Synthetic Metals 245 (2018) 32–41

Contents lists available at ScienceDirect

Synthetic Metals

journal homepage: www.elsevier.com/locate/synmet

Synergetic effect in a self-doping polyaniline/TiO_2 composite for selective adsorption of heavy metal ions

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ARTICLE INFO

Keywords:
PANi(ES^+)/TiO_2(O-) heterojunction structure
Heavy metal ions
Selective adsorption
Synergistic adsorption
Mechanism

ABSTRACT

Design and synthesis of adsorbents with high adsorption selectivity are important for the treatment of the wastewater which contains multiple metal ions. Herein, a PANi(ES^+)/$TiO_2(O^-)$ composite is the subject of an investigation into the synergetic effect of a polymer/metal oxide composite and the mechanism of selective adsorption towards heavy metal ions. The self-doping nature of $TiO_2(O^-)$ to PANi was first discovered through characterizations including FT-IR, zeta potential analysis, TGA, XRD, SEM-EDS, TEM-EDS, N_2 adsorption-desorption isotherm and isotherm investigation for Pb (II), Zn (II) and Cu (II) in single/multiple metal ion system, which was confirmed to contribute to the novel selectivity of the PANi/TiO_2 composite of $Zn^{2+} > Pb^{2+} >> Cu^{2+}$ in a multiple metal ion system. The synergistic mechanism between the conjugated polymer and metal oxide for selective adsorption was discussed and proposed subsequently, which was suggested that the metastability of the doped state of PANi (ES^+) would result in the dedoping of the $TiO_2(O^-)$ in a non-acid solution (pH = 5), further leading to the doping of cationic heavy metal ions on $TiO_2(O^-)$. The mechanism we proposed can satisfactorily explain the selective adsorption properties of the polymer/metal oxide composite system and provide general guidance for designing an adsorbent with expected selective adsorption properties for water treatment.

1. Introduction

Currently, large amounts of wastewater containing various heavy metal ions such as Pb(II), Zn(II), Cu(II), *etc.* are being released into natural water system, resulting in serious water contamination and threats to human health [1,2]. Therefore, the heavy metal ions in wastewater should be removed and recycled before the water is discharged into the environment. So far, the removal of heavy metal ions from wastewater can be achieved by employing various methods including chemical precipitation [3], ionic exchange [4], coagulation [5], membrane separation [6], adsorption [7], *etc*. Among them, adsorption is widely investigated and applied due to its simplicity, high selectivity, low cost and excellent efficiency [8–10]. To achieve high adsorption efficiency in wastewater that contains multiple metal ions, considerable attention needs to be paid to the design and synthesis of adsorbents with high adsorption selectivity and adsorption capacity. However, few investigations into materials with these properties have been carried out.

Electroactive polymers such as polyaniline (PANi), polypyrrole (PPy) and polythiophene (PTh) with intrinsic redox properties and interesting doping and dedoping capabilities have been identified as candidates for adsorbents [7,8,11]. The polymer, PANi has attracted considerable research interest in recent years as an adsorbent [11]. Aniline polymers have the general form of $[(\text{-B-NH-B-NH})_y(\text{-B-N=Q=N-})_{1-y}]_n$, in which Q and B represent the quinoid and benzenoid ring, respectively. Therefore, it can exist mainly in four forms shown in Scheme ***S1***: i) the fully oxidized form, pernigraniline (PNA, y = 0); ii) 75% oxidized form, nigraniline (NA, y = 0.25); iii) 50% oxidized form, emeraldine base (EB, y = 0.5); iv) fully reduced form, leucoemeraldine base (LB, y = 0) [12]. Among them, the emeraldine base is the most common form, and can be doped into the emeraldine salt (ES) conducting state. The stability of the ES can be tuned by the solution pH, by which the doping process can be well controlled [12]. The ES will retain the doping ions when dry, however it will undergo dedoping gradually when it is in water with a pH greater than 4 [12,13]. Therefore, PANi with this interesting property will be taken into consideration when a PANi adsorbent is being designed.

In order to obtain an adsorbent with sensitive selectivity, heterogenous materials can be introduced to synergistically assist the PANi to selectively adsorb heavy metal ions [14]. Metal oxides are widely

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https://doi.org/10.1016/j.synthmet.2018.08.006
Received 10 June 2018; Received in revised form 1 August 2018; Accepted 10 August 2018
0379-6779/

regarded as encouraging adsorbents in this respect [15]. It has been reported that Mn oxides show special adsorption affinity toward Cu(II) [16] and Fe oxides possess unique affinity to Pb(II) [17], while Zn(II) can be greatly attracted to Si oxides [18]. Therefore, the synthesis of conducting polymers with metal oxides has been extensively researched. V. Gilja et al. [19], X. Li et al. [20] and M. Vaez et al. [21] investigated the synergetic effect between PANi and TiO_2 in the photocatalytic degradation of dye. In the synergetic mechanism they provided in these investigation, PANi played an important role in protecting the TiO_2 surface from the blockage of intermediates while TiO_2 absorbs photons with energy higher than 3.2 eV to generate the excited states of electron and hole pairs to oxidize the dye into CO_2 and H_2O. In addition, several interesting selective adsorption properties were also noted in investigations of PANi based metal oxides. S.A. Nabi et al. [22] prepared a PANi/Ti(V) tungstate composite, and showed selective adsorption for Pb(II), Hg(II), Bi(III) and Zr(IV). The reason of the selectivity was ascribed to the radius of the ions. In contrast, special affinity to Cu(II) and Pb(II) was acquired for PANi/Al_2O_3 in investigation conducted by S. Piri et al. [23] when the ions have to compete with Zn (II), Ni(II), Co(II) and Cd(II). Moreover, Q. Zhang et al. [24,25] prepared PANi/ZrP with or without carbon nanotubes (CNTs), observing that PANi/zirconium phosphate (ZrP) with CNTs showed better affinity to Pb(II) due to complexation with oxygen derived from P-O-H on the ZrP, while the composite without CNTs obtained in acetonitrile exhibited an affinity to Ni(II) due to artificial amino acids on ZrP to Ni(II), even though Ni(II) has a smaller radius than usually expected for heavy metal ions with such high affinity. Therefore, it can be seen that there still are many contradictions to the conclusions made previously for the selective adsorption mechanism, and the theory proposed before cannot satisfactorily explain the selectivity of the polymer/metal oxide composite. These contradictions can seriously restrict adsorbent design. While the combination of polymer and metal oxides produce the selective adsorption for heavy metal ions, the mechanism for the synergetic effect remains unknown. Therefore, a reasonable and convincing mechanism for the selective adsorption and the synergistic adsorption should be investigated and proposed.

To solve this problem, a PANi capable of doping and dedoping was chosen to synergistically combine with $TiO_2(O^-)$ in this study. The doping states, composite structure, textural properties and interaction of/between PANi and $TiO_2(O^-)$ were characterized using FT-IR, zeta potential analysis, TGA, XRD and N_2 adsorption-desorption isotherm. Adsorption experiments including kinetic, isotherm in single/multiple metal ion system were designed and performed to illuminate the individual and competitive adsorption properties for Pb(II), Zn(II) and Cu (II). Finally, a hypothesis for the synergistic mechanism between the polymer and $TiO_2(O^-)$ and the selective adsorption mechanism of polymer/$TiO_2(O^-)$ for heavy metal ions were verified by the results. The mechanism we proposed may provide insight to the nature of adsorption and may guide the design of adsorbents with selectivity towards certain heavy metal ions.

2. Experimental

2.1. Chemicals

The chemicals (AR grade) used in this investigation were all purchased from Sinopharm Chemical Reagent Co., Ltd (China). Specifically, aniline was purified by distillation, and stored in the refrigerator in the dark. The heavy metal ion solutions employed in the adsorption investigations were prepared from $Pb(NO_3)_2$, Cu $(NO_3)_2{\cdot}3H_2O$ and $Zn(NO_3)_2{\cdot}6H_2O$, respectively with ultrapure water.

2.2. Synthesis of the PANi(ES), TiO_2(OH) and PANi(ES^+)/$TiO_2(O^-)$ composite

The PANi(ES^+)/$TiO_2(O^-)$ composite was synthesized by chemical oxidative polymerization. The ratio of TiO_2 and aniline monomer was optimised in our previous work [26]. Specifically, the TiO_2 was prepared through the typical sol-gel hydrolysis. 20 mL of titanium (IV) isopropoxide (0.033 mol) was added in the aqueous solution (2.64 g). The obtained TiO_2 was then dispersed in 100 mL (0.1 $mol{\cdot}L^{-1}$) of HNO_3 solution (Caution! HNO_3 is highly corrosive!), followed by adding 1.8 mL of aniline to the TiO_2 suspension (Caution! Aniline may cause cancer!). After stirring for 30 min, 22.8 g of ammonium persulphate (0.1 mol) was dispersed in the solution and was left for reaction to another 6 h at ambient temperature (Caution! Ammonium persulphate is corrosive!). The composite was filtrated and dried at 50 °C. The PANi (ES) and TiO_2(OH) used for comparison in this investigation were also synthesized using the same procedure, either without TiO_2 or aniline and ammonium persulphate being added.

2.3. Characterization

The Fourier transform infrared spectra (FT-IR) of the PANi(ES), TiO_2(OH) and PANi(ES^+)/$TiO_2(O^-)$ composite used for the functional group characterization before and after metal ions adsorption were performed on a BRUKER TENSOR 37 FT-IR spectrometer by the KBr pellet method in the experimental range from 4000 to 400 cm^{-1}. The zeta potential investigation for the doping degree study was conducted on a Malvern Zetasizer Nano ZS90. The thermogravimetric analysis (TGA) used for the thermal stability study and the component inspection was performed on a Setaram Labsys Evo in N_2 flow with a heating rate of 10 °C min^{-1}. X-ray diffraction (XRD) patterns were acquired on an X'Pert PRO Diffractometer using a Cu-Kα radiation method. The N_2 adsorption and desorption isotherms were recorded on a Builder SSA-4200. The features including specific surface area, total pore volume and average pore radius were calculated using a Builder analysis software. A Shimadzu UV2600 spectrophotometer was applied for the solid UV–vis NIR spectra investigation on the PANi(ES^+)/$TiO_2(O^-)$ composite synthesized through the Buchwald-Hartwig reaction. The scanning electron microscopy (SEM) and energy dispersive spectrometer (SEM-EDS) images were recorded on a JSM-6700 F to investigate the morphology of sample. A JEM model 2100 electron microscope was used to acquire the transmission electron microscopy (TEM) and energy dispersive spectrometer (TEM-EDS) images. The initial and residual concentrations of the heavy metal ions were determined on an inductive coupled plasma emission spectrometer (ICPE-9000, Shimadzu).

2.4. Adsorption experiments

In the adsorption experiments, the dose of adsorbent was kept at the optimal concentration of 2 $g{\cdot}L^{-1}$ with the solution volume of 20 mL. All experiments were performed using a benchtop shaking incubator (ZWY-100H, Zhicheng, Shanghai, China) with controllable temperature, and the agitation speed was kept at 200 rpm. The initial solution pH, which was determined using a TISAB (PXSJ-216F, Leici, Shanghai, China) by calibration in every test, was kept at 5 to avoid the influence of precipitation of heavy metal ions on the adsorption.

To study the isotherm in the single metal ion solution, Pb^{2+}, Zn^{2+} and Cu^{2+} solutions with various initial concentrations were applied at 15, 25, 45 °C, respectively for 3 h. The initial concentrations of Pb^{2+} were 100, 200, 300, 400, 600, 800 $mg{\cdot}L^{-1}$, respectively, while the initial concentrations of Zn^{2+} and Cu^{2+} were 10, 50, 100, 200, 400, 600 $mg{\cdot}L^{-1}$, respectively. To investigate the selectivity of the composite, a Pb^{2+}, Zn^{2+} and Cu^{2+} mixed solution with initial concentrations of 50, 100, 200, 300 and 400 $mg{\cdot}L^{-1}$ of each metal ion were used at 25 °C for 3 h. To study the effect of pH, solutions with initial pHs from 1 to 5 were employed for 3 h, and the initial heavy metal ion concentration was kept at 200 $mg{\cdot}L^{-1}$. The initial pH was adjusted using dilute HNO_3 and NaOH solutions.

The adsorption capacity in the adsorption experiments and the recycling efficiency in the recycling experiments were calculated as