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A comparative adsorption study of sulfamethoxazole onto graphene and graphene oxide nanosheets through equilibrium, kinetic and thermodynamic modeling

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ABSTRACT

Adsorption properties of sulfamethoxazole (SMX) as an antibiotic were promoted by graphene nanosheet (GNS) and Graphene oxide nanosheet (GOS). The five factors influencing the adsorption of SMX (initial SMX concentration, initial solution pH, amount of adsorbent, temperature and contact time) were studied. The results showed that adsorbent dosage of 0.010 mg, initial pH∼6 and contact time ∼110 min are optimum for both systems. The monolayer adsorption capacity (q_m) decreased with the increase of the temperature from 25 °C to 45 °C. Non-linear regressions were carried out in order to determine the best fit model for each system. To do this, 8 error functions were applied to predict the optimum model. Among various models, Redlich–Peterson and Koble–Corrigan isotherm models represented the equilibrium adsorption data of SMX while kinetic experimental data were well fitted by pseudo second-order model on both adsorbents. The study showed that GOS can be used as a more efficient adsorbent for the adsorption of SMX from water solution.

1. Introduction

Recently, the demand for pharmaceuticals and personal care products (PPCPs) has nearly paralleled to the escalating population (Liu et al., 2014). The pharmaceutical industry has expanded to produce hundreds of tons of synthetic chemicals per year (Huang et al., 2012). In particular, antimicrobials and their metabolites appear in significant amounts in water supplies. Although no evidence exists showing that human health is affected by minute doses of antibiotics, changes have been observed in ecosystem functions over long periods of time (Huang et al., 2012). Studies have determined a rising level of antimicrobial-resistant organisms in the environment. In addition to antimicrobial resistance, the studied bacteria displayed a delay in cell growth and limited denitrification (Hassard et al., 2015).

The majority of these frequently-used compounds and their metabolites are not completely removed by the treatment systems, with removal efficiencies reported between zero and 90% (Bhandari et al., 2008). Because of increasing the usage rate of PPCP, lack of efficient removal technology and the environmental risks associated with PPCP occurrence, there is a reason to develop new materials and processes in treatment systems in order to eliminate antibiotics from the environment.

A class of antimicrobial drugs commonly found in wastewater effluent is sulfanilamides. These compounds are a subset of chemicals containing the sulfonamide functional

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group, to which numerous prescription drugs belong. Sulfonamide drugs consist of anti-diabetic agents, anticonvulsants, diuretics, protease inhibitors and beta-blockers. These compounds are of concern due to their expansive use and inability to be readily biodegraded in the environment, despite the fact that many sulfonamides are photodegradable in surface waters (Benitez et al., 2011). Sulfanilamide antimicrobials interfere with microbiological mechanisms by mimicking essential bacterial enzymes, making the compounds possibly detrimental to secondary wastewater treatment processes.

SMX (Fig. 1s) is a broad-spectrum biostatic sulfanilamide which has become a point of interest because of its prevalence in contaminated wastewaters at concentrations correlated to bacterial resistance and genetic mutations in organisms (Ghauch et al., 2013). Although SMX is therapeutically active by itself, it is often paired with trimethoprim (TMP), creating a synthetic antibacterial combination drug that affects the biosynthesis of nucleic acids and proteins in bacteria. The SMX-TMP drug is one of the most highly prescribed antibiotics for treating bladder, lung, and ear infections. Sulfa allergies and liver toxicity are posed as common side effects in consumers of this antibiotic. The human body does not fully metabolize the compound, causing about 30% to be excreted in its original pharmaceutically active form (Dias et al., 2014).

In addition, in the case of SMX it is approximated that from 10 to 30% of the ingested dose is excreted via urine in its original form (Masters et al., 2003; Zhang et al., 2010a). Indeed, SMX has been detected in concentrations that range from dozens to hundreds of $\mu g\,L^{-1}$ in sewage samples and from 14.8 to 297 $ng\,L^{-1}$ in surface waters. Research suggests that such antibiotics can induce bacterial resistance and are suspected to cause liver cancer (Wang et al., 2013a). Persistence of antibiotics in aquatic environment is mainly due to their widespread consumption, low biodegradability and hydrophilic nature. Therefore, buildup of these potentially harmful compounds in aquatic environment can pose long-term threat to aquatic and surrounding life. SMX was chosen for this adsorption study due to its frequent occurrence in surface waters (Ghauch et al., 2013; Qi et al., 2014). Taking into account the widespread use of sulfonamides and their potential environmental effects, it is important to develop new technologies for removing SMX and similar compounds from points of discharge. Current water and wastewater treatment processes are advanced oxidation, photolysis and adsorption. Adsorption is known to be an effective treatment technique for the removal of organic micropollutants such as pharmaceuticals and pesticides (Nam et al., 2015; Rostamian et al., 2011). Conventional and natural adsorbents (e.g., activated carbon, carbon nanotubes, zeolites, etc) have thus been studied widely regarding the removal of micropollutants (Ji et al., 2010a; Ji et al., 2010b; Saman et al., 2015; Zhang et al., 2010a).

Graphene nanosheet (GNS) as a new family of carbon nanomaterial has unique and superior properties including excellent thermal conductivity (5300 $W\,m^{-1}K^{-1}$), mobility of charge, mechanical properties (Young's modulus, ∼1100 GPa), electrical conductance (∼2000 $S\,cm^{-1}$), specific magnetism properties and large surface area (Ersan et al., 2015). Recently, GNS and graphene oxide sheet (GOS) were used as adsorbents to remove dyes, hydrocarbons, heavy metal ions from aqueous solutions, and showed high adsorption amount and fast adsorption rates (Akkaya Sayğılı et al., 2015; Wang et al., 2015).

The GOS and GNS characteristic structures and electronic properties make interact strongly with organic molecules via non-covalent forces, such as hydrogen bonding, π–π stacking, electrostatic forces, van der Waals forces, and hydrophobic interactions (Pyrzyńska and Bystrzejewski, 2010). Their nanosized structures also endow them some advantages such as rapid equilibrium rates, high adsorption capacity and effectiveness over a broad pH range (Mauter and Elimelech, 2008). Activated carbon (granular, powder and etc) is conventional adsorbent but Graphene is the next-generation adsorbent. Adsorption of SMX onto carbonaceous materials was due not only to the large surface area but also to π–π electron donor acceptor interactions and electrostatic attraction between adsorbate and adsorbent. In accordance with its large specific surface area and π-electron-rich aromatic structure, graphene has demonstrated high adsorption capacities (hundreds of milligrams per gram) for a range of organic compounds through strong π–π interaction, such as heavily used antibiotic, pharmaceuticals, naphthalene, acrylonitrile, biphenyl and so on. GOS is laminated from GNS and has many carbons and various functional groups such as carboxylic(ACOOH), hydroxyl (AOH), and epoxy (ACCO)groups on its surface (Wang et al., 2013b).

There are only a few studies focusing on the systematic investigations of GOS adsorption of antibiotics in environmentally relevant aqueous systems (Chen et al., 2015). Among these researches, π–π interactions (or π–π stacking) are commonly invoked to explain adsorption rate and extent for many organic compounds due to the wide availability of delocalized π electrons at the graphene surface which can overlap non-covalently in a stacking arrangement with π electrons within benzene rings of organic adsorbate. Hydrophobic interactions, electrostatic interactions, other diverse π interactions and dispersion interactions (van der Waals), and hydrogen bonding with oxygen-bearing impurities (e.g. carboxyl functional groups) may also be important sorption mechanisms depending on adsorbate and adsorbent properties. Charged surface functional groups may improve the wettability of material surfaces, improve colloid stability, promote electrostatic attraction or repulsion, and alter π electron donating character of C sp^2 (Zhang et al., 2010b).

This study systematically compares and investigates the performance of GNS and GOS as potent adsorbents to removing SMX, as well as the factors influencing sorption of SMX, including temperature, pH of solution, contact time of interaction and initial SMX concentration. Adsorption isotherm, kinetic and thermodynamic parameters have been estimated from experimental results and error analysis was also used to find best fit model. These findings would progress our essential understanding about SMX adsorption mechanisms to better design the water treatment process applications. Also GNS can be coated on solid matrix for separation and purification in industrial reactors (Ji et al., 2009; Wang et al., 2013a) or even it can be used as an adsorbent in any wastewater samples for removing SMX. The experimental results can help us to determine the optimum conditions for environmental applications.

2. Method and theory

2.1. *Preparation and characterization of adsorbents*

GNS and GOS were purchased from US Research Nanomaterials (USA). The characterization and properties of the adsorbents reported by manufacturer are tabulated in Table 1s.