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Novel N-doped CNTs stabilized Cu_2O nanoparticles as adsorbent for enhancing removal of Malachite Green and tetrabromobisphenol A

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HIGHLIGHTS

- Novel N-doped CNTs stabilized Cu_2O nanoparticles for organic pollutants removal.
- PVP@CNTs-Cu_2O exhibited enhanced adsorption performances for MG and TBBPA than CNTs.
- Wide pH range, excellent salt resistance and rapid rate of MG adsorption were obtained.
- FTIR and XPS were used to analyze the adsorption mechanisms of MG and TBBPA.

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ABSTRACT

A newly designed N-doped CNTs stabilized Cu_2O nanoparticles (PVP@CNTs-Cu_2O) were fabricated and used to remove organic pollutants such as Malachite Green (MG) dye and tetrabromobisphenol A (TBBPA). The introduction of PVP here not only could stabilize Cu_2O nanoparticles, but also act as active sites for adsorption of organic pollutants. The hybrid mesoporous adsorbent exhibited excellent adsorption performances for MG and TBBPA, which were mainly because of the synergistic effects of inorganic species and polymer. The maximum adsorption capacities of MG and TBBPA by PVP@CNTs-Cu_2O were 1495.46 and 116.72 mg/g, respectively, significantly higher than pristine CNTs (417.58 and 68.03 mg/g, respectively). The adsorption of MG was independent of ionic strength. In contrast, the increase in ionic strength significantly inhibited the adsorption of TBBPA. Freundlich isotherm model fitted well with the experimental data of both MG and TBBPA adsorption, indicating the heterogeneous surface of PVP@CNTs-Cu_2O. PVP@CNTs-Cu_2O demonstrated rapid adsorption rates for both MG and TBBPA, and their adsorption kinetics were analyzed by the pseudo-first-order, pseudo-second-order and Elovich kinetic models. The possible mechanisms of MG and TBBPA adsorption was further explored by means of FTIR and XPS. High adsorption capacity, rapid kinetics, good reusability as well as simple preparation were important advantages for the practical application in MG and TBBPA removal by PVP@CNTs-Cu_2O.

1. Introduction

The development of modern industry and agriculture along with the rapid urbanization caused an extreme large amount of wastewater discharging in recent years, thus leading to serious water pollution problems and attracting more and more concerns all over the world. Organic pollutants in wastewater have direct and potential effects on aquatic biodiversity and water quality. Their toxic effects can even do harm to population health and cause a series of diseases. Various synthetic dyes are widely used in textile, printing, paper, plastics, leather, food, cosmetics, rubber and other industries. Most synthetic dyes are toxic and stable, which are difficult to degrade due to their complex chemical structure. Malachite Green (MG) is a basic dye of triphenylmethane type and discharge of MG in water can give undesirable color, reduce sunlight penetration and cause damage to aquatic life even at very low concentrations due to its carcinogenic, genotoxic, mutagenic and teratogenic properties [1]. Tetrabromobisphenol A (TBBPA), one of the most widely used brominated flame retardants (BFR) around the world, has been recognized as an emerging contaminant and a potentially toxic endocrine-disruptor. Manufacture, use and disposal of various materials containing TBBPA may lead to TBBPA release into the environment. The worldwide usage and limited water solubility may result in TBBPA persistence in the environment and the contamination of organisms and environment

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mediums. TBBPA and its derivatives have been detected in different environment matrices, including soil, water, sediments, dust and organisms [2,3]. TBBPA is highly lipophilic (log K_{ow} = 4.5) with the potential to bioaccumulate, which can cause various negative effects on mammalian and human physiology due to its extensive use, toxicity and persistence [4,5]. Thus, it is necessary and important to develop effective techniques for removal of organic dyes and TBBPA from contaminated environment.

A number of technologies have been employed to remove organic pollutants from aqueous environment including chemical precipitation, membrane separation, chemical oxidation, photocatalytic degradation, adsorption, biological treatment, etc. Notably, adsorption has been proven to be one of the most promising approaches for removal of organic pollutants due to its high efficiency, low cost, simple operation, regeneration and sludge-free process. Various adsorbents such as active carbon [6], clay minerals [7], metal oxides [8], natural and synthetic materials [9,10] have been reported to deal with organic pollutants. Novel adsorbents with high adsorption capacity, fast kinetics, simply and easily controlled preparation, no toxic chemicals and less energy-consuming are in great demand.

In recent years, carbon nanotubes (CNTs) have received great attention for the potential applications in environmental remediation due to its large specific surface area, small size, hollow and layered structures. It has been reported that CNTs could be used as a promising adsorbent for the removal of gas [11], dyes [12], heavy metal ions [13] and organic compounds [14]. However, the adsorption performances of CNTs for the target pollutants are not satisfactory, possibly due to the serious aggregation of nano-sized CNTs, poor interaction between CNTs and adsorbate and limited availability of active sites on the surface. Thus, much efforts have been made to design and synthesize novel types of composite based on CNTs with organic and inorganic materials. The resulting composite materials would integrate the properties and advantages of each component and make the composites exhibit synergic or complementary performances. The unique structure and properties of CNTs enable them to be used as supporter for coating or anchoring different types of low-cost materials especially using metallic or oxide nanoparticles. Gong et al. prepared magnetic multiwall carbon nanotube (MMWCNT) adsorbent for effective cationic dye removal and the prepared MMWCNT adsorbent displayed the main advantage of separation convenience [15]. Wang et al. used Mn oxide-coated carbon nanotubes (MnO_2/CNTs) as an adsorbent for Pb(II) removal. Their studies showed that MnO_2/CNTs was superior to CNTs with the significant improvement of Pb(II) adsorption [16]. Farghali et al. reported that the decoration of MWCNTs with $CoFe_2O_4$ nanoparticles showed high adsorption capacity for methylene blue from water [17]. However, functionalization using organic ligands not only can introduce different kinds of functional groups which can react with target pollutants through physical and chemical forces but also endow novel materials with high activity and stability. Ji et al. found that 3-aminopropyltriethoxysilane modified MWCNTs/Fe_3O_4 (MWCNTs/Fe_3O_4-NH_2) exhibited better adsorption properties for TBBPA and Pb(II) than MWCNTs/Fe_3O_4 [18]. Nabid et al. used multiwalled carbon nanotubes/poly(2-amino thiophenol) as a solid-phase extraction sorbent for separation and preconcentration of Cd(II) and Pb(II). Their studies showed that the novel nanocomposite exhibited a high affinity for heavy metals due to the presence of S and N groups [19]. Chatterjee et al. prepared chitosan hydrogel beads with multiwalled carbon nanotubes impregnation (CS/CNT) for the removal of congo red dye. Their study showed that 0.01% CNT impregnation was the most useful for enhancing the adsorption capacity [20]. Therefore, surface modification of CNTs using organic ligands and inorganic species would combine the properties and advantages of both them and greatly improve the functionalities and properties.

To obtain this goal, the main objective of this work was to develop a novel hybrid adsorbent based on the polymer and inorganic species by employing polyvinylpyrrolidone (PVP) and CNTs to stabilize metallic nanoparticles. Metallic nanoparticles such as cuprous oxide (Cu_2O) have attracted intensive attention for the applications in various fields including catalysis, semiconductor, environmental remediation, etc. due to its low cost, high surface area and high surface reactivity as well as excellent catalytic activity. Ma et al. prepared several Cu_2O-MgAl-LDH composites and found that Cu_2O-Mg_7A_{l5}-LDH composite exhibited superior adsorption capacities and photocatalytic property for Orange II dye [21]. Liu et al. reported that mesoporous Cu_2O submicrospheres have high affinity to methylene orange (MO) with adsorption capacity of 48.38 mg/g and can adsorb MO from mixture dyes selectively [22]. PVP, a polar polymer, is commonly applied as a stabilizer in the synthesis of composite materials to control aggregation, size and shape of nanoparticles [23]. N in C—N and O in C=O in N-vinylpyrrolidone monomer of PVP chain can act as active sites to react with cations, molecules, particles or polymers through hydrogen bonding, coordination reaction and other forces [24–26]. Immobilization of Cu_2O nanoparticles into the polymer matrix would provide novel composites with enhanced properties and functionalities. Herein, a new composite adsorbent was successfully synthesized by chemical deposition of Cu_2O nanoparticles on PVP-stabilized CNTs using ascorbic acid as reducing agent. CNTs with large specific surface area, hollow and layered structures can act as a supporter for anchoring nanoparticles and effectively prevent the aggregation of nanoparticles. Meanwhile, N- and O-containing functional groups in PVP can coordinate with Cu_2O to form coordination complexes, which can effectively reduce aggregation of nanoparticles and CNTs, and consequently give high reactivity of composite adsorbent. To date, few studies have been reported on the preparation of novel composite materials with excellent properties for the removal of TBBPA from wastewater. Thus, the resulting PVP@CNTs-Cu_2O was applied as an enhanced adsorbent for removal of organic MG dye and TBBPA from wastewater, which would exhibit the enhanced adsorption performances due to the synergistic effects of polymer and inorganic species. PVP@CNTs-Cu_2O was characterized using BET surface area, elemental analysis, scanning electron microscope (SEM), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). Adsorption characteristics of PVP@CNTs-Cu_2O were conducted in terms of the removal of MG dye and TBBPA in aqueous solution by using batch adsorption technique under the experimental conditions in which the effects of initial pH, adsorbent dosage, initial pollutant concentration, contact time, temperature and ionic strength were investigated. The equilibrium relationships between PVP@CNTs-Cu_2O and organic pollutants were analyzed using adsorption isotherms including Langmuir, Freundlich, Tempkin and D-R models. Adsorption kinetics of PVP@CNTs-Cu_2O for organic pollutants were described by the pseudo-first-order model, pseudo-second-order model and Elovich equation. Adsorption mechanisms of MG and TBBPA by PVP@CNTs-Cu_2O were also explored by means of FTIR and XPS.

2. Materials and methods

2.1. Materials and chemicals

Multiwalled carbon nanotubes (CNTs) (OD < 8 nm and length of 10–30 μm) were obtained from Chengdu Organic Chemical Co., Ltd., Chinese Academy of Sciences (China). TBBPA was purchased