) is a synthetic non-steroidal anti-inflammatory drug (NSAID) with analgesic and antipyretic properties, comparable or superior to other NSAIDs. It widely used for treatment of primary dysmenorrhea, relief of mild to moderate pain, and for relief of the signs and symptoms of rheumatoid arthritis (Blair & Plosker, 2015; Chuasuwat et al., 2009; Derry, Wiffen, & Moore, 2016; Gibofsky, Hochberg, Jaros, & Young, 2014). Diclofenac (DF) appears to be one of the most concerning compounds because it has been extensively found in influents and effluents of wastewater treatment plants as well as drinking water (Andrew Lin, Yang, & Lee, 2015; Nam et al., 2015). It is also considered to be harmful to aqua lives as well as vultures hence it considered as emerging micropollutants which is a topic of actual concern for international scientific and legislative communities (Álvarez, Ribeiro, Gomes, Sotelo, & García, 2015). In this context, there is an increasing demand for competent methods to remove pharmaceuticals from wastewater. Most employed

processes for the removal of pharmaceutical pollutants including filtration, biological treatment and photocatalytic degradation (Jauris et al., 2016; Rad, Irani, & Barzegar, 2015; Rzeszutek & Chow, 1998). Moreover, advanced oxidation processes have been extensively used for the treatment of pharmaceutical wastes (Almeida, Garcia-Segura, Bocchi, & Brillas, 2011; De Luna, Veciana, Su, & Lu, 2012) but these techniques are associated with problems such as excessive time requirements, high costs and high energy consumption. Among the various techniques currently proposed, adsorption process assumes great evidence, because of its high efficiency and simplicity. It is a process in which pollutants are transferred from the effluent to a solid phase thereby decreases exposure of living organisms to hazardous species (Saucier et al., 2015; Sun, Schüssler, Sengl, Niessner, & Knopp, 2008). In recent years, various types of adsorbents were employed for diclofenac adsorption including; Metal Organic Frameworks (MOFs), clay, graphene, ZnO, waste materials, activated carbon, and zeolites (Baccar, Sarra, Bouzid, Feki, & Blaquez, 2012; De Oliveira et al., 2016; Graouer-Bacart, Sayen, & Guillon, 2016; Hassan, Abdel-Shafy, & Mansour, 2016; Kaur & Datta, 2014; Mariah, Matthias, & Douglas, 2016; Nielsen & Bandosz, 2016). Despite of good performance, these adsorbents show some drawbacks regarding to economic feasibility, effectiveness, and regeneration (Jiang, Yang, Zhang, Yang, & Wang, 2015).

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Magnetic ionic liquids are emerging anionic compounds with various functional groups and a magnetized component within their structure that enables them to act as weak individual magnet. Compared with traditional adsorbents, magnetic ionic liquids possess low resistance to mass transfer, which making them kinetically fast (Khani, Sobhani, & Beyki, 2016; Tian & Row, 2011). To improve the stability of the sorbent coating as well as improving extraction-to-extraction reproducibility, polymeric ionic liquids (PILs) were introduced as a class of reusable coating materials (López-Darias, Anderson, Pino, & Afonso, 2011). The thermal stability, reproducibility, as well as tunability of magnetic polymeric ionic liquids make them particularly attractive candidates as sorbent coatings (López-Darias, Pino, Meng, Jared, & Ana, 2010 Ruiz-Aceituno, Sanz, & Ramos, 2013). Combination of polymeric ionic liquids with layered materials such as layered double hydroxides (LDHs); generate advanced material with remarkable improvement of mechanical, thermal, optical, and physicochemical properties compared with the pure polymer or conventional composites. In other words, LDHs – ionic liquid polymer composite exert synergic effect on adsorption of anionic species (Chitrakar et al., 2005; Leroux & Besse, 2001; Sinha Ray, Maiti, Okamoto, Yamada, & Ueda, 2002; Yang, Sun, Zhang, Wang, & Zhao, 2003). Based on these viewpoints magnetic CaAl layered double hydroxide – cellulose ionomer was synthesized and employed for diclofenac sodium adsorption. Ionomer composed from pyridinium chloride component with hydrophilic property as well as anion exchange capability. Combination of these characteristics with anion exchange capability of LDH generates efficient anion exchange platform for DF uptake. Effective parameters on DF adsorption i.e, pH, time, adsorbent dosage and ionic strength were optimized and isotherm as well as kinetic models was studied.

## 2. Experimental

### 2.1. Materials

Aluminium chloride, CaCl<sub>2</sub>, urea, Iron(II) chloride tetrahydrate, NaOH, cellulose, epichlorohydrin (EPH), and pyridine were supplied from Merck (Darmstadt, Germany). Standard solutions of DF (1000 mg L<sup>-1</sup>) were prepared with dissolving of DF sodium salt in 2 mL of ethanol and then diluted to appropriate volume with distilled water. The pH adjustments were performed with 0.1 mol L<sup>-1</sup> of HNO<sub>3</sub> and NH<sub>3</sub>.

### 2.2. Instruments

The prepared materials were characterized by powder X-ray diffraction analysis using a Phillips powder diffractometer, X'Pert MPD, with Cu-Kα ( $\lambda = 1.540589 \text{ \AA}$ ) radiation in  $2\theta$  range of 2–100°. FE-SEM analysis carried out using HITACHI S 4160 instrument. Fourier transformed infrared spectra (FT-IR) were measured with Equinox 55 Bruker with ATR method over the wavelength of 400–4000 cm<sup>-1</sup>. Magnetization measurements were recorded using a vibration sample magnetometer (VSM) (Lake Shore Model 7400, Japan). Thermal gravimetric analysis (TGA) and energy dispersive X-ray (EDX) were recorded with a TA-Q-50 and Oxford ED-2000 (England), respectively. The N<sub>2</sub> adsorption–desorption isotherms were measured on Nova Station A system. A digital pH-meter (model 692, Herisau, Metrohm, Switzerland) was used for the pH adjustment. A Perkin-Elmer LS 50 spectrofluorimeter equipped with xenon discharge lamp and quartz cell were used to record fluorescence measurements.

### 2.3. Synthesis of LDH and magnetite polymeric ionomer

In a typical synthetic run, 2.0 g of CaCl<sub>2</sub>, 2.17 g of AlCl<sub>3</sub>·6H<sub>2</sub>O and 3.7 g of urea were dissolved in 80 mL methanol by stirring at room temperature for 30 min. The solution was transferred into an autoclave and then kept to 150 °C for 6 h. After cooling to room temperature, the whit precipitate was collected by centrifugation and washed several times with water and ethanol. Finally, the product was dried at 80 °C for 6 h. For preparing cellulose solution, about 1.0 g of microcrystalline cellulose was added to 40 mL distilled water (containing 6.0 g of urea and 4.0 g of NaOH) in 100 mL volumetric flask and magnetically stirred for 5 min. The flask was placed in a refrigerator freezer at 0 °C for 1 h until a clear transparent gel was obtained. To prepare magnetic cellulose – LDH (MCL), 2.5 g of Iron(II) chloride tetrahydrate was dissolved in 100 mL distilled water containing 0.5 g of LDH, and then the cellulose solution was poured into the LDH – iron solution under magnetic stirring. After stirring for 10 min the mixture was irradiated sonically at 60 °C for 1 h. Obtained black precipitate was filtered, washed with distilled water and dried at 70 °C for 5 h. To prepare, magnetite polymeric ionomer, 1.3 g of MCL was stirred in 150 mL of NaOH solution (0.1 mol L<sup>-1</sup>) for 2 h then, 5.0 mL of EPH was added to the suspension and stirred at room temperature for 6 h. The mass was collected with external magnetic field, washed with water, acetone and ethanol, and then ultrasonically dispersed at 80 mL of ethanol for 10 min. After addition of 2.0 mL of pyridine, the mixture was refluxed at 70 °C for 24 h along with stirring. After cooling to room temperature, the product was collected magnetically, washed with ethanol and distilled water and dried at 50 °C for 4 h. Ionomer structure has been schematically illustrated in Fig. S1.

### 2.4. Adsorption experiment

DF adsorption experiments were performed with batch method. For this purpose, the pH of DF solutions (0.5–200 mg L<sup>-1</sup>) was adjusted to 9 and 10 mg of the sorbents (MCL or ionomer) were added to each solution. Final volume was 10 mL. After shaking for appropriate time, the solid mass was collected and the concentration of DF in the supernatant was determined by fluorescence spectroscopy. To do this, 1.0 mL of supernatant was poured in a quartz cell and irradiated with ultraviolet radiation at 275 nm as excitation wavelength. Fluorescent emission appeared at 364 nm (Fig. S2). Same procedure was employed to determine the peak intensity of standard diclofenac solutions (diclofenac concentration in the range of 0.5–40 mg L<sup>-1</sup>). DF concentration in supernatant was calculated through fitting its fluorescent peak intensity with the plot of standard diclofenac solutions.

## 3. Results and discussion

### 3.1. Characterization of the materials

The XRD analysis was used to verify the crystallinity of CaAl – LDH and magnetic ionomer. The pattern of LDH (Fig. S3a) showed a series of sharp reflections at low  $2\theta$  values and clear low intense peaks at high  $2\theta$  values. The peaks around  $2\theta^\circ$  of 8.28 and 23 corresponding to (002) and (004) faces as the angle of the first peak indicated the interlayer d-spacing of 10.67 Å. The observed diffractions are indexed to pure hexagonal phase matched to reference pattern (PDF 78–1219). The sharp reflections with high intensity corresponding to (002), (004), and (006) planes indicate well-formed distorted “Brucite-like” layers (Zhang et al., 2012). In the XRD pattern of magnetic ionomer the characteristic peaks of cubic Fe<sub>3</sub>O<sub>4</sub> are dominant. The pattern show scattering at  $2\theta^\circ = 30.26, 35.34, 43.22, 53.55, 57.23, \text{ and } 63.32$  equal to the (220), (311),

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