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Synthesis of zinc-carboxylate metal-organic frameworks for the removal of emerging drug contaminant (amodiaquine) from aqueous solution

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ABSTRACT

We herein report the removal of amodiaquine, an emerging drug contaminant from aqueous solution using [$Zn_2(fum)_2(bpy)$] and [$Zn_4O(bdc)_3$] (fum = fumaric acid; bpy = 4,4-bipyridine; bdc = benzene-1,4-dicarboxylate) metal–organic frameworks (MOFs) as adsorbents. The adsorbents were characterized by elemental analysis, Fourier transform infrared (FT-IR) spectroscopy, and powder X-ray diffraction (PXRD). Adsorption process for both adsorbents were found to follow the pseudo-first-order kinetics, and the adsorption equilibrium data fitted best into the Freundlich isotherm with the R^2 values of 0.973 and 0.993 obtained for [$Zn_2(fum)_2(bpy)$] and [$Zn_4O(bdc)_3$] respectively. The maximum adsorption capacities foramodiaquine in this study were found to be 0.478 and 47.62 mg/g on the [$Zn_2(fum)_2(bpy)$] and [$Zn_4O(bdc)_3$] MOFs respectively, and were obtained at pH of 4.3 for both adsorbents. FT-IR spectroscopy analysis of the MOFs after the adsorption process showed the presence of the drug. The results of the study showed that the prepared MOFs could be used for the removal of amodiaquine from wastewater.

Introduction

Increased applications of pharmaceuticals and personal care products (PPCPs) in various activities of man over the past decades has resulted in the occurrence of high levels of these products in wastewater thereby increasing the spate of contamination of water bodies by these products and their attendant health risk (Wolfová et al., 2013). Primarily, PPCPs reach the environment either as excreted product of human and animal metabolism or in effluents released by pharmacies, hospitals, and manufacturing industries. Residual concentrations of these chemicals have been reported to be present in industrial effluents discharged into the environment, thereby finding their way into water bodies (Huang et al., 2011; Nikolaou et al., 2007). The development and efficiency of pharmaceutical products for the treatment of various diseases such as malaria has made them almost indispensable to man.

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Malaria is known to be a global burden due to the fact that it affects and kills about 800,000 people annually and puts at risk about 3.3 billion people (Korenromp et al., 2013). Malaria is a disease transmitted by infected mosquitoes *via* the strains of malaria parasites (*Plasmodium falciparum, Plasmodium vivax, Plasmodium ovale, Plasmodium malariae* and *Plasmodium knowlesi*). The *P. falciparum* strain is known to be most prevalent of the 5 strains, causing severe malaria which is the most frequent cause of death for children under five years of age in Sub-Saharan Africa and about 91% of the annual deaths (Korenromp et al., 2013). Resistance of the *P. falciparum* to the common anti-malarial drugs like sulphadoxine/pyrimethamine (which is an antimalarial drug that has the sulphonamide antibiotic effect and the antiprotozoan effect of pyrimethamine), chloroquine, and amodiaquine (which is a phenyl substituted analogue of chloroquine), posed a major challenge to the fight against the prevalence of the malaria disease in Africa (Koram et al., 2005). In order to address this problem, the World Health Organization (WHO) recommended the arteminisin-based combination therapy (ACT) to combat the emergence and spread of drug-resistant uncomplicated malaria (Koram et al., 2008; Fehintola et al., 2011). One of such ACT drugs recommended was Amodiaquine/Artesunate (Hodel et al., 2010; Kopel et al., 2012).

Amodiaquine (4-((7-chloroquinolin-4-yl)amino)-2-((diethylamino)methyl)phenol) shown in Fig. 1, has been used widely for the prevention and treatment of malaria, and other conditions of arthritis (Wittes, 1987; Karunajeewa, 2015). It is an analogue of chloroquine (a phenyl substituted analogue) found to be effective against some strains of *P. falciparum,* and also a member of the 4-aminoquinolines which were considered as most important antimalarial drugs for several decades. As a result, it is commonly found in wastewater as well as drinking water. Thus, its removal is necessary to eliminate its contamination of water.

Several strategies have been proposed for the removal of PPCPs from wastewater. These strategies include phototransformation (Ereira et al., 2007), membrane nanofiltration (Koyuncu et al., 2008), sedimentation, chlorination (Boyd et al., 2003, 2005), precipitation, adsorption (Marin et al., 2010; Li et al., 2011; Zhang et al., 2012), and ozonation (Ernes et al., 2003). The adsorption process has been proven to be very effective due its advantages over other techniques, which includes low cost, excellent removal efficiency and its applicability over a large range of adsorbent and adsorbate concentrations (Bajpai et al., 2014). Therefore, the development of adsorbent materials, which will be efficient for the removal of emerging contaminants such as PPCPs from wastewater, is very important (Huang et al., 2011). Among the various adsorbents, such as mesoporous silica, zeolites, metal–organic frameworks (MOFs), biomaterials and activated carbon commonly used for adsorptive removal, and separation and purification of contaminants, MOFs have intrinsic characteristics that make them unique and different from the other adsorbents.

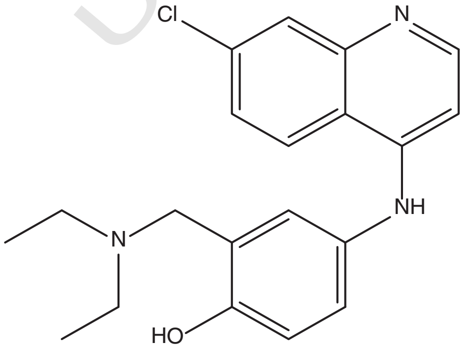

Fig. 1 – Chemical structure of amodiaquine.

The application of MOFs in the removal of PPCPs was first reported by Jhung and co-workers (Hasan et al., 2012). The liquid-phase adsorption of naproxen and clofibric acid as representative of PPCPs were carried out using two MOFs iron-benzenetricarboxylate (MIL-100-Fe) and chromium-benzenedicarboxylate (MIL-101) and their adsorption rate and adsorption capacities were compared to those of activated carbon. The removal efficiency was reported to decrease in the order of MIL-101 > MIL-100-Fe > activated carbon in both parameters. The fast adsorption rate of MIL-101 was explained in terms of its larger pore size. The adsorption process was more favorable at lower solution pH on MIL-101 and the adsorption mechanism was therefore interpreted as simple electrostatic interaction between the PPCPs and MIL-101. This pioneer study suggested that MOF type materials could be applied in the adsorptive removal of PPCPs in contaminated water. Several other reports on the removal of PPCPs using MOFs and MOF derivatives have been well documented (Seo et al., 2016, 2017; Ahmed et al., in press; Bhadra et al., 2017).

The structures of metal–organic frameworks (MOFs) consist of metal ions and organic ligands linked together *via* coordination bonds (Fan and Yan, 2012). They possess permanent porosity and have unique properties such as large surface areas (1000–10,400 m^2/g), high thermal stability with tunable polarity and nanoscale pore sizes (Yaghi et al., 2003; Rowsell and Yaghi, 2004). MOFs have therefore been variously applied in catalysis (Corma et al., 2010), separation (Li et al., 2012; Xie et al., 2011), gas storage (Getman et al., 2011), drug delivery (Taylor-Pashow et al., 2009) and more importantly as adsorbents (Tella and Owalude, 2014).

Many metal–organic frameworks have been synthesized by solvent-based solvothermal and reflux techniques at temperatures between 25 to approximately 220°C. In the recent past, a number of functional metal–organic framework materials have been reported based on these techniques. A metal–organic framework material constructed from Zn(II) and the ligand 2,5-di(3′,5′-dicarboxylphenyl)pyridine has been reported (J.-Q. Liu et al., 2016). The compound was demonstrated to possess the ability to selectively sense nitrobenzene and therefore can be employed in detection of explosives. The study also showed that the metal–organic framework materials displayed multifarious applications for selective adsorption of Fe^{3+} ions and dyes and their subsequent separation from solutions. A metal–organic framework based on the ligand 5-nitroisophthalate and co-ligand 2,2′-dimethyl-4,4′-bipyridine has also been reported (Ma et al., 2015). These ligands were functionalized by incorporating hydrophobic functional groups, such as, methyl and nitryl in their structures. The resulting MOF is hydrostable with a 3D dia topology and highly selective in busulfan payloads. High

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