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A comprehensive adsorption study and modeling of antibiotics as a pharmaceutical waste by graphene oxide nanosheets

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ABSTRACT

The adsorption behavior of tetracycline (TCN), doxycycline (DCN) as the most common antibiotics in veterinary and ciprofloxacin (CPN) onto graphene oxide nanosheets (GOS) in aqueous solution was evaluated. The four factors influencing the adsorption of antibiotics (initial concentration, pH, temperature and contact time) were studied. The results showed that initial pH ~ 6 to 7 and contact time ~ 100 – 200 min are optimum for each drug. The monolayer adsorption capacity was reduced with the increasing temperature from 25 °C to 45 °C. Nonlinear regressions were carried out in order to define the best fit model for every system. To do this, eight error functions were applied to predict the optimum model. Among various models, Hill and Toth isotherm models represented the equilibrium adsorption data of antibiotics while the kinetic data were well fitted by pseudo second-order (PSO) kinetic model (DCN and TCN) and Elovich (CPN) models. The maximum adsorption capacity (q_{max}) is found to be in the following order: CPN > > DCN > TCN, obtained from sips equation at the same temperature. The GOS shows highest adsorption capacity towards CPN up to 173.4 mg g^{-1}. The study showed that GOS can be removed more efficiently from water solution.

1. Introduction

The supply of water for human consumption and the wastewater treatment are the biggest challenges of this century (Rostamian and Behnejad, 2017). The occurrence of pharmaceutical active compounds (PACs) and their metabolites in the water cycle are widely documented across the globe and although their presence in drinking water is sporadic and in trace. However, PACs are recognized as emerging contaminants due to their bioactivity, wide usage and potential health and ecological risks (Sobsey and Bartram, 2002). Tetracyclines, fluoroquinolones, sulfonamides and trimethoprim are classes of synthetic antibiotics used extensively in human and veterinary medicine. Tetracyclines are antibiotics used for the treatment of a variety of infections and they are commonly applied in agriculture and aquaculture for growth promotion and disease treatment (Sayğılı and Güzel, 2016).

A vast variety of materials, including silica, active carbon, polymer/composites and graphene oxide, are utilized as adsorbents to remove contaminants from water (De Gisi et al., 2016; Thines et al., 2017). Among those adsorbents, graphene oxide (GOS) has shown excellent performance, due to its porous structure and plentiful oxygen-containing functional groups. GOS has a number of hydroxyl, carboxyl and epoxy groups on its two-dimensional graphene framework surface, thus bringing about strong interactions with organic structures as well antibiotics and high modifiability. Most drugs have an appropriate interaction with GOS via π – π stacking (Rostamian and Behnejad, 2016). The oxygen atoms of GOS and delocalized conjugated π electrons on the surface of the GOS make it extremely hydrophilic and provide the capability to apply GOS in the aquatic and biological environment. Actually a few studies are focusing on the studies of GOS adsorption of antibiotics in the environment (Ashfaq et al., 2017; Chen et al., 2015; Rostamian and Behnejad, 2016). Among these published researches, π – π interactions are commonly invoked to illustrate adsorption rate which can overlap in a stacking arrangement with π electrons within the benzene ring in the organic adsorbate structure. Hydrophobic, electrostatic, other diverse π interactions, dispersion (van der Waals) interactions and hydrogen bonding with oxygen-containing impurities (for example carboxyl functional groups) may also be considerable adsorption mechanisms depending on adsorbent and adsorbate properties (Goswami et al., 2017).

This study systematically investigated the performance of GOS as a potent adsorbent to remove some antibiotics. The parameters of adsorption isotherm, kinetic and thermodynamic have been measured and calculated from experimental results as well as error analysis also applied to detect best-fit model. Kinetic modeling is very important in wastewater treatment for the reason of providing insights into the reaction pathways, the mechanism and behavior of the adsorption process

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(Subbaiah and Kim, 2016). It is notable to look into the kinetics process to predict at which rate antibiotic is removed and to design the appropriate adsorption filtering process. These results would progress our essential understanding about antibiotics adsorption mechanisms to better design the waste water treatment process applications (Ji et al., 2009; Wang et al., 2013). The experimental results can help us to determine the optimum conditions for environmental applications.

2. Method and theoretical background

2.1. Experiment methods, characterization of GOS and antibiotics

All chemicals were purchased in analytical grade and all the solutions were made with distilled water thorough the experiment. Each stock solution was prepared in conical flasks and stirred magnetically. A stock solution of adsorbate (antibiotic) was prepared by dissolving its required amounts in 1000 mL of distilled water. All stock solutions were fresh and prepared on the same day of the experiment. The pH of the aqueous solution was adjusted using suitable concentrations of nitric acid or sodium hydroxide aqueous solutions. The adsorbent was prepared from US Research Nanomaterials (USA). The purity, thickness, number of layers and diameter of GOS are 99.5%, 2 – 18 nm, less than 32 layers and 10 – 50 μm respectively. The CHN analysis shows C and H percent is 43.4932% and 0.2585%. The specific surface area of GOS is 123 $m^2 g^{-1}$. TCN, DCN and CPN antibiotics (China) were given by Iran Darou Company (Iran, Tehran) as a gift (purity ≥ 97%). SEM and TEM images of GOS (Fig. 1a, b) displayed dense sheets loosely distributed on the basal planes to create groove areas. The two-dimensional and flat structures of GOS enable the exposure of active sites on the surfaces of GOS to antibiotics.

To the best of our knowledge, a main point in the interaction between adsorbent and adsorbate is the chemical structure of the adsorbent. The XRD pattern of GOS (Fig. 1c), showing a peak at $2\theta = 10$, indicates oxygen-containing functional groups on the surface. Previous works also reported the XRD peaks of GOS at $2\theta = 10.2 – 10.6$ and described the occurrence of peaks in the presence of O-attached functional groups on the adsorbent surface via the increment of d-spacing after the oxidation of graphite (Ai et al., 2011).

2.2. Adsorption of pharmaceutics

A stock solution of each antibiotic was prepared by dissolving its required amounts (5 – 250 mg of antibiotic) in 500 mL of distilled water. Solutions of desired concentration were prepared by diluting the stock solution using distilled water. The suspension was shacked overnight and wrapped in an aluminum foil to avoid possible photodegradation of antibiotic. The antibiotic solutions were protected from light during the experiment and used on the same day of production. All of the experiments were performed in batch conditions using 10 mL of each antibiotic solution and 0.0100 g of GOS. Shaker was used (150 rpm) at three temperatures (25.0, 35.0, 45.0 °C) in order to mix the antibiotic suspensions. After that, the solution was filtrated and the residual concentrations of antibiotics in the solutions were measured using UV–vis spectrophotometer (Shimadzu UV 2550, Japan) at a maximum wavelength of 350 nm for TCN, 346 nm for DCN and 280 nm for CPN, via measuring the concentration by plotting a calibration curve.

2.2.1. Study of adsorption isotherms

The maximum amount of antibiotic adsorbed onto GOS is calculated from the isotherm curves and recorded as q_e (mg g^{-1}) at each equilibrium concentration of antibiotic (C_e (mg L^{-1})) (Fontana et al., 2016).

As shown in Table S1, Redlich-Petersen and Sips models adapted Langmuir and Freundlich parameters in their models to indicate differences on adsorption at high concentration versus low concentration of adsorbate in the solution (Rostamian and Behnejad, 2017). Koble-Corrigan model is an empirical model with three parameters representing adsorption isotherm data (Koble and Corrigan, 1952). Also, Toth isotherm model is an empirical equation that is advantageous in describing heterogeneous adsorption systems satisfying both low and high boundaries of the concentration. Hill model describes the binding of molecules onto the homogeneous surface making adsorption a cooperative phenomenon case with the ligand binding ability at one site on the molecule and may change various binding sites on the same molecule (Hill et al., 1951). To adapt the various aspects of each adsorption system, it is essential to study which adequate model best describes the experiment results (Najafi et al., 2011). Wolfram Mathematica v.9.0 software was used to perform the regression analysis and the parameters are reported and discussed.

2.2.2. Study of kinetic adsorption

Kinetic experiments were performed to confirm when the equilibrium is reached. 10 bottles with 10.0 mg masses of adsorbent and constant concentration of antibiotic are used for each experiment, for each initial concentration of antibiotic at 25 °C. Samples were kept away from the light during the experiment. After the definite time, each sample was filtered and remaining concentrations of antibiotic were measured at UV–vis spectrophotometer (Shimadzu UV2550, Kyoto, Japan). The equilibrium concentration is plotted on the adsorption curve to confirm if the equilibrium concentration is consistent with the isotherm data. The experimental data is plotted on q_t versus time (min). The experiment was triplicated with each antibiotic. The sorption capacity q_t (mg g^{-1}) of adsorbents was calculated using this equation (Rostamian et al., 2011):

$$q_t = \frac{C_0 - C_t}{W} \times V, \quad (1)$$

where C_0 is the initial antibiotic concentration (mg L^{-1}) and C_t is the remaining antibiotic (mg L^{-1}) at time t, V is the volume of antibiotic solutions (L) and W is the mass of adsorbent (g).

The main objective of this stage is to maximize the realization of system design while minimizing experimental expense. The first goal is to understand the adsorption mathematical model parameters to foresee and evaluate the model adequacy. The adsorption mechanism can happen in its chemical or physical form. A resistance can be associated with each step and integrated into each kinetic model. The largest resistance corresponds to the slowest step and consequently determines the overall rate-limiting step to adsorption. The models are tabulated in Table S1 (Rostamian et al., 2011).

The good fit of this model demonstrates that the adsorption driving force determined by ($q_e - q_t$) was proportionate to the number of free adsorption sites for antibiotic, while the kinetic of process was administered by chemisorption (Rostamian et al., 2011). Hence, the kinetic rate is an important parameter to determine the transport of antibiotic in the solution.

2.2.3. Error functions analysis

As known, linear regression has been one of the best tools describing the best fitting which mathematically analyses the adsorption systems and checks the theoretical hypothesis of a model. The eight mathematically precise error functions were employed and the obtained parameters were tabulated in Table S2. In these equations, q_{meas} is the measured antibiotic concentration; q_{calc} is the calculated antibiotic concentration with model, n is the number of observations in the experimental data and $\overline{q_{calc}}$ is the average of q_{calc} (Rostamian et al., 2011).

3. Results and discussion

3.1. Effect of pH on adsorption capacity

In water treatment systems, the pH of influent water varies according to the sources of water and amounts to 4.8 – 9.5 in surface