Journal of Environmental Management 209 (2018) 205–215

Contents lists available at ScienceDirect

Journal of Environmental Management

journal homepage: www.elsevier.com/locate/jenvman

Research article

Application of as-synthesised MCM-41 and MCM-41 wrapped with reduced graphene oxide/graphene oxide in the remediation of acetaminophen and aspirin from aqueous system

Samson O. Akpotu, Brenda Moodley*

School of Chemistry and Physics, University of KwaZulu-Natal, Westville Campus, Durban, 4000, South Africa

ARTICLE INFO

Article history:
Received 16 October 2017
Received in revised form
11 December 2017
Accepted 16 December 2017

Keywords:
As-synthesised
MCM-41
Graphene oxide
Reduced graphene
Pharmaceuticals
Adsorption

ABSTRACT

In this study, ASM41 (as-synthesised MCM-41), MCM-41, MCM-41 encapsulated with graphene oxide (MCM-41-GO) and reduced graphene oxide (MCM-41-G) were fabricated and utilized in the remediation of acetaminophen and aspirin from water. A surfactant template (cetyltrimethylammonium bromide) was added to ASM41 to make it more hydrophobic and its effects on the remediation of acetaminophen and aspirin from wastewater was studied. To further improve the adsorption capacity of the adsorbent, MCM-41 was encapsulated with GO and G which also aided in easy separation of the adsorbent from the aqueous solution. Comparative studies of the adsorption of acetaminophen and aspirin on all four adsorbents were investigated. Batch adsorption studies of acetaminophen and aspirin were carried out to determine the effects of pH, initial concentration, time and adsorbent dose. Adsorption mechanism was through EDA, π-π interactions, and hydrophobic effects. Data from sorption kinetics showed ASM41 had the highest q_m value for aspirin (909.1 mg/g) and MCM-41-G had the highest q_m value for acetaminophen (555.6 mg/g). The significant adsorption by ASM41 can be attributed to increased hydrophobicity due to the retention of the surfactant template. Thermodynamic studies revealed the adsorption process as spontaneous and exothermic. Desorption studies revealed that adsorbents could be regenerated and reused for adsorption.

1. Introduction

Acetaminophen (Acet) and aspirin (Asp) (Fig. SI 1) are over-the-counter (OTC) drugs that are water soluble and are not completely broken down by human metabolism and can be excreted into sewage systems and find their way into water bodies (Khetan and Collins, 2007). Pharmaceuticals are not easily remediated from water bodies by conventional water treatment methods and are regarded as “pseudo-persistent” (Carballa et al., 2004; Tambosi et al., 2010). In South Africa, recent studies have shown the presence of pharmaceuticals in the environment and particularly in wastewater effluent, rivers and dams (Agunbiade and Moodley, 2014; Gumbi et al., 2017). This has therefore generated serious concern for scientists and the public. Pharmaceuticals have been implicated in genotoxicity, aquatic toxicity, creation of resistance in pathogenic microbes and as endocrine disruptors (Khetan and Collins, 2007). Due to their persistence and adverse effects, there is a need for remediation. Adsorption is a reliable technique in the removal of pollutants from wastewater, because of its efficiency and ease of use. Other advantages include no toxic by-products and recyclability of adsorbents (Al-Khateeb et al., 2014).

Graphene oxide (GO) and graphene (G) are carbonaceous materials with various application in different fields with huge potential in adsorption. GO has functional groups such as hydroxyls, ketones, epoxides and carboxyl groups, thus making it easily immobilised on a substrate and as an excellent binder for organic groups (Li et al., 2015; Liu et al., 2013). Nonetheless, it is not easily separated from the adsorbate. Graphene was rediscovered and characterised by Novoselov et al. (2004). It is one carbon atom thick, arranged in a honey comb lattice structure with a theoretical surface area of ~2630 m^2/g, a rich π-system, excellent electrical, thermal and mechanical properties (Liu et al., 2013; Yang et al., 2015). It has excellent hydrophobic properties enabling it binding easily to organic pollutants. However, its full potential is often not fully exploited because it forms aggregates of nanosheets in aqueous solution, which reduces the surface area and adsorption

---

* Corresponding author.
E-mail address: moodleyb3@ukzn.ac.za (B. Moodley).

https://doi.org/10.1016/j.jenvman.2017.12.037

capabilities. In a bid to enable G/GO to reach maximum adsorption potential, the materials must be immobilised on a substrate. To overcome these challenges, a new class of material termed periodic mesoporous silica-graphene oxide/graphene composites have been developed. Mobil Catalytic material (MCM-41) has excellent properties, such as high surface area, homogenous pores, narrow pore size distribution, low toxicity, good biocompatibility (Datt et al., 2012) and thermal stability (Ghorbani et al., 2013). MCM-41 is synthesised through a liquid crystal templating mechanism and removal of the template (surfactant) is through high temperature calcination or refluxing with strong acids. The template free (surfactant free) MCM-41 now has a uniform, hexagonally ordered structure with a rigid shape around the expelled surfactant molecules (Akpotu and Moodley, 2016).

Despite MCM-41 advantageous properties, adsorption of organic molecules by MCM-41 remains a challenge. Nevertheless, studies have shown that the interaction between pharmaceutical pollutants and MCM-41 are weak (Teo et al., 2016) and also in aqueous solution it is strongly hydrophilic and adsorbs water molecules (Gibson, 2014). Hence, it is imperative to modify MCM-41 surface to enhance the interacting bonds and improve sorption capacity. Hydrophobization of MCM-41, by replacing hydrophilic Si—OH with hydrophobic functionalities, can cause a significant increase in the adsorption of organic molecules (Shadmani et al., 2016). To improve the hydrophobicity of MCM-41, the uncalcined as-synthesised form (ASM41) was used for the removal of organic pollutants (Gibson, 2014). Retaining the surfactant template in the MCM-41 mesopores will result in increased sorptive properties for hydrophobic pharmaceuticals in aqueous solution. This was proven when Mangrulkur and co-workers, successfully adsorbed phenol and chloro-phenol with ASM41, which gave a high sorption capacity as compared to pristine MCM-41. The higher sorption capacity was attributed to the surfactant template, which improved hydrophobic properties of ASM41.

In a bid to develop materials with greater hydrophobicity and improved sorption capability, hybrid sorbents with a hydrophobic surface and large surface area are required. Wang et al. (2010) developed a GO periodic mesoporous silica (GO-PMS) composite with improved thermal, mechanical and electrical properties used for energy storage. The coating of PMS serves 3 main purposes: first, it helps with an improved dispersion of reduced graphene (RGO)/GO because of their hydrophobic nature; second, it creates a better separation of the adsorbent and adsorbate in water and thirdly, the immobilisation on PMS helps provide a hybrid adsorbent with improved surface area and better hydrophobic properties. In a bid to surmount these challenges MCM-41 was synthesised and coated with GO and RGO.

In this study, we report the fabrication and effectiveness of novel ASM41 (as-synthesised MCM-41), MCM-41, MCM-41 encapsulated with GO (MCM-41-GO) and RGO (MCM-41-G) and their application in the remediation of Acet and Asp from wastewater. The presence of the surfactant and GO and G will increase the hydrophobicity of the adsorbent leading to increased adsorption capacities. In addition, an investigation to evaluate the effect of surfactant (CTAB) on adsorption of Acet and Asp from wastewater on MCM-41 and ASM41 was carried out. Adsorption kinetics, adsorption capacities and desorption studies were determined. This study would be useful in determining effective adsorption conditions, optimising sorption parameters and provision of a comprehensive understanding of adsorption mechanism. Acet and Asp were selected as model pharmaceutical pollutants to determine the efficiency of the adsorbents as probe molecules and in understanding the adsorption mechanism. The relative low cost of synthesis of ASM41 and MCM-41, coupled with the simple procedure of encapsulation with RGO/GO and their high efficiency in adsorption makes these materials excellent for the removal of pharmaceutical pollutants from wastewater.

2. Experimental

2.1. Materials and chemicals

Natural graphite powder, methanol (HPLC grade), hydrazine monohydrate (80%), 3-aminopropyl triethoxysilane (APTES, 99%), HCl (37%), $KMnO_4$, tetraethylorthosilicate (TEOS, 98%) and the pharmaceuticals acetaminophen (Acet) and aspirin (Asp) were obtained from Sigma-Aldrich. Absolute ethanol (Merck), cetyltrimethyl ammoniumbromide (CTAB 99%+) (Calbiochem), H_2SO_4 (98%), H_2O_2 (35%) and H_3PO_4 (80%) were obtained from Promark. All the reagents were analytically pure and were used without further purification. MilliQ water was used in the preparation of the standard solutions and the mobile phase used in chromatography analysis.

2.2. Synthesis of MCM-41 and as-synthesised MCM-41 (ASM41)

MCM-41 was synthesised using a modified method from (Akpotu and Moodley, 2016). CTAB (2.4 g) was dissolved in 120 mL of double-distilled deionised water at room temperature. A 10.25 mL portion of ammonium hydroxide was added to a the CTAB and water, under stirring. About 10 mL of ethanol was also added to the mixture. The mixture was stirred for 30 min and a 10 mL of aliquot of tetraethylorthosilicate (TEOS) was added to the clear solution and stirred rigorously at 300 rpm for 1 h. The resulting slurry was vacuumed filtered, washed with double-distilled deionised water to obtain a pH of 7, leading to the removal of the CTAB (structure directing agent) and the NH_3 solution. The resultant powder was dried in a vacuum oven at of 110 °C for 24 h. The resultant powder was gently broken with a pestle and ground before calcining at 550 °C for 5 h at a ramp rate of 2 °C/min to ensure the removal of CTAB. This product was labelled as MCM-41. The uncalcined form of MCM-41 is referred to as as-synthesised MCM-41 (ASM41), where the surfactant/SDA was not calcined and retained in the MCM-41 template.

Detailed methods of the activation of MCM-41 (Akpotu and Moodley, 2016), synthesis of NH_2-MCM-41 (Akpotu and Moodley, 2016) and GO (Marcano et al., 2010) are provided in the supplemental information (SI).

2.3. Synthesis of MCM-41-GO and MCM-41-G

In this encapsulation procedure, NH_2-MCM-41 was dispersed and sonicated in water. GO (10 mg/L) previously sonicated for 2 h was added to the suspension and pH adjusted to 7 by adding NH_4OH whilst stirring. It was stirred continuously for 8 h and left to settle for 1 h. The product was filtered, washed with water and dried in a vacuum oven for 6 h at 50 °C. This was labelled as MCM-41-GO. In the synthesis of MCM-41 reduced graphene oxide (MCM-41-G), a similar procedure was adopted but the synthesis temperature was 80 °C and hydrazine monohydrate was added to the mixture to reduce GO to reduced GO. The mixture was stirred for 8 h, left to settle for 1 h, filtered, washed with water and dried under vacuum. The solid black product was oven dried in a vacuum at 80 °C for 6 h. This was labelled MCM-41-G.

2.4. Characterisation of synthesised adsorbents

The morphology and microstructure of the adsorbents were analysed by field emission scanning electron microscopy (FESEM, Zeiss instrument, 10 kV operating voltage), and high-resolution