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Removing oil droplets from water using a copper-based metal organic frameworks

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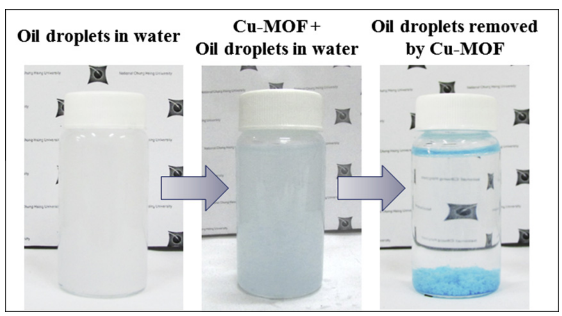
HIGHLIGHTS

- Oil removal from water by a copper-based MOFs, HKUST-1, is demonstrated.
- HKUST-1 exhibits a promising oil-removal capacity of 4000 mg g^{-1}.
- Effects of salts, surfactants, pH of emulsions on removal capacity are examined.
- HKUST-1 can be regenerated conveniently by washing with ethanol.

GRAPHICAL ABSTRACT



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ABSTRACT

To recover oil during manufacturing processes or to eliminate oil pollution in wastewaters, oil droplets must be separated from water. Among the current techniques for oil removal, adsorption appears to be one of the simplest. Metal Organic Frameworks (MOFs) have recently been proposed as adsorbents to remove contaminants from water owing to their high surface area and versatile tunability. Interestingly, only a few studies looked at the use of MOFs to remove oil droplets and several unknowns remain regarding the mechanism and the potential of this approach. Here, we propose to use a copper-based MOFs, HKUST-1, to separate oil droplets from water. HKUST-1 is synthesized and characterized using XRD, FTIR, N_2 sorption analysis and thermogravimetric analysis. The kinetic and equilibrium constants of the oil/water separation are determined; HKUST-1 exhibits a high removal capacity, about six times higher than a commercial activated carbon. This performance can be further improved via addition of salts and surfactants, and change of pH. HKUST-1 is successfully regenerated via an ethanol-washing process and its capacity remains about constant up to 5 cycles. The kinetics of the oil/water separation follows a pseudo second order, while the adsorption isotherm can be fitted using the Langmuir model.

1. Introduction

Oil droplets in water can be found in many industries such as petroleum [1–3], pharmaceuticals [4,5], food processing [6,7] and metal manufacturing [8]. Domestic wastewater also contains high concentration of oil derived from plant, animal, synthetic fat and human wastes [9]. Separation of oil from water can be desired to recover the oil from manufacturing processes or to eliminate oil pollution in water [10–13].

Up to date, many techniques have been employed to separate oil droplets from water including filtration [14–16], chemical destabilization [17], electrocoagulation [18,19], flotation [20–23], or adsorption. Among these techniques, adsorption appears to be

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one of the most attractive methods to remove contaminants owing to its simple design and relatively low initial cost [24]. Common adsorbents for oil removal include granular activated carbon, natural fibers, agricultural wastes and minerals [25–28]. Since the physical and chemical properties of adsorbents (e.g., surface areas, pore volumes, and surface functional groups) significantly influence their removal capacity, strategies to tune these materials must be thoughtfully implemented in order to improve the efficiency of separating oil from water [3].

A new type of porous network material named Metal Organic Frameworks (MOFs) has attracted great attention among the scientific community [29–31]. These materials are synthesized by combining metal ions and organic ligands to form a porous crystalline network. With their exceptional physical and chemical properties, MOFs have had a significant impact on disciplines related to gas storage and adsorption [32–34], catalysis [35–37], drug delivery [34,38], and sensing [39].

Recently, a number of studies started to evaluate the feasibility of MOFs to remove contaminants from water such as metal ions [40], dyes [41], and other organic compounds [42], revealing that MOFs can be stable in the aqueous environment and exhibit great capacity to separate the targeted contaminants. As a promising porous material, we expect MOFs to be capable of removing oil droplets from water. If successful, MOFs could be used not only in wastewater treatments but also for the separation of hydrophobic compounds from hydrophilic solvents in a variety of applications, including biological systems, food processing, pharmaceuticals or analytic chemistry. To the best of our knowledge, only a few studies have been conducted to evaluate this potential application of MOFs-related materials [43,44].

Thus, we propose to use MOFs for the separation of oil droplets from water. In this study, a copper-based MOFs, HKUST-1 (or CuBTC), was selected owing to its stability in water [45] as well as extensive applicability in many fields, including catalysis [46–49], analytic chemistry [50,51], separation [52], gas storage [53], sensor [54], etc. In addition, HKUST-1 is relatively straightforward to synthesize as it is made of commercially available ligands and it forms under mild conditions. The material performance was compared to that of a granular activated carbon. We investigated the reaction kinetics by three common kinetics models: the pseudo first order equation, the pseudo second order equation and the intraparticle diffusion. Adsorption isotherms were also modeled by two common isotherm models: Langmuir isotherm and Freundlich isotherm. We examined the effects of additions of NaCl and CTAB, and change of the pH on the removal capacity. The recyclability was also tested using a rapid and convenient method to regenerate HKUST-1 by washing with ethanol.

2. Experimental

2.1. Materials and methods

Copper acetate monohydrate ($Cu(CO_2CH_3)_2 \cdot H_2O$) was purchased from Scharlab S.L. (Spain); benzene-1,3,5-tricarboxylic acid (H_3BTC) was purchased from Alfa Aesar (England). D.I. Water (D.I.) was prepared to exhibit less than 18 MΩ cm; ethanol was purchased from Merck. Soybean oil was obtained from Fwusow Industry Co.; sodium chloride (NaCl) pellets and cetrimonium bromide (CTAB) were purchased from Sigma–Aldrich. Granular activated carbon was purchased from Merck (average size of 1.5 mm).

2.2. Synthesis of copper-based MOF, HKUST-1

The copper-based MOFs, HKUST-1, was synthesized and activated according to the procedure reported by Münch and Mertens [50]. In a typical synthesis, 0.299 g (1.5 mmol) copper acetate monohydrate was dissolved in 25 ml D.I. water and heated at 100 °C for 1 h. A 25 ml of ethanol solution containing 0.210 g of H_3BTC was prepared and added to the solution of copper acetate monohydrate. The resulting mixture was stirred at 60 °C for 1 h and subsequently at 25 °C for 12 h. The final product was filtered and washed several times with ethanol to obtain the blue powder. To activate HKUST-1, the blue powder was heated at 100 °C at reduced pressure for 24 h.

2.3. Characterization of HKUST-1

The powder X-ray diffraction patterns (PXRD) of HKUST-1 were obtained using an X-ray diffractometer (PANalytical) with copper as an anode material (40 mA, 45 kV). Infrared (IR) spectroscopic analysis of HKUST-1 was conducted using an infrared spectrometer (Jasco 4100). The surface area of HKUST-1 was determined by a nitrogen adsorption and desorption at 77 K using a Micrometrics ASAP 2020 surface area analyzer. To analyze the morphology of as-synthesized HKUST-1, a field emission scanning electron microscopy (FE-SEM) (JEOL JSM-6700F) was used.

2.4. Batch tests for oil droplets removed by HKUST-1

Oil-in-water (O/W) emulsion was prepared according to the procedure reported by Wang et al. [3]. Typically, a mixture of soybean oil (1 ml) and D.I. water (18 ml) was ultrasonicated using an ultrasonicator (Heat Systems Ultrasonics, USA) to obtain a concentrated O/W emulsion. This emulsion was then diluted to a desired concentration by addition of D.I. water. The concentration of oil droplets in water was measured as reported by Zouboulis and Avranas [21] using a turbidimeter (HACH 2000) with a sensitivity of 0.01 NTU. The emulsion turbidity was then converted to the concentration of oil using a standard reference line which was established by measuring the concentrations of oil in a series of standard O/W emulsions with known turbidities using the chemical oxygen demand method (COD). The conversion of the COD concentrations to the concentrations of soybean oil was calculated based on the average formula of soybean oil (i.e., $C_{55}H_{98}O_6$) [55]. The correlation coefficient of the line (R^2) was higher than 0.99 and the standard reference line was examined periodically to ensure its validity over the course of this study.

The removal of oil droplets from water using HKUST-1 was evaluated by a batch-type adsorption test, in which a 20-ml emulsion with a desired concentration was poured in a glass vial and bulk HKUST-1 powder was then added to the vial. The removal reaction was proceeded in a temperature-controlled orbital shaker at 300 rpm.

2.5. Recyclability test of HKUST-1

A recyclability test of HKUST-1 to remove oil droplets was performed using regenerated HKUST-1. To regenerate HKUST-1, the oil-rich HKUST-1 was dissolved in ethanol and the resulting mixture was placed on the orbital shaker at 300 rpm for 2 h at ambient temperature to remove the oil on HKUST-1. The ethanol-washed HKUST-1 was centrifuged to collect HKUST-1 powder which then was placed in a vacuum oven to remove the residual solvent to obtain the regenerated HKUST-1.

2.6. Thermogravimetric analysis of oil-adsorbed HKUST-1

To investigate weight loss of HKUST-1 and the oil-rich HKUST-1 as a function of temperature, the derivative thermogravimetric (DTG) analysis was conducted using a thermogravmetric analyzer (TGA) (ISI, Michigan, USA) with a carrier gas of nitrogen. The