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Adsorption equilibrium and kinetic studies of Pb^{2+}, Cu^{2+} and Cd^{2+} on zeolite 4A/reduced graphene oxide composite

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Abstract

Reduced graphene oxide is a material widely used in technological applications. The synergism between reduced graphene oxide and zeolite allows the creation of a hybrid material with unique and improved properties, which can be used in several research areas, such as catalysis, adsorption, gas separation and energy storage. The use of this composite was investigated to evaluate the adsorption capacity for Pb^{2+}, Cd^{2+} and Cu^{2+} from aqueous solution. Batch adsorption studies at 303 K were performed. Three equilibrium isotherm models – Langmuir, Freundlich and Redlich-Peterson – were applied to represent the experimental data. Two kinetic models were assessed in order to represent the adsorption capacity according to the contact time. Redlich-Peterson model has shown to be the most adequate model to represent the metals adsorption equilibrium experimental data. A second-order kinetic model was selected to represent the time of metals adsorption. The composite shown to have a great potential for application as an adsorbent for Pb^{2+}, Cd^{2+} and Cu^{2+} removal, reaching adsorbed amounts of 141, 34 and 28 mg g^{-1}, respectively.

Keywords: Metal ions; adsorption; equilibrium isotherms; reduced graphene oxide.

1. Introduction

The discharge of chemical contaminants, such as heavy metal ions, found in industrial wastewater are potential hazard to human health. Those metal ions in human organism may cause liver, lungs, nervous system and reproductive system diseases[1, 2].

Over the past decades, various methods have been applied for toxic and radiative metal ions removal [3]. However, such methods have not shown to be very cost-effective. Adsorption then has become an attractive technology to remove metal ions from wastewater due to its relative operational low cost [4].

An efficient adsorption process relies on the choice of the adsorbent material. Graphene oxide (GO) is a 2D carbon nanomaterial that presents novel properties. It has been considered as a promising material for the removal of heavy metals due to its chemical characteristics including surface charge and polarity, surface chemistry and purity.[4, 5].

This study focuses on the performance of a zeolite 4A/ reduced graphene oxide composite to remove heavy metals (Pb^{2+}, Cu^{2+} and Cd^{2+}) in aqueous solution by adsorption technique. To do so, adsorbent dosage tests, adsorption equilibrium isotherms and adsorption kinetic were assessed.

2. Methods

2.1. Composite preparation

Graphene oxide (GO) was prepared using the tour method that can be found in [6]. Then, zeolite 4A and produced GO were mixed in a proportion of 75% and 15%, respectively, resulting in a dark-coloured paste. This paste was shaped into a cylindrical pellet with dimensions of 5 mm of height and 3 mm of diameter. Z4A-rGO was then prepared using a thermal reduction method [7]; the material was heated at 573 K for 2 hours in a furnace.

2.2. Adsorption equilibrium study

To obtain the equilibrium isotherms measurements, the heavy metal solutions were separately prepared dissolving certain amount of mass in 2 L of distilled water. The specific concentrations for adsorption equilibrium measurements of the metal ions were then prepared by adding deionized water in the previous concentrated solution. Then, 0.1 g of the composite Z4A/rGO was added in separate flasks containing 25 mL of different concentrations of Pb^{2+}, Cu^{2+} and Cd^{2+} in CH3COONa/CH3COOH buffer (pH = 5.0). The concentrations of the studied metals were 0.02, 0.05, 0.08, 0.1, 0.15, 0.2, 0.3, 0.5, 0.8, 1.0, 1.5, 2.0 mmol L^{-1}. All adsorption equilibrium isotherm measurements were performed at 303 K. After the tests, the amount of metal in solution was determined with the aid of the flame atomic absorption spectrophotometer. The adsorbed amount of metals (q_e, mg g^{-1}) was then computed by Equation (1):

$$q_e = \frac{(C_0 - C_e)}{m_{ads}} \times V \qquad (1)$$

where C_0 and C_e (mg L^{-1}) are the initial and equilibrium concentration, respectively. V(L) is the liquid volume and m_{ads} denotes the adsorbent mass (g).

The relation between adsorbate and adsorbent can be represented by adsorption equilibrium models. In order to represent the experimental adsorption isotherm data, Langmuir (Equation (2)), Freundlich (Equation (3)) and Redlich-Peterson (R-P) (Equation (4)) models were fitted to the experimental one.

$$q_e = \frac{q_s k_L C_e}{(1 + k_L C_e)} \qquad (2)$$

$$q_e = k_F (C_e)^{1/n} \qquad (3)$$

$$q_e = \frac{k_{RP} C_e}{[1 + \alpha (C_e)^{\beta}]} \qquad (4)$$

where q_s denotes the maximum adsorption capacity, k_L is the Langmuir constant and C_e represents the concentration at the equilibrium condition, k_F is the Freundlich constant, $1/n$ is the heterogeneity parameter, k_{RP} and α are the constants of the Redlich-Peterson isotherm, respectively. β is an exponent that is related to the heterogeneous nature of the adsorbent.

2.3. Contact time study

For the evaluation of contact time influence of ions adsorption in batch studies, the adsorbent material was added to the solution in the following time intervals; 1, 3, 7, 10, 15, 20 and 45 min. The final concentration of solutions was analysed, and the results were presented in terms of q_t (mmol g^{-1}). In order to verify the well-representative adsorption kinetic model, the linear driving force (LDF) (Equation (5)) and pseudo-second order (Equation (6)) models were applied [8].

$$\frac{d\bar{q}_t}{dt} = k_{LDF}(q_e - \bar{q}_t) \qquad (5)$$

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \qquad (6)$$

Where q_e and $\bar{q}_t$ (mg g-1) are the adsorbed amount at equilibrium and the volume-average adsorbed concentration at time t (min), respectively. k_{LDF} (min-1) and k_2 (g_{ads} min^{-1} mg^{-1}) are the adsorption rate constant.

3. Results

3.1. Adsorption isotherm

The adsorption isotherms of metal ions on Z4A/rGO at 303 K are presented in Fig. 1. The experimental data are represented by the black symbols, the lines represent the equilibrium models calculated according to the Langmuir, Freundlich and Redlich-Peterson equations.

Pb^{2+} presented the highest ion adsorbed amount, followed by Cd^{2+} and Cu^{2+}. Also, it can be

seeredlichn that Pb^{2+} presented a high discrepancy of adsorption capacity on Z4A/rGO when compared to the others two materials studied.
The R-P model presented the most well-fitted results for all the three adsorbed ions.

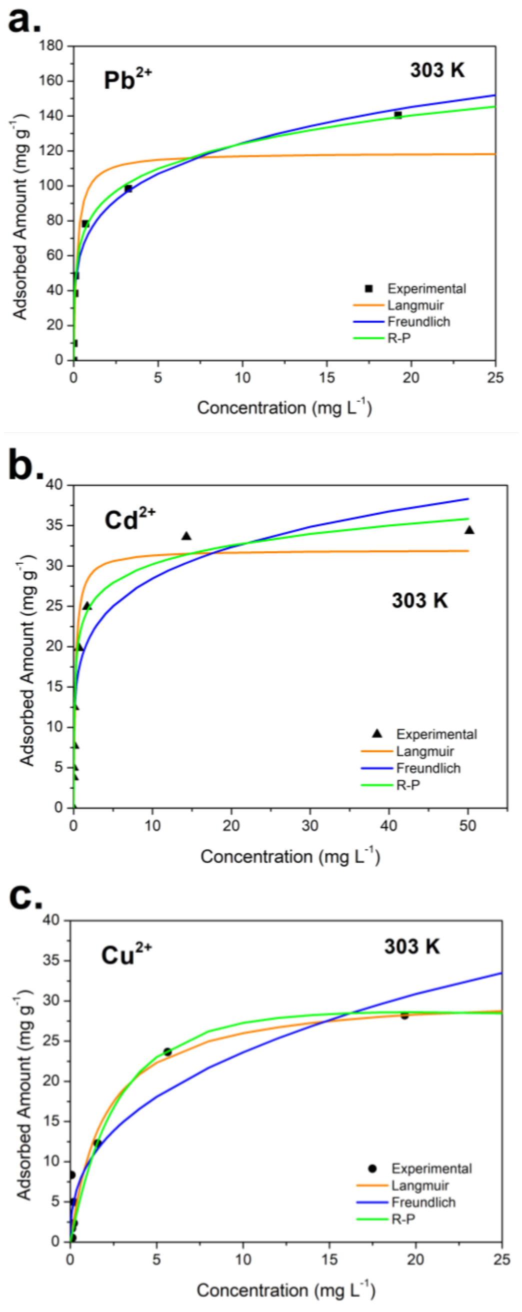
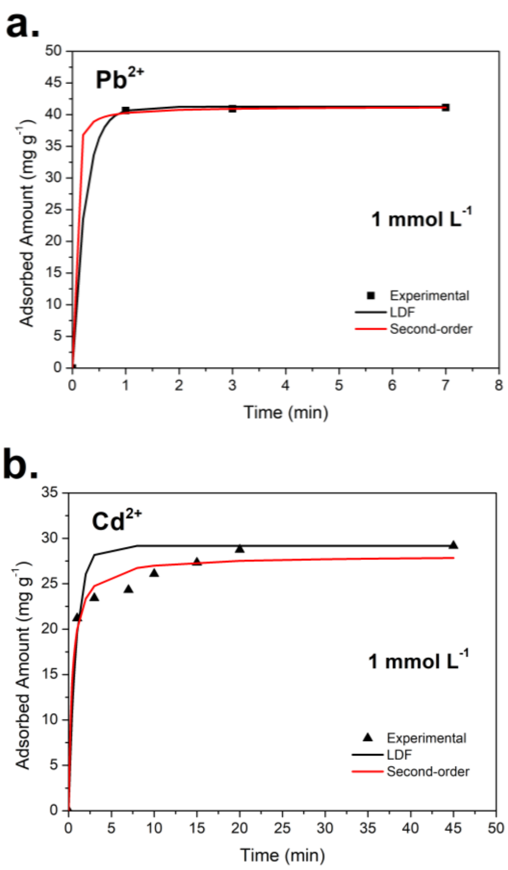


Fig. 1. Adsorption equilibrium isotherm data of (a) Pb^{2+}, (b) Cd^{2+} and (c) Cu^{2+} ions; Equilibrium (scatter) and fitted models; Langmuir (orange line), Freundlich (blue line) and R-P (green line).

3.3. Adsorption kinetic

Fig. 2 shows the adsorption kinetic of ions Pb^{2+}, Cd^{2+} and Cu^{2+} in a solution with concentration of 1 mmol L^{-1}. Fig. 2a shows that Pb^{2+} is rapidly adsorbed. Cd^{2+} and Cu^{2+} reach the adsorbed amount at equilibrium approximately at the same time. In those cases, the second-order model better represented the experimental data, although the LDF also represented them quite well.



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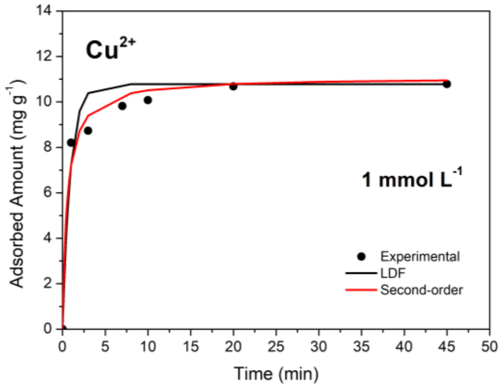

Fig. 2. Adsorption kinetic of (a) Pb^{2+}, (b) Cd^{2+} and (c) Cu^{2+} for a solution concentration of 1 mmol L^{-1}; Experimental data (scatter) and fitted models; LDF (black line) and Second-order (red line).

4. Conclusion

The Pb^{2+} ion has shown to be preferably adsorbed on Z4A/rGO over the others two metals ions Cd^{2+} and Cu^{2+} evaluated, the latter presenting the lower adsorbed amount. Since R-P has more parameters than Langmuir and Freundlich models, it presented as the most representative isotherm model for all three ions studied. The second-order kinetic model presented better results, although LDF model also present satisfactory ones. Due to the fast kinetic of ions adsorption, both models may be feasible to represent the kinetic data. For further studies, performing experiments at higher and lower temperatures, followed by variations of pH, can provide more details about metal ions adsorption on Z4A/rGO.

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