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Hydroxyl-functionalized Graphene from Spent Batteries as Efficient Adsorbent for Amoxicillin

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A chemically exfoliated graphene, functionalized with hydroxide, was prepared and used as an adsorbent for the removal of amoxicillin from aqueous solutions. This nanocomposite was recovered from chemically exfoliated graphite rods present in spent zinc-carbon batteries. The graphene-OH was determined to have a sheet-like morphology with high surface area ($A_{s,BET}$ = 181 m^2 g^{-1}) . Its adsorption characteristics were observed at different adsorption time, initial amoxicillin concentrations, and adsorbent dosage to establish the kinetics, isotherm, and optimal adsorption conditions. Pseudo-first-order and pseudo-second-order models were used to study the kinetics, while Freundlich and Langmuir models were used to study the adsorption isotherms. Results showed that amoxicillin adsorption fitted with Langmuir isotherm with higher correlation than the Freundlich isotherm and followed the pseudo-second-order rate model. The removal efficiency increased as the adsorbent dosage was also increased. Similarly, increasing the adsorbent dosage from 1 g/L to 20 g/L, the adsorption capacity decreased from 36 mg/g to 4 mg/g. For recyclability, the adsorptivity of graphene – OH was shown to be slightly decreasing over the 5-cycles (99.75 % to 95.37 %). Based on the results, hydroxyl-functionalized graphene demonstrated high industrial potential for amoxicillin wastewater treatment.

1. Introduction

A pharmaceutical antibiotic as a water contaminant is detrimental to humans and the environment (Balarak et al., 2017). Antibiotic compounds present in the marine environment, which originates mainly from the pharmaceutical industry and the usage of animals and humans, is an emerging problem as it may enable the proliferation of drug-resistant bacteria. One of the considered important antibiotics used commercially is Amoxicillin which has high resistance to bacteria and has a great spectrum against a large variety of microorganisms (Yaghmaeian et al., 2014). Hence, the wastewater containing this antibiotic must be treated properly before being released into the environment.

Several techniques have been reported in the removal of amoxicillin from aqueous substances and some of which are membrane separation (Benitez et al., 2011), Fenton oxidation (Zha et al., 2014), ozonation (Andreozzi et al., 2005), and adsorption (Moussavi et al., 2013). The adsorption process is regarded as an exceptionally efficient method of removing water contaminants even at extremely low concentrations (< 1 mg/L) (Secondes et al., 2014). This method is easy and applicable in removing prevalent substances with low operating costs compared to other methods (Ahmad & Hameed, 2010). The adsorption technique includes the benefits of ease of use, low price, high effectiveness, and no risk of extremely toxic by-products.

Graphene and its composite materials are gaining importance as nano adsorbents. Graphene, a two-dimensional nanomaterial having a single-atom graphite layer, has attracted great interest in many application areas (including wastewater treatment) due to its unique physicochemical properties (Ali et al., 2019). Applications of graphene in various fields have fortified not only the growth of substance-bound extended graphene single layers but also connected materials like reduced graphene oxide (rGO) (Le et al., 2020) and graphene oxide (GO) (Zunita et al., 2020).

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In this study, electrochemical exfoliation was used to produce graphene from spent zinc-carbon batteries. Year by year, solid waste batteries increase due to the high demand for portable electronic devices. To reduce the waste's impact on the environment, some battery waste components must be reused. Herein, a functionalized adsorbent material from graphite rods of waste zinc-carbon batteries was synthesized and investigated its properties. Hydroxyl-functionalized graphene from electrochemically exfoliated graphite rods was synthesized and tested for its efficacy for the adsorption of amoxicillin. Its kinetics, isotherm, recyclability, and optimal adsorption conditions in terms of contact time, initial amoxicillin concentrations, and adsorbent dosage were also determined.

2. Materials and methods

Main raw materials include waste zinc-carbon batteries and amoxicillin (AMX). Procedures detailed below involved in the synthesis of hydroxyl-functionalized graphene include electrochemical exfoliation of graphite rod from zinc-carbon batteries to recover graphene, followed by dissolution of graphene in NaOH solution. The graphene-OH were then subjected to characterization and adsorption experiments.

2.1 Research materials

Graphite rods were obtained from spent zinc-carbon batteries. Sulfuric acid (98 % H_2SO_4, RCI Labscan Ltd.) was used for electrochemical exfoliation of graphite rods. Sodium hydroxide (98.5 % NaOH, Scharlau) was used for the hydroxyl-functionalization of graphene.

2.2 Research procedure

Electrochemical exfoliation of graphite rod

Two (2) graphite rods were connected separately to a power source (10 to 14 V) and submerged in 250 mL of approximately 1.0 molar (M) sulfuric acid. The electrochemical reaction exfoliated the graphite rod to form graphene. After consuming all the graphite rods, graphene was filtered out from the solution and was dried at 60 ˚C for 6 hours.

Synthesis of graphene-OH nanocomposite

Four (4) grams of electrochemically exfoliated graphene was mixed with 80 mL of 2.0 M NaOH and was stirred vigorously for 10 minutes at room temperature. The mixture was transferred to a 100 mL Teflon-lined stainless autoclave and was reacted at 180 ˚C for 2 h. After cooling to room temperature, the product was sonicated for 8 hours, filtered, washed with distilled water until the filtrate was neutral, and was oven-dried at 80 ˚C to obtain the graphene-OH nanocomposite.

Characterization of graphene-OH nanocomposite

The nanoscopic morphology of the synthesized graphene-OH was analyzed using a scanning electron microscope (SEM, Hitachi SU150, Japan) equipped with energy dispersive X-ray (EDX). Fourier-transform infrared (FTIR) spectra of samples were recorded with KBr pellet using a Shimadzu 8400 spectrophotometer. Porosity and surface area were determined by N_2 adsorption – desorption at 77 K with a Brunauer-Emmett-Teller (BET) analyzer (BEL: BELSORP-MINI, Japan).

Adsorption experiments

The adsorption characteristics of graphene-OH was observed at different adsorption time, initial AMX concentrations, and adsorbent dosage to establish the kinetics, isotherm, and optimal adsorption conditions. Graphene-OH was dispersed in a certain volume of AMX solution (V) and agitated (150 rpm) at a specified time (t). Simulated AMX solutions were prepared by dissolving the powdered AMX tablet in distilled water (DW) at desired initial concentration (C_o). Samples were taken after the graphene-OH was separated from the solution using a syringe with filter to determine the concentration at time t (C_t) or until equilibrium AMX concentration (C_e) was reached. AMX removal efficiency and equilibrium adsorption capacities were determined considering the mass of graphene-OH dispersed into the AMX solution.

3. Results and discussion

Characterization of graphene-OH nanocomposite to describe its surface morphology is necessary to further understand its adsorptive properties which were evaluated through: AMX's adsorption kinetics, isotherms, effect of solid to liquid (S/L) ratio, and recyclability to evaluate the overall efficiency of graphene as AMX adsorbent.

3.1 Characterization

The graphene-OH synthesized from spent-batteries appears to have sheet-like morphology (Figure 1a), which indicates successful exfoliation. It has a surface area of 182.1 $m^2\ g^{-1}$ (Figure 1a) with some mesopores as

indicated by the BJH plot (Figure 1b inset). The graphitic nature of both GO and sGO samples were characterized by D-band, and G-band observed in the Raman spectra (Figure 1c), indicating sp^2 carbon in a 2D hexagonal lattice and sp^3 carbon atoms of defects and disorder, respectively. The intensity ratio of D-band to G-band (I_D/I_G) of around 1.44 in the graphene-OH sample suggested the presence of disorder carbonaceous content, which was grafted with oxygen functional groups during the hydrothermal functionalization process. It also shows different oxygen configuration in its structures. The characteristic peaks of hydroxyl (3050–3700 cm^{-1} and 1070 cm^{-1}) with all C–OH vibrations from COOH and H_2O, C=O stretching (1739 cm^{-1}), O-H deformation (1402 cm^{-1}), and C-O stretching vibration (1109 cm^{-1}) were observed.

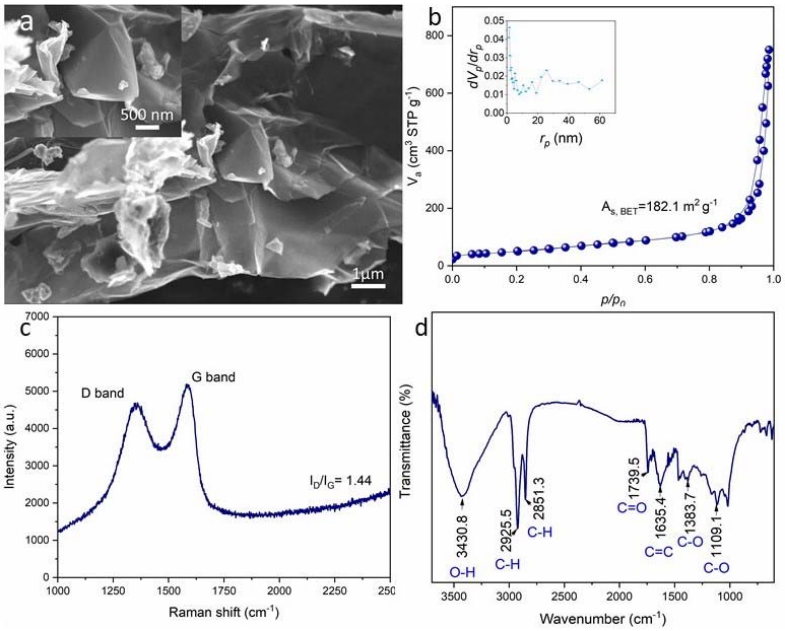

Figure 1: SEM images (a), adsorption-desorption isotherms with BJH plot inset (b), Raman analysis (c), and FTIR analysis (d) of graphene-OH.

3.2 Kinetics of AMX adsorption

Examination of the behavior of amoxicillin adsorption and potential rate-controlling steps such as mass transport and chemical reaction processes were done using kinetic models, pseudo-first-order (PFO, Eq. 1), and pseudo-second-order (PSO, Eq. 2) equations. Non-linear regression analyses were carried out to derive equilibrium adsorption capacity (q_e) and rate constants k_1 (first-order) and k_2 (second-order) based on the calculated adsorption capacity at any time t (q_t).

$$q_t = q_e(1 - e^{-k_1 t}) \quad (1)$$

$$q_t = q_e\left(\frac{q_e k_2 t}{1 + q_e k_2 t}\right) \quad (2)$$

Derived constants (Table 1) and non-linear fitting (Figure 2b) shows that correlation (r^2) coefficient of the PSO is greater than that of PFO kinetic model. This implies that the rate of AMX adsorption onto graphene-OH was affected mainly by the availability of active adsorption sites on the adsorbent rather than the concentration of the AMX in the solution (Moussavi et al., 2013). The adsorption mechanism of graphene-OH includes an interaction between the base functional group and amoxicillin chemically (Citraningrum et al., 2007). The AMX adsorbed increased rapidly in the first 120 minutes (Figure 2a), which can be attributed to the high amount of available adsorption sites initially. However, adsorption capacity started to approach equilibrium at t = 1440 minutes, implying relatively fast adsorption kinetics.

Table 1: Kinetic parameters of amoxicillin adsorption onto graphene-OH.

Pseudo-first-order			Pseudo-second-order		
q_e (mg g^{-1})	k_1 (min^{-1})	r^2	q_e (mg g^{-1})	k_2x10^{-5} (g mg^{-1} min^{-1})	r^2
28.18	0.002	0.97	34.85	6.25	0.98

C_o = 40 mg L^{-1}, pH = 7, S/L ratio = 1 g L^{-1}, and T = 25 °C

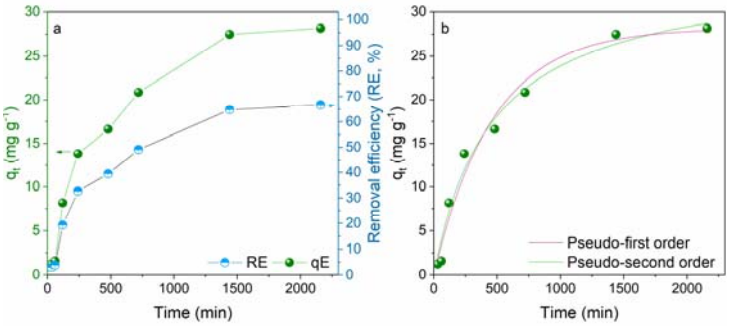

Figure 2: Equilibrium adsorption capacity and removal efficiency plotted vs. time.

3.3 Isotherms of AMX adsorption

Adsorbate-adsorbent interaction was determined through isotherm studies, varying initial AMX concentrations. The percentage of removal (RE) decreased with increasing initial amoxicillin concentration for graphene-OH adsorbent (Figure 3a), but q_e increased with the increase of C_o. The lower uptake at higher concentration resulted from an increased ratio of the initial adsorption number of moles of the AMX to the available surface area. The C_o is the primary driving force to overcome the mass transfer resistance of the AMX between the aqueous and solid phases (Aljebori & Alshirifi, 2015). Therefore, at higher C_o, the number of ions competing for the available sites on graphene-OH surface was high, resulting in higher q_e.

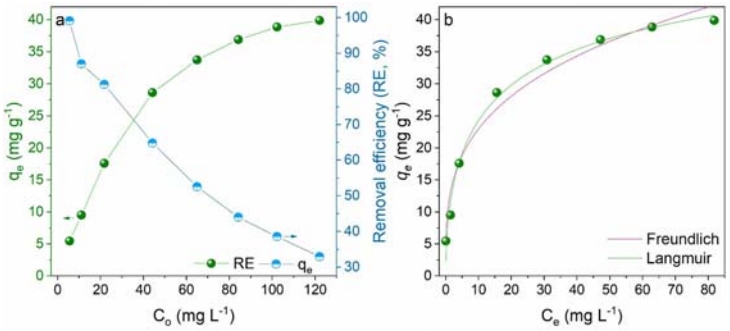

Figure 3: Equilibrium adsorption capacity and removal efficiency plotted vs. time.

Langmuir (Eq. 3) and Freundlich isotherms (Eq. 4) had been utilized to assess the equilibrium characteristics of the adsorption processes. Considering the equilibrium AMX concentration (C_e, mg L^{-1}), Langmuir (K_F, L g^{-1}), and Freundlich (K_L, L g^{-1}) constants, Freundlich exponent (n, g L^{-1}) and the theoretical maximum monolayer saturation adsorption capacity (q_m).

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{3}$$

$$q_e = K_F C_e^{\frac{1}{n}} \tag{4}$$

The equilibrium data for AMX adsorption was fitted with both the Langmuir and Freundlich isotherms (Figure 3b), and non-linear regression analysis determines the calculated parameters (Table 2). Langmuir isotherm has a higher correlation than the Freundlich isotherm. This suggests that a monolayer of AMX was adsorbed on a fixed number of identical and localized sites in the graphene-OH lattice, contrary to the Freundlich model, which assumes a heterogeneous adsorbent surface (Zhang, L. & Zhang, Y., 2014). The derived q_m = 59.55 mg AMX/g graphene-OH is comparable or higher than those in the literature (42.25 mg g^{-1} Balarak et al., 2017, 5.5 mg g^{-1} Zhang et al. 2014, 47.37 mg g^{-1} Putra et al., 2009).

Table 2: Isotherm constants of AMX adsorption in Graphene-OH.

Langmuir			Freundlich		
q_m (mg g^{-1})	K_L (L mg^{-1})	r^2	n	K_F (L g^{-1})	r^2
59.55	0.20	0.99	3.45	11.80	0.97

pH = 7, S/L ratio = 1 g L−1, and T = 25 °C

3.4 Effect of *S/L* (g L^{-1})

In AMX adsorption, adsorbent and adsorbate interaction plays a critical role; hence adsorbent dosage was varied based on the solid (adsorbent) to liquid (adsorbate) ratio (*S*/L, g L^{-1}) (Figure 4). All parameters like temperature and pH were held constant. For the quantitative removal at 1 g L^{-1} to 20 g L^{-1} of graphene-OH, an increase from 44 % to 100 % was recorded. Evidently, the removal efficiency increases as the adsorbent dosage was increased. This was due to the number of available adsorption sites increasing with adsorbent dosage, resulting in a higher adsorption capacity. Similarly, increasing the adsorbent dosage from 1 g L^{-1} to 20 g L^{-1}, the adsorption capacity decreased from 36 mg/g to 4 mg/g. The main attribute to this effect is the interactions between the particles, such as aggregation leading to a decrease in the adsorbent's total surface area and an increase in diffusion path length (Akcay et al., 2009). Additionally, the rise in adsorption capacity is pertinent to the increase in initial pollution concentration gradient (Kakavandi et al., 2013).

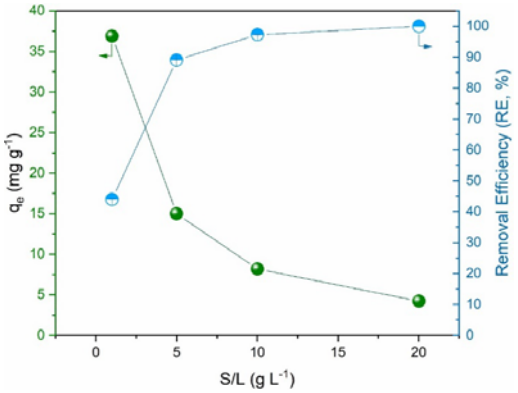

Figure 4: Effect of adsorbent dosage to the adsorption of AMX onto graphene-OH at varied solid to liquid (S/L) ratio, C_o = 40 mg L^{-1}, pH = 7, and T = 25 °C.

3.5 Recyclability of graphene-OH

The potential recyclability of graphene-OH is highly important to evaluate its overall efficiency and applicability. Its recyclability was measured in terms of its adsorptive and desorptive efficiency of graphene–OH after five adsorptive-desorptive cycles (Figure 5). The adsorptivity of graphene – OH was shown to slightly decrease over the 5-cycles (99.75 % to 95.37 %, Figure 5). During the 3rd, 4th, and 5th cycles, the adsorptive efficiency started to decline in slightly larger increments. Furthermore, the desorptive efficiency showed not to have any substantive variations. Functionalized graphene-based nanomaterials, such as graphene – OH, have high adsorption capacity, high desorptivity, and high recyclability (Fraga et al., 2018). This entails that graphene – OH has the stability for long-term use.

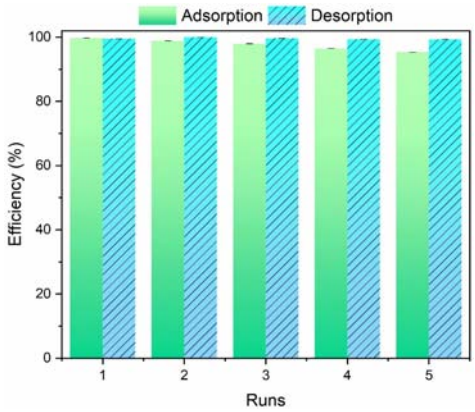

Figure 5: Adsorption-desorption of AMX onto and from graphene-OH at C_o = 80 mg L^{-1}, S/L = 10, pH = 5, and T = 25 °C.

4. Conclusions

Graphene-OH from spent batteries were successfully synthesized from spent batteries with a surface area of 182 m^2 g^{-1}. It was eventually used for AMX adsorption with q_m = 59.5 mg g^{-1} at *t* = 1440 minutes. The AMX

uptake process followed a Langmuir-type behavior and a pseudo-second-order rate of adsorption. Graphene-OH also exhibited material stability and high adsorption performance consistency implying its potential to treat AMX contaminated wastewater.

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