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Synthesis of MIL-101@nanoporous graphene composites as hydrophobic adsorbents for oil removal

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ABSTRACT

The marine environment is being more and more polluted by oil spills on a daily basis, posing a serious threat to humans. The substances possessing high adsorption capacity and hydrophobic nature, generally play an important role in crude oil adsorption from aqueous solutions. The synthesis of new porous materials has attracted attention of many researchers in a large number of systems. Metal Organic Frameworks such as MIL-101(Cr) with high surface area and pore volume have been widely investigated to use in many applications such as separation. To enhance the MIL-101′s properties, hybrid composites with high specific surface area and pore volume have been considered.

MIL-101 and MIL-101@ nanoporous graphene (NPG), which have been fabricated for the first time, with different nanoporous graphene contents (30, 60, and 90 wt%) were herein synthesized via a solvothermal method .The prepared adsorbents were characterized using field emission scanning electron microscopy (FE-SEM), Transmission electron microscopy (TEM), X-ray diffraction (XRD), FT-IR spectroscopy, thermal gravimetric analysis (TGA), adsorption of nitrogen at 77.4 K, and contact angle (CA). The high oil adsorption capacity (14 g/g) was achieved for the synthesized adsorbents with the high surface area of MIL-101 (4293 m^2/g) and MIL-101@NPG 60 wt% (4642 m^2/g), and the high pore volume of MIL-101 (2.42 cm^3/g) and MIL-101@NPG 60 wt% (2.62 cm^3/g). The results show that the crude oil adsorption capacity enhanced by adding NPG to the virgin MIL-101, which is higher than that of previous scientific reports. The conformity of various adsorption models, including Freundlich, Langmuir, Temkin, and Dubinin–Radushkevich (D-R) to the equilibrium data were evaluated, and among which Freundlich isotherm model gave the best fitting result. The synthesized adsorbents can be further reused for several times, with no significant adsorption loss capacity and hydrophobicity.

1. Introduction

Organic waste contaminates the aquatic environment heavily. Industrial activities are the main reason why oil spills release into the oceans and other water resources (1–3). Human activities, including drilling, storing, transporting, waste management, and accidental releases of oil are the main sources for oil pollutions in marine environment. Production of novel materials to remove oil spills from water are becoming more and more indispensable since industrial water pollutions are rising (4). Many approaches have been used for the oil spills removal such as bioremediation, combustion, skimming, using chemicals like dispersants, and sorbents (5). Among them, adsorption process is one of the most favorable methods which can be utilized for many of pollutants, including oil spills (6–9). Oil sorbents play a significant role in oil spill clean-up and separation of oil from water (10). Moreover, selective adsorption process has some advantages, including simple application, relatively low cost, low energy consumption, and no by products (11,12). High oil adsorption capacity and surface area, low water pickup, and excellent reusability are the most important criteria for selecting an appropriate oil sorbent such as graphene foams (13–20). New porous materials have recently attracted particular attentions (21,22). One of the most popular materials possessing these features is metal-organic frameworks (MOFs). MOFs have been known as highly efficient adsorbents due to their fascinating structures and unusual properties such as ultrahigh surface areas, uniform but tunable cavities, and tailorable chemistry. MOFs are a group of porous adsorbents having large pore volume and surface area. MOFs are made of metal clusters and organic linkers. MOFs, therefore, have properties of both groups of organic and inorganic materials (23). There are more than 20,000 different MOFs with regard to differences between metal clusters

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and organic linkers. The surface area of MOFs is generally more than that of common porous materials such as zeolites or carbons, and it is typically within the range of 1000 to 10,000 m^2/g (24). A large number of approaches have been applied for synthesis of MOFs, *e.g.*, hydrothermal/solvothermal, microwave, electrochemical, mechanochemical, and sonochemical methods (25).

MIL-101 (the chromium terephthalate metal–organic framework, (MIL, Material Institute Lavoisier)) has been reported to be one of the most porous MOFs up to now with high hydrothermal/chemical stability and desirable textural properties, considered as a promising material for functional application among the MOFs. In addition to its highly porous nature, functional modification on MIL-101 can be easily achieved through direct or indirect approaches (26). Despite its prominent properties such as high specific surface area and pore volume, the large free volume within its framework makes them typically prone to self- interpenetration, preventing high porosity. Hence hybrid composite adsorbents should be made to improve its stability and adsorption performance for practical application. In recent years, many researches were conducted to fabricate MOFs with graphitic components. Several hybrid nanocomposites, such as MOFs/hierarchical porous carbon (27), MOF-5/AGO (Aminated Graphene Oxide) (28), MOFs/MWCNTs (Multi-Wall Carbon Nano-Tube) (29), MIL-53/GNP (Graphene Nano-Plates) (30), and MIL-101/SWCNT (Single-Wall Carbon Nano-Tube) (31) were synthesized and subsequently used as adsorbents. The adsorption performance in most of these synthesized adsorbents was increased. Nanoporous graphene (NPG), synthesized in our previous work, has high surface area (411 m^2/g), and high capacity for the sorption of crude oil (105.4 g/g) without any further modifications or secondary treatments (32). The presence of functional groups in the NPG such as hydroxyl, carbonyl, and carboxyl groups can make interactions between oxygen groups and metal centers in MIL-101′s structure, and it can be done via a simple solvothermal reaction. Thus the introduction of NPG to the synthesized MIL-101, which has the highest surface area among the synthesized MIL-101 s in the world (33), can dramatically improve the surface area and pore volume, and finally the adsorption capacity would increase sharply. Herein, we demonstrated that the synthesis of the novel hybrid MIL-101 and nanoporous graphene (MIL-101@NPG) nanocomposites, used as adsorbents for the oil spills removal. To the best of our knowledge, this is the first research introducing a new MIL-101 and NPG hybrid with different contents of NPG. It is worth nothing that surface area (4642 m^2/g) and pore volume (2.62 cm^3/g) of the synthesized adsorbents in this study (MIL-101@NPG) are the highest amount, reported for other synthesized hybrids until now.

It is found that by adding nanoporous graphene (NPG) to MIL-101, the pore walls inside MIL-101 can be modified so that the hydrophobicity and oleophilicity of the MIL-101 incredibly elevated. The results were verified by characterization studies. The synthesized adsorbents were characterized using FE-SEM, TEM, XRD, FT-IR, TGA, BET, and contact angle (CA) and the adsorption isotherms analyses were also investigated. As a matter of fact, the high surface area results in high oil adsorption capacities of prepared hybrid nanocomposites, *i.e.* an excessive desire to adsorb organic pollutants. The hybrid nanocomposite sorbents were prepared, namely MIL-101, MIL-101@NPG 30 wt%, MIL-101@NPG 60 wt%, and MIL-101@NPG 90 wt%.

2. Experimental

2.1. Chemicals

Chromium nitrate (Cr $(NO_3)_3 \bullet 9H_2O$, Loba chemie), 1.4-benzene dicarboxylic acid (H_2BDC, Merck), ethanol (99.5%, ACS reagent), and deionized water were used with no further purification. Nickel nitrate (Ni $(NO_3)_2 \bullet 6H_2O$) and citric acid ($C_6H_8O_7.H_2O$) were provided from Sigma–Aldrich (Saint Louis, MO, USA). The oil used in this study was obtained from Bahergan company (API = 28.01, specific gravity = 0.89, and viscosity at room temperature = 28.4 poise). All materials were used as received.

2.2. Synthesis of the adsorbents

2.2.1. MIL-101

1 Cr: 2 H_2BDC: 265 DI ratio was used, in order to synthesize MIL-101(Cr). Hence Cr $(NO_3)_3 \bullet 9H_2O$ (4.00 g, 10 mmol) and H_2BDC (3.32 g, 20 mmol) were dissolved in DI water (2650 mmol, 48 mL) and stirred for 30 min. The mixture was loaded in a Teflon-lined autoclave at 220 °C for 8 h, and then the system was naturally cooled to room temperature. The mixture was filtered using a Whatman filter paper to remove the recrystallized terephthalic acid. The green product was centrifuged at 9000 rpm for 10 min, and subsequently washed with ethanol and last centrifuged for 10 min three times. The final MIL-101 without HF was obtained after drying at room temperature overnight. The MIL-101 samples were purified using a two-step process (first step: using hot ethanol, and second step: using aqueous NH_4F solution). At first, 1 g solid sample was treated in 56 cm^3 ethanol at 80 C for 4 h. The green precipitate was then separated using centrifugation at 9000 rpm for 20 min; afterward, it was washed using ethanol and centrifuged at 12,000 rpm for 15 min (to ensure that the final product is pure enough, the process of washing and centrifugation were repeated three times). The solids were finally dried at room temperature. In the next step, the obtained sample was dispersed in an aqueous solution of 30 mM NH_4F, and placed in an oven set at 60 °C for 5 h. The resulting green MIL-101 solids were then separated by centrifugation at 12,000 rpm for 15 min, and washed with hot water and centrifuged at 12,000 rpm for 5 min (to ensure that the final product is pure enough the process of washing and centrifugation were repeated five times) to remove traces of NH_4F. The resulting solids were naturally dried at room temperature. The ratio of sample to the NH_4F solution was 1 g to 100 cm^3 (33).

2.2.2. Nanoporous graphene (NPG)

The nanoporous graphene (NPG) was prepared by employing the chemical vapor deposition (CVD) method in a catalytic base. Methane gas has been used as a carbon source in an electrical furnace (diameter of 50 mm and a length of 120 mm, heating up to 900–1100 °C), and nickel oxide nanocatalyst has been prepared as a catalytic base. Nickel nitrate (Ni $(NO_3)_2 \bullet 6H_2O$, 5.8 g) and citric acid ($C_6H_8O_7.H_2O$, 4.2 g) were entirely dissolved in deionized water (100 ml) to synthesize NiO nanoparticles. The prepared solution was stirred for about 12 h at 70 °C. A translucent green gel was formed, followed by water removal via evaporation. The gel was subsequently aged and dried at 110 °C for 24 h and calcined at 400 °C for 4 h. NiO nanoparticles were subsequently loaded into a quartz tube, followed by heating to 1100 °C and maintaining under a gas mixture, composed of methane and hydrogen (4 and 1, respectively). The furnace was subsequently cooled to ambient temperature at fast (3 °C/s) and slow (0.3 °C/s) cooling rates. In order to purify the NPG, and get rid of the metal nanocatalysts, the product was stirred in 18% HCl solution for 16 hours at ambient temperature. The sample was last rinsed several times, and dried overnight at 100 °C (9, 34).

2.2.3. MIL-101 @ nanoporous graphene (NPG) hybrid nanocomposites

Three different types of MIL-101@NPG hybrid nanocomposites in 30, 60, and 90 wt% were synthesized under the same conditions as mentioned in Section 2.2.1. The MIL-101 synthesis was done in the presence of different concentrations of NPG (0.6, 1.2, and

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