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Efficient removal of phenol and aniline from aqueous solutions using graphene oxide/polypyrrole composites

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ABSTRACT

A novel approach was developed to fabricate graphene oxide/polypyrrole (GO/PPy) composites via dielectric barrier discharge (DBD) plasma technique in nitrogen and room temperature conditions, and characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier transformed infrared spectroscopy (FT-IR), thermal gravimetric analysis (TGA), and X-ray photoelectron spectroscopy (XPS) in details. The sorption of phenol and aniline on the GO/PPy composites from aqueous solutions was investigated as a function of contact time, solid content, pH and initial concentrations of sorbates. The sorption capacities of phenol and aniline on the GO/PPy composites were much higher than those of phenol and aniline on many of today's materials. The sorption of phenol and aniline on GO/PPy composites obeyed the Langmuir model, and was mainly attributed to ion exchange, π–π electron donor–acceptor (EDA) interaction, hydrophobic interaction and Lewis acid–base interaction. The thermodynamic parameters calculated from the temperature-dependent sorption isotherms suggested that phenol and aniline sorption on GO/PPy composites was an endothermic and spontaneous process. Moreover, GO/PPy composites could be regenerated through the phenol and aniline desorption by ethanol, and cycling reused without obvious decrease of sorption capacity. All these results indicated that the GO/PPy composites were suitable materials for the preconcentration of phenol and aniline from aqueous solutions in environmental pollution management.

1. Introduction

Phenol and aniline, as ionizable organic contaminants, are extensively found in the effluents from dyestuffs, petrochemicals, pesticides and pharmaceuticals [1,2]. The relatively high solubility in water makes phenol and aniline possible to transport favorably in the environment. They have been classified in the list of prior pollutants by most national Environmental Protection Agencies (EPA) owing to their potential harm to the environment and mutagenic and also carcinogenic effects to human health at relative low concentrations. The USEPA, the Central Pollution Control Board (CPCB) and the European Union (EU) have set an effluent standard of 1.0 mg/L of phenol, aniline and their derivatives for the safe and sanitary discharge of industrial and agricultural effluents. Phenol and aniline influence the objectionable taste and odor of drinking water at the concentration of 0.005 mg/L. Moreover, fatal doses can be absorbed through the skin and chronic phenol and aniline exposure would damage organs including spleen, pancreas and kidneys. Acute poisoning would cause severe gastrointestinal disturbances, lung edema, circulatory system failure, kidney malfunction and convulsions. The readily reaction of aniline makes the hemoglobin easily to be converted into methaemoglobin to prevent the oxygen uptake in the blood. For the sake of public health and environmental safety, many studies have focused on the efficient elimination of phenol and aniline from aqueous solutions such as photocatalytic oxidation [3], electrolysis [4], sorption [5], biodegradation [6] and membrane [7]. Among these methods, sorption technique has been widely used in the preconcentration and solidification of aromatic pollutants due to its low cost, easy operation and wide adaptability. Efficient cleanups of phenol and aniline by artificial sorbents such as carbon nanotubes [8–11], activated carbon [12,13], porous media [14,15], nanoparticles [16] and polymers [17–19] have been investigated. However, the limited sorption capacities and efficiencies hinder their practical applications in real work. Therefore, the development of available sorbents with excellent sorption capacities for the removal of organic pollutants from aqueous solutions is of great importance.

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Graphene, a single-atom-thick nanosheet with two dimensional sp^2-hybridized carbon structures, has attracted a tremendous research interest in recent years owing to its excellent mechanical strength [20], high electrical conductivity [21] and good thermal stability [22]. Graphene and its derivatives have been developed in multidisciplinary fields, such as clean energy [23], photonic devices [24] and sensors [25]. The large theoretical specific surface area of graphene (~2620 m^2/g) indicates its potential for the sorption of organic pollutants in environmental pollution cleanup. Nevertheless, the solubility of GO is quite limited, and can form aggregates irreversibly in most solvents due to Van der Waals forces between the layers of GO [26,27]. The absence of effective ways to disperse graphene in aqueous solutions makes it difficult to be applied widely. Therefore, huge efforts have been made to synthesize GO-based materials and to explore the potential applications by attaching different kinds of functional groups to the carbon backbone [28–34].

Polypyrrole (PPy), a traditional conducting polymer with high atmospheric stability, facile synthesis, low cost and uniquely electronic and redox properties, has been studied extensively [35–37]. In order to keep the charge neutrality of positively charged nitrogen atoms in PPy, some of the counter ions would be incorporated into the growing polymer chains [38]. The existence of positively charged nitrogen atoms in PPy presents strong affinity toward different kinds of organic contaminants. All the promising properties together with the ease of functionalization and processability make graphene oxide/polypyrrole (GO/PPy) composites for the applications in filtration separation and sorption [39–42].

To the best of our knowledge, the conventional approaches applied for the fabrication of graphene–polymer composites including in-situ polymerization [43,44], melt blending [45,46], and solution mixing [47,48], are usually complicated with multiple steps. Moreover, chemical approaches would inevitably introduce different kinds of additional pollutants. The crucial point is that the abovementioned synthetic methods are relatively fierce, leading to the structural damages and changes of material properties. With this in mind, the development of effective and facile approaches for the construction of GO/PPy composites is greatly desirable and remains a great challenge. As an effective process operated in the atmospheric-pressure environment, dielectric barrier discharge (DBD) technique for the surface activation and modification of materials has attracted great concerns in recent decades. Compared with the conventional polymer processing, DBD technique has superior properties for its reduced energy requirement, highly distributed active species, short operation time, enhanced catalyst activation and low environmental pollution [49]. Numerous chemically active species can activate the material surfaces without altering the main surface properties of the bulk. The activated sites are easy to form chemical bonds with polymers and to graft the polymers on the material surfaces [50]. Furthermore, different gases including reductive, oxidative and inactive ones can be applied as the plasma sources to introduce varieties of elements or functional groups which are desired to improve the properties of composites. Plasma discharging process is also easier to be controlled by changing relevant parameters. The high controllability makes the product quality of plasma technique much better than that of conventional chemical methods, and the mass production in the near future will also guarantee its wide applicability. All these advantages make DBD plasma technique superior to other synthetic methods.

In this study, we focused on a novel approach to modify GO by DBD plasma induced polymerization of pyrrole monomer in nitrogen and room temperature conditions. The application of as-synthesized GO/PPy composites as sorbents for the removal of phenol and aniline from aqueous solutions was investigated by batch experiments. The effect of environmental factors such as contact time, solid content, pH, temperature and initial concentrations of sorbates was studied. Furthermore, the reusability was also conducted to evaluate the potential in possible real applications.

2. Experimental

2.1. Synthesis of GO/PPy composites

GO nanosheets were prepared using modified Hummers method by oxidation of natural flake graphite [51]. Typically, 4.0 g of graphite powder, 3.0 g of $NaNO_3$ and 300 mL of concentrated H_2SO_4 were mixed together under vigorous stirring and an ice-water bath condition. 18.0 g of $KMnO_4$ was added into the mixture slowly for 2 h. Then the suspension was stirred continually for another 5 d at room temperature. Afterwards, 560 mL of H_2SO_4 (5.0 wt.%) was added into the suspension for 2 h with vigorous stirring at 98 ± 2 °C. Then the temperature was decreased to 60 °C, and 12 mL of H_2O_2 (30 wt.%) was added into the suspension to eliminate the excess $KMnO_4$, and the mixture was stirred for 2 h further. The color of the mixture was converted from dark brown to yellow. After centrifugation at 23,000 rpm for 60 min, the solid phase was dispersed by using vigorous stirring and ultrasonic water bath. The centrifugation and ultrasonication were recycled for several times, then the sample was rinsed with 10% HCl and Milli-Q water sequentially until the solution was almost neutral. Finally a homogeneously aqueous dispersion of GO ($2.0\ g\cdot L^{-1}$) was obtained for further use.

0.3 g of freshly distilled pyrrole monomer was added into 50 mL of the above GO suspension under ultrasonication. The reactor was a quartz tube with an inside diameter of 4 mm and a length of 170 mm. A copper wire with a diameter of 0.75 mm was installed into the quartz tube as an electrode. The DBD plasma treatment was carried out for 30 min with a voltage of 100–110 V and a power of 200 W. The obtained sample was rinsed with Milli-Q water and ethanol thoroughly to remove residual pyrrole monomer and homopolymer, and then the suspension was dried by the vacuum freeze-drying technique. The as-prepared material was named as GO/PPy composites. PPy polymers were synthesized without adding GO solutions by DBD plasma induced polymerization of pyrrole monomer with the same parameters as mentioned above.

2.2. Characterization

The GO/PPy composites were characterized by SEM, XRD, FT-IR, TGA and XPS techniques in detail. The SEM images were obtained by using a JEOL JSM-6330F instrument operated at the beam energy of 15.0 kV. FT-IR spectra were recorded on a Nicolet Magana-IR 750 spectrometer by using KBr pellets over a range from 400–4000 cm^{-1}. Powder XRD patterns were performed by using a (Philips X'Pert Pro Super X-ray) diffractometer with Cu Kα source ($\lambda = 1.54178$ Å).TGA measurements were taken by using a Shimadzu TGA Q5000 V3.15 Build 263 thermogravimetric analyzer from 40 °C to 700 °C at a heating rate of 10 $°C\cdot min^{-1}$ with an air flowing rate of 75.0 $mL\cdot min^{-1}$. XPS spectra were performed in a VG Scientific ESCALAB Mark II spectrometer equipped with two ultrahigh vacuum chambers.

2.3. Batch sorption experiments

The sorption experiments of phenol and aniline on GO/PPy composites were investigated by using batch technique in 8 mL glass vials equipped with polytetrafluoroethylene-lined screw caps under ambient conditions. The stock suspensions of GO/PPy composites, sorbates and NaCl solutions were added into glass vials to achieve the desired concentrations of different components. In this process, the solution pH was adjusted by adding negligible volumes of 0.01 or 0.1 M HCl or NaOH solution. Afterwards the glass vials were oscillated for 48 h to ensure the sorption equilibrium. The solid and liquid phases were separated by centrifugation at 8000 rpm for 25 min. The concentrations of phenol and aniline were analyzed by ultraviolet–visible (UV–vis) spectroscopy at the wavelength of 270 and 230 nm, respectively. The distribution coefficient (K_d), sorption percentage (%) and the amount of