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Application of novel metal organic framework, MIL-53(Fe) and its magnetic hybrid: For removal of pharmaceutical pollutant, doxycycline from aqueous solutions

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ABSTRACT

As a pharmaceutical pollutant, doxycycline causes contamination when enters into the environment. In this research MIL-53(Fe), and its magnetic hybrid MIL-53(Fe)/Fe_3O_4 were synthesized and employed for removal of doxycycline from aqueous solutions. The adsorbents were characterized by XRD, SEM, BET, FTIR, EDAX, VSM and TG-DTG technique. The effect of different variables such as DOC concentration, pH, contacting time, and adsorbent dose on the removal efficiency was studied and under optimized conditions the adsorption capacity of 322 mgg^{-1} was obtained. The adsorption process was kinetically fast and the equilibration was attained within 30 min. The used adsorbent was easily separated from the solution by applying external magnetic field. The regenerated adsorbent retained most of its initial capacity after six regeneration steps. The effect of ionic strength was studied and it was indicated that removal of doxycycline from salt-containing water with moderate ionic strengths was quite feasible. Langmuir, Freundlich, Tempkin and Dubinin–Redushkevich isotherms were employed to describe the nature of adsorption process. The sorption data was well interpreted by the Longmuir model.

1. Introduction

The worldwide utilization of pharmaceuticals compounds causes an overgrowing pollution of aquatic environments (Mansouri et al., 2015). There are serious concerns regarding certain pharmaceutical compounds such as antibiotics, anti-parasiticides, anti-mycotics and anti-cancer medicinal even if to date there is no clear evidence of short-term health effects on humans. These products are especially intended to kill their target organism or target cells and might prove to be the most important pharmaceutical compounds affecting human health via environmental exposure (Mudgal et al., 2013).

Among different kinds of pharmaceuticals pollutant, antibiotics are more often find than others. They are discharged in their original or metabolized forms into the environments by domestic wastewaters and pharmaceutical sewage. Since no legal demands have been inflicted for discharge of these compounds into the surface water, they have stimulated increasing concerns (Zhou et al., 2012). Doxycycline is one the famous antibiotics which generally used to treat many infected diseases and also used as growth ingredient in animal feeding (Carolina Kogawa and Nunies Salgado, 2012). Elimination of antibiotics by conventional waste treatment methods is commonly imperfect (Chao et al., 2014).

It is necessary to develop more efficient technologies to remove these antibiotics from the polluted waters and waste streams. Many technologies such as chemical oxidation (Mansouri et al., 2015), ionic treatment (Mudgal et al., 2013), photodegradation (Zhou et al., 2012), adsorption (Ötker Uslu and Akmehmet Balcioğlu, 2009), electrochemical process (Carolina Kogawa and Nunies Salgado, 2012) and, fenton (Zhang et al., 2015) methods have been developed to improve the quality of polluted waters by antibiotics. These methods possess some limitation and drawbacks including imperfect removal efficiency, and producing more toxic intermediate substances. Adsorption has been proved to be an economic, effective and attractive technology to achieve our expectation due to its simplicity on operation and availability of a wide range of sorbents (Chao et al., 2014). Several adsorbents, including mesoporous silica (Brigante and Avena, 2016), black tea and pomegranate peel (Hassan and Ali, 2014), graphene-like layered molybdenum disulfide (Chao et al., 2014), Fe_3O_4 (Ghaemi and Absalan, 2015), and sea buckthorn biocarbon (Zhang et al., 2016) have been investigated.

Metal–organic frameworks (MOFs) are crystalline porous compounds made of metal ions and organic linkers. The pore size and

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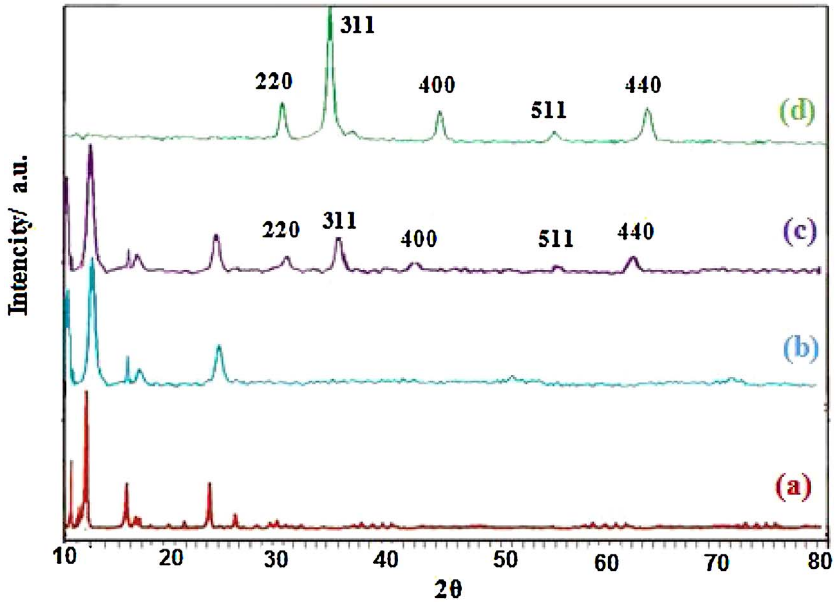

Fig. 1. XRD pattern of standard mil-53(Fe) (a), synthesized MIL-53(Fe) (b), synthesized MIL-53(Fe)/Fe_3O_4 (C), Fe_3O_4 (d).

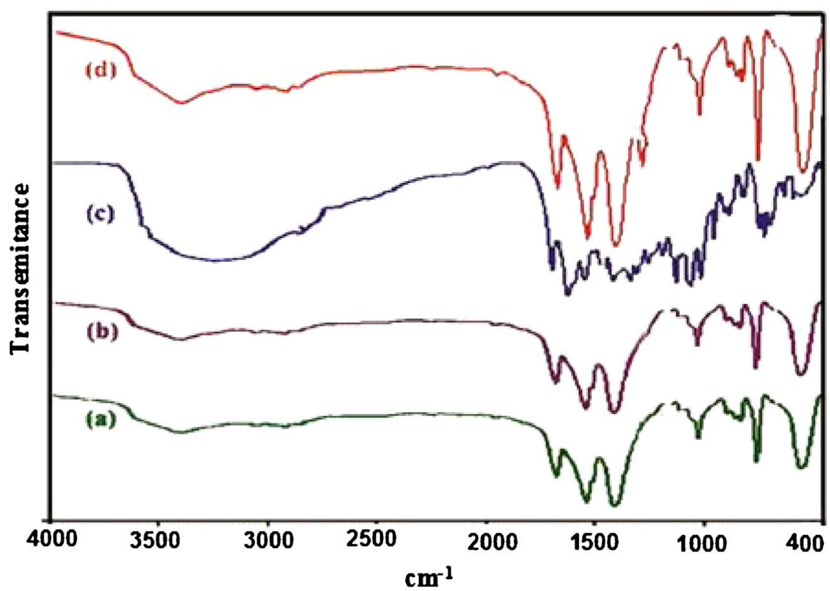

Fig. 2. FT-IR spectra of MIL-53(Fe) (a), MIL-53(Fe)/Fe_3O_4 (b), DOC (c) and DOC MIL-53(Fe)/Fe_3O_4 loaded with DOC (d).

geometry of MOF can be tailored to make them suitable compounds for many applications. Moreover, due to their high resistance, high surface area, and large pore volume they have attracted extensive interests for adsorptive elimination of hazardous materials (Wei et al., 2016). Incorporation of MOFs into magnetic material structure is a new approach to combine the porosity and magnetism and to make new materials for adsorptive separation (Wu et al., 2014). Among the MOFs, the MIL-53(M^{III}) family due to huge chemical versatility, high chemical stability and high surface area occupies an outstanding situation (Yılmaz et al., 2016).

In this work, we synthesized a magnetic nontoxic iron (III) carboxylate MOFs named MIL-53 (Fe). This compound was magnetized and was used for removal of doxycycline from aqueous solution under different experimental conditions.

2. Experimental

2.1. Materials

Terephthalic acid (1,4-BDC, %97) was purchased from Aldrich, Ferric chloride ($FeCl_3{\cdot}6H_2O$ 98%), *N,N*-dimethylformamide (DMF 99.8%), ferrous chloride ($FeCl_2{\cdot}4H_2O$, 98%), hydrochloric acid (HCl, 37%), sodium hydroxide (NaOH, 97%) were purchased from Merck Company (Germany). DOC (99%) was obtained from Sigma–Aldrich Chemical Company.

2.2. Synthesis and magnetization of MIL-53(Fe)

MIL-53(Fe) was prepared according to the procedure described by Ruowen Liang (Liang et al., 2015). A mixture containing iron (III) chloride, terephthalic acid in N, N-dimethylformamide (DMF) was transferred to a Teflon-lined autoclave and heated at 150° C for 12 h. The product was separated and the remaining DMF was removed by