

## Effect of aniline on cadmium adsorption by sulfanilic acid-grafted magnetic graphene oxide sheets



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### ABSTRACT

Cd(II) has posed severe health risks worldwide. To remove this contaminant from aqueous solution, the sulfanilic acid-grafted magnetic graphene oxide sheets (MGOs/SA) were prepared and characterized. The mutual effects of Cd(II) and aniline adsorption on MGOs/SA were studied. The effects of operating parameters such as pH, ionic strength, contact time and temperature on the Cd(II) enrichment, as well as the adsorption kinetics and isotherm were also investigated. The results demonstrated that MGOs/SA could effectively remove Cd(II) and aniline from the aqueous solution and the two adsorption processes were strongly dependent on solution pH. The Cd(II) adsorption was reduced by the presence of aniline at pH < 5.4 but was improved at pH > 5.4. The presence of Cd(II) diminished the adsorption capacity for aniline at pH < 7.8 but enhanced the aniline adsorption at pH > 7.8. The decontamination of Cd(II) by MGOs/SA was influenced by ionic strength. Besides, the adsorption process could be well described by pseudo-second-order kinetic model. The intraparticle diffusion study revealed that the intraparticle diffusion was not the only rate-limiting step for the adsorption process. Moreover, the experimental data of isotherm followed the Freundlich isotherm model.

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### 1. Introduction

Water pollution due to the indiscriminate disposal of different contaminants is a global environmental problem. For example, many industrial processes such as chemical manufacturing, battery manufacturing, metalliferous mining and leather tanning generate large quantities of wastewater containing various concentrations of Cd(II) [1]. Exceeding the micronutrient level of human body, Cd(II) ions affect the enzyme activity because of replacing Zn(II) ions in metallo-enzymes, and cause a number of acute and chronic disorders, such as renal damage, emphysema, hypertension, testicular atrophy and skeletal malformation in fetus [2,3]. For environmental protection, it is necessary to remove Cd(II) contaminated wastewater prior to its discharge to the environment. Compared with other disposal processes, adsorption is proved to be an effective method for the removal of toxic metal ions from wastewater as it is simple and economically viable.

A lot of organic and inorganic materials have been applied to remove various contaminants such as heavy metal ions and

organic substances. Attention has been focused on graphene oxide (GO) in recent years because it has a lot of oxygen-containing groups, such as hydroxyl, epoxide, carbonyl and carboxyl groups, which are essential for the high adsorption of contaminants. However, after the adsorption is carried out, the GO is difficult to be separated from the solution using traditional separation methods due to its hydrophilic nature [4]. The problem can be solved using magnetic technology. Actually, some studies had reported the synthesis of magnetic graphene oxide composites [5–8]. These composites were synthesized by loading magnetic nanoparticles on the GO sheets surface, which could be easily collected from water with the help of an external magnetic field. However, the loaded Fe<sub>3</sub>O<sub>4</sub> particles on the GO surface may result in the loss of adsorption capacity because some groups of the GO are occupied by the magnetic nanoparticles. Several chemical reagents, such as EDTA [9] and ethylenediamine [10], demonstrated some positive benefits for enhancing the adsorption capacity of GO when they were used to modify the GO. Sulfanilic acid contains a sulfo group and an amino group, which can form stable chelates with metal ions. So, graft of sulfanilic acid on the magnetic graphene oxide surface may increase the adsorption ability of the composite.

It is well known that organic substances and metal ions are co-existing contaminants in wastewater, and organic substances can

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react with metal ions, thereby influencing the removal of metal ions [11]. Aniline is an important chemical compound which is well known for its wide applications in the manufacture of dyestuffs, rubbers, pesticides, plastics and paints [12]. It is frequently found in industrial effluents and surface water due to its disposal, which cause a series of environmental problems [13]. Aniline and Cd(II) are often used together in many industrial processes such as chemical manufacturing, leather tanning, dyeing, and rubber manufacturing. Therefore, there is a high possibility that aniline and Cd(II) ions exist in mixed contaminant systems. The amino group of aniline can form stable complexes with metal ions. Besides, the aniline can interact with GO-based composites through strong  $\pi$ - $\pi$  interaction in aquatic systems [11]. Both of these may affect the adsorption behaviors of Cd(II) ions on GO-based composites.

The objectives of this study were to: (1) prepare and characterize sulfanilic acid-grafted magnetic graphene oxide sheets (denoted as MGOs/SA) and apply them as adsorbent for effective decontamination of Cd(II) from aqueous solution; (2) study the mutual effects of Cd(II) and aniline adsorption on MGOs/SA; (3) investigate the effects of the process parameters on Cd(II) adsorption; (4) study the adsorption mechanism with kinetics and isotherm models.

## 2. Materials and methods

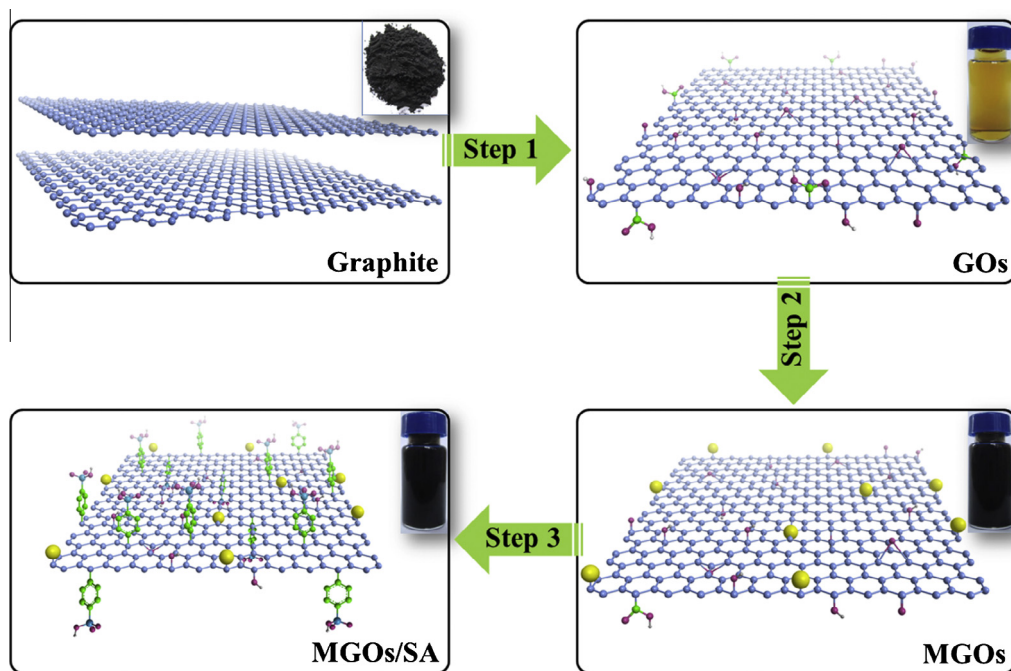
### 2.1. Synthesis of MGOs/SA

Graphene oxide sheets (GOs) were prepared from natural graphite by modified Hummers method [14]. Briefly, 6 g graphite powder, 5 g  $K_2S_2O_8$  and 5 g  $P_2O_5$  were added into 24 mL of  $H_2SO_4$  (98%) and stirred at 80 °C for 4.5 h. Then, 1 L of Milli-Q water was added and left overnight. The mixture was washed thoroughly and dried under vacuum at 60 °C. The residue was collected and put into 240 mL cold (0 °C)  $H_2SO_4$  (98%), and then 5 g  $NaNO_3$  and 30 g  $KMnO_4$  were added gradually and the mixture was continually stirred below 20 °C for 4 h. Then, the reaction was carried out at

35 °C for 2 h. Next, 0.5 L of water was added slowly and the mixture was stirred for another 6 h at 90 °C. After that, 1 L water and 40 mL  $H_2O_2$  (30 wt.%) were added to the mixture, and stirred for 2 h at room temperature. The paste was washed repeatedly with HCl (10%) and Milli-Q water and then sonicated for 2 h and a GOs solution was obtained. The magnetic graphene oxide sheets (MGOs) were prepared by coprecipitating  $Fe^{2+}$  and  $Fe^{3+}$  ions with ammonia solution in the GOs solution [8]. Typically, 200 mL mixed solution of  $FeCl_3$  (0.1 mol/L) and  $FeCl_2$  (0.05 mol/L) was added to 400 mL GOs solution (5 mg/mL) with stirring. Chemical precipitation was achieved at 85 °C under vigorous stirring by addition of ammonia solution and the pH was kept to 10 for 45 min. Then the sample was rinsed with Milli-Q water until the solution was neutral and a MGOs suspension was obtained. The sulfanilic acid-grafted magnetic graphene oxide sheets were synthesized from MGOs suspension in aryl diazonium salt solution [15]. The diazonium salt solution was prepared as the following: 0.5 g of sulfanilic acid and 0.4 g of  $NaNO_2$  were added to 20 mL NaOH solution (1%), and then 20 mL ice water and 1 mL of concentrated HCl were added into the mixed solution and stirred for 20 min at 0 °C. Next, the diazonium salt solution was added to 400 mL MGOs suspension in an ice bath and stirred for 4 h. The obtained MGOs/SA were rinsed with Milli-Q water for several times and stored at room temperature. Fig. 1 shows the preparation sketch of MGOs/SA.

### 2.2. Characterization

The X-ray diffraction (XRD) pattern of the MGO/SA composites was obtained on a Rigaku D/max-2500 diffractometer equipped with a rotating anode and Cu  $K\alpha$  source. The magnetic property was characterized by magnetization curve using a vibrating sample magnetometer (Lake Shore 7410, USA). The morphology of the MGOs/SA was characterized by field-emission scanning electron microscopy (FESEM, JSM 6700F, Japan). The zeta potential of MGOs/SA was obtained by Zeta Sizer and Nano series equipped with a microprocessor unit (ZEN3690, Malvern, UK).



**Fig. 1.** Schematic representation of the synthesis processes of MGOs/SA from graphite: (Step1) oxidation of natural graphite to graphite oxide, followed by ultrasonication; (Step2) preparation of MGOs by loading magnetic nanoparticles on the GOs surfaces through chemical coprecipitation method; (Step3) formation of MGOs/SA by grafting sulfanilic acid on the MGOs surfaces.

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