Modification of sand with iron and copper derived from electroplating wastewater for efficient adsorption of phosphorus from aqueous solutions: A combinatorial approach for an effective waste minimization

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ABSTRACT

The focus of the this work is to develop mesoporous silica and amine modified sand loaded with iron (Fe) and copper (Cu) species from electroplating wastewater for a further removal of phosphorus (P) from wastewater. First, it is shown that Fe or Cu supported sand adsorbent can effectively remove phosphorus (P) from aqueous solutions. The influence of pH, initial ion concentration (C_0), contact time (t) on the adsorption of P by both sand adsorbents was studied. The maximum adsorption efficiency at room temperature reached 98% for the Fe-supported adsorbent under conditions of pH = 4, C_0 = 25 mg/L, t = 180min and 96.3% for the Cu-supported sand under conditions of pH = 2, C_0 = 5 mg/L, t = 120min respectively. The kinetics of P adsorption by the Fe or Cu supported sands followed the pseudo second-order kinetic model, while the adsorption isotherms fitted the Langmuir model. Based on the above results, an iron and copper co-supported sand adsorbent was prepared successfully by encapsulating Fe and Cu from a copper electroplating wastewater. In the meantime, Cu in the electroplating wastewater was reduced from 222 to 0.12 mg/L. This wastewater derived sand-based adsorbent had the same efficiency as the Fe-supported sand adsorbent. It was used to remove P from aqueous solution until the residual P in solution met China National Standard of WastewaterEmission. By this way, a dual approach to synergistically purify both anions and cations polluted wastewaters is developed.

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1. Introduction

Phosphorus (P) in wastewaters is mainly from farm activity (especially the application of fertilizers), municipal wastewater discharges (especially the household cleaners) and industrial emissions (Kataki et al., 2016). P contamination in water resource has been greatly concerned as it poses unacceptable ecological risks to plants, animals (Roy, 2017). Excess of P in surface water can cause excessive growth of suspended organic matters, blocking out sunlight and reducing oxygen supply for creatures in water (Roy, 2017). The threshold limits of P in water vary dependent on countries, water types and effluent origins, etc. (Loganathan et al., 2014). For

examples, the total P limit stated in the Clean Water Act of American Environmental Protection Agency is 50 μg/L (https://www.epa.gov/wqs-tech/water-quality-standards-regulations-nebraska, 2015). The European Union considers a total P concentration below 0.01−0.07 μg/L as a standard for excellent river waters (European Commission, 2009). The limits of P in water discharges in China are 0.5 and 1 mg/L for 1st the 2nd class industrial emissions respectively (GB 8978, 1996).

There are many methods for the removal of P from wastewaters, including chemical coagulation and flocculation process (Amuda and Amoo, 2007), biological treatment (Rubio-Rincón et al., 2017), membrane separation (Bódalo-Santoyo et al., 2004) and adsorption method (Kim et al., 2011), etc. However, the chemical precipitation method may cause a secondary pollution due to the generation of P-containing sediments or sludges. The biological removal of P requires a long operation time and strict conditions.

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The membrane technology suffers from expensive cost and energy consumption. The adsorption method is advantageous over the other methods, because it is economic, efficient and easy to operate and now widely used (Loganathan et al., 2014) in wastewater purification. Many kinds of adsorbents have been developed, such as metal oxides or hydroxides (Park et al., 2017; Cui et al., 2016)), titania-functionalized graphene oxide (Sakulpaisan et al., 2016), polymeric ligand exchangers (Kney and Zhao, 2004) and porous materials (Huang et al., 2017) for the effective removal of P contaminants in wastewaters. For example, Park et al. (2017) coated sulfonated polymer with Fe−Ti bimetal oxides for the removal of phosphorus from membrane bioreactor effluents. The authors concluded that Ti doping and Ca binding to mixed metal oxide layers substantially enhanced the adsorption rate and capacity of the coated beads due to the formation of more positively charged surfaces and calcium phosphate. The mixed metal oxides coated beads were highly selective to phosphate ions against Cl^-, NO_3^-, and SO_4^{2-} ions. Cui et al. (2016) synthesized a ferric hydroxide-coated cellulose nanofiber hybrid for the removal of phosphate from wastewater. It was shown that the adsorption of phosphate can be described by the Langmuir isotherm and the pseudo-second-order models. And the phosphate adsorption was mainly due to electrostatic attraction and ligand exchange mechanisms. Kney and Zhao (2004) developed a polymeric ligand exchanger (PLE) by immobilizing copper ions onto a commercially available chelating resin. A pilot test showed that the PLE could selectively remove phosphate and nitrate from secondary municipal wastewater effluent.

Mesoporous silica is one of the most widely studied adsorbents for adsorbing P from wastewaters (Huang et al., 2017). While pure mesoporous silicas although have large surface areas, pore volumes and controllable pore size distribution, their adsorption performance is still not ideal for a practical application. Metal doping porous silica skeletons (Han et al., 2015) and amino-functionalization of the mesopores (Hamoudi et al., 2007) are effective strategies to greatly enhance the efficiency of mesoporous silicas toward P in wastewater.

The search for cheap adsorbents is always a central task in developing practicable adsorption technology (Gupta et al., 2009). Natural minerals (Moharami and Jalali, 2013) and wastes such as sludges (Devi and Saroha, 2017) have been successfully tried by different groups. Among the adsorbents used for the removal of P from wastewaters, silica sand may be advantageous over the others due to its low cost and natural abundance. Bubba (Bubba et al., 2003) demonstrated the capacities of 13 Danish sands towards P via batch adsorption experiments. With an initial P concentration of 320 mg/L, the maximum capacity was 1.1 mg/g sand. However, natural sands generally have low capacities toward P in water (Jiang et al., 2014). It was reported that Cu^{2+}, Fe^{3+}, Al^{3+}, Ca^{2+} and other metal ions had high affinity for P (Park et al., 2017; Del Bubba et al., 2003; Zavareh et al., 2017; Arias et al., 2006). Therefore, sands could be modified by these cations to improve its efficiency in removing P in water. For example, Arias (Arias et al., 2006) coated quartz particles with iron and aluminum oxides to increase the adsorption of P by the sand. A higher sorption capacity was shown for Al-coated sand than Fe-coated sand. It was proposed that the interaction between Fe-coating and P was mainly electrostatic, while the interaction between Al-coating and P included both electrostatic interaction and hydrogen bonds between orthophosphate and aluminum hydroxide.

In this work, silica sand was first modified with porous SiO_2 coating in order to increase its surface area. The coated silica sand was further functionalized with amino groups. Then, the porous silica and amine doubly modified sand was loaded with Fe (III) or Cu (II) to improve its adsorption capacity toward P. The adsorption of P from aqueous solutions with respect to the effect of pH, initial concentration, contact time, adsorption kinetics and isotherms were studied. Following these studies, the modified sand was first applied to uptake Fe and Cu simultaneously from a real electroplating wastewater. Then the Fe and Cu co-supported sand was further used to adsorb P from a synthetic wastewater. The dual approach of adsorption cations and anions by the modified sand provides a wider and a better platform for waste minimization.

2. Experimental section

2.1. Modification of sand with mesoporous silica

A natural silica sand sized 200−350 μm was from a sea sand deposit quarry in the southern part of China. All other chemicals used in the experiments were of analytical grade. The modification of the sand was as follows. First, 100 g of silica sand was pre-treated with 50% hydrochloric acid (HCl) solution for 1 h at room temperature to remove dissolvable metal ions on the sand surface and this was followed by rinsing with distilled water and drying. To coat the sand with silica gel, 6 g of the treated sand and 1.08 g of cetyltrimethylammonium bromide (CTAB) were put in 100 mL of H_2O in a conical flask under stirring at 333 K for 10 min. Thirty milliliters of sodium hydroxide (NaOH,0.3 M) and 4.5 mL of tetraethyl orthosilicate (TEOS) were then added to the mixture. The mixture was stirred for 3 h at room temperature. After the reaction, the sample was collected by filtration and washed with distilled water and dried in air. The procedures were repeated four times for multiple coating silica gel onto the sand. The product obtained was calcined at 823 K for 6 h to generate mesoporous silica coated sand. This sample was designated as mesosilica@Sand.

2.2. Amino functionalization of modified sand (mesosilica@Sand)

The mesosilica@Sand was further amino-functionalized. Briefly, 5 g of the mesosilica@Sand was mixed with 3 mL of (2-Aminoethylamino) propylmethyldimethoxysilane (AAPTS) and 90 mL of anhydrous toluene under stirring at 388 K for 9 h. After the reaction, the sample was collected by filtration, followed by washing with methanol and drying at 363 K for 3 h. The amino-modified silica sand was encoded as NH_2-Sand.

2.3. Supporting of iron or copper onto the surface of NH_2-Sand

For the synthesis of Fe-supported sand, 1 g of NH_2-Sand was put into 25 mL of isopropyl alcohol solution of $Fe(NO_3)_3 \cdot 9H_2O$ with a concentration of 0.1 mol/L for 1 h at 298 K. The product was collected by filtration and washed with isopropyl alcohol. The final sample was dried at 363 K for 2 h and designated as Fe−NH_2-Sand. Cu−NH_2-Sand was prepared following the same steps as Fe−NH_2-Sand. $CuCl_2 \cdot 2H_2O$ with a concentration of 0.25 mg/L was used as Cu source.

2.4. Encapsulation of Fe and Cu from electroplating wastewater by NH_2-Sand

One gram of the NH_2-Sand was added to 25 mL of copper electroplating wastewater to encapsulate Fe and Cu onto the surface of NH_2-Sand. The initial pH of the copper electroplating wastewater was 2.03. The concentrations of Cu^{2+} and Fe^{3+} in the waste liquid were 222 mg/L (≈ 0.0035 mol/L) and 2714 mg/L (≈ 0.048 mol/L), respectively. The mixture was stirred for 1 h at 298 K. The sample was collected by filtration, dried at 363 K and named as W−NH_2-Sand.

The preparation of sand based adsorbent described above is