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Selective removals of heavy metals (Pb^{2+}, Cu^{2+}, and Cd^{2+}) from wastewater by gelation with alginate for effective metal recovery

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HIGHLIGHTS

- Gelation with alginate can rapidly remove heavy metal ions from wastewater.
- Pb^{2+} can be selectively removed by alginate when Cu^{2+} and Cd^{2+} are present.
- FTIR and XPS analyses indicate the role of —OH and $—COO^-$ in metal gelation.
- Calcination of the gels can obtain PbO, CuO, and CdO nanopowders for metal recovery.

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ABSTRACT

A novel method that uses the aqueous sodium alginate solution for direct gelation with metal ions is developed for effective removal and recovery of heavy metals from industrial wastewater. The experimental study was conducted on Pb^{2+}, Cu^{2+}, and Cd^{2+} as the model heavy metals. The results show that gels can be formed rapidly between the metals and alginate in less than 10 min and the gelation rates fit well with the pseudo second-order kinetic model. The optimum dosing ratio of alginate to the metal ions was found to be between 2:1 and 3:1 for removing Pb^{2+} and around 4:1 for removing Cu^{2+} and Cd^{2+} from wastewater, and the metal removal efficiency by gelation increased as the solution pH increased. Alginate exhibited a higher gelation affinity toward Pb^{2+} than Cu^{2+} and Cd^{2+}, which allowed a selective removal of Pb^{2+} from the wastewater in the presence of Cu^{2+} and Cd^{2+} ions. Chemical analysis of the gels suggests that the gelation mainly occurred between the metal ions and the $—COO^-$ and —OH groups on alginate. By simple calcination of the metal-laden gels at 700 °C for 1 h, the heavy metals can be well recovered as valuable resources. The metals obtained after the thermal treatment are in the form of PbO, CuO, and CdO nanopowders with crystal sizes of around 150, 50, and 100 nm, respectively.

1. Introduction

Contamination of water and soil by heavy metals has been a serious and long-lasting environmental problem. Lead, copper, and cadmium are three common types of heavy metals that have been found in industrial wastewaters, including discharges from metal plating, mining activities, smelting, and battery manufacturing [1]. Heavy metals are not biodegradable and can be accumulative in the ecosystems and human bodies as well [2]. Lead is toxic to humans via interaction with the sulfhydryl group of proteins, resulting in disruption of the metabolisms and biological activities of many proteins [3]. Copper can causes various types of acute and chronic disorders in human, such as hemochromatosis and gastrointestinal catarrh [4,5]. The accumulation of cadmium in human bodies can cause itai-itai disease and renal abnormalities, including proteinuria and glucosuria [6,7]. The harms of heavy metals to the environment and public health have made the removal of such metals a top priority in wastewater treatment. Meanwhile, these metals are valuable resources that should be recovered as much as possible from the wastes.

The methods commonly used for the removal of metals from wastewater include chemical precipitation, ion exchange, membrane filtration, and adsorption [8–11]. Chemical precipitation is generally reliable and widely used; however, this process yields a

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large volume of sludge that presents little value and a great difficult for metal recovery. Ion exchange can efficiently remove heavy metals from wastewater and it can be readily used for small-scale industrial applications. However, ion exchange has drawbacks, such as not suitable for high-strength wastewaters due to a rapid saturation of the resins [12]. Membrane filtration, e.g., nanofiltration or reverse osmosis, can remove heavy metal ions with a high efficiency, but problems such as the high cost, process complexity, membrane fouling and low permeate flux, have hindered its application in heavy metal removal [13]. Adsorption is considered as one of the most effective techniques for the removal of heavy metals from wastewater owing to its low initial cost and process simplicity [14]. However, the subsequent treatment of the adsorbents can greatly increase the treatment cost and often cause secondary pollutions.

Besides these methods, gelation by sodium alginate has been proposed as a novel and effective method for heavy metal removal and recovery. Alginate is a highly promising material for biosorption of heavy metals because of (a) its low cost and wide availability as a major product of brown algae [15] and (b) its high affinity toward heavy metals via gelation [16–20]. Studies have been conducted to use alginate for the removal or recovery of heavy metals from aquatic solutions. Jang et al. [21] reported the recovery of Cu^{2+} from a synthetic aqueous solution in a loop fluidized bed reactor with the alginate and calcium alginate spheres. Cu^{2+} could be removed by a two-step approach: direct dispensing of sodium alginate to absorb the metals from the solution followed by the addition of partially coagulated calcium alginate spheres to "polish" the effluent. Torres et al. [22] tested the biosorption of gold and silver ions from the aqueous solutions using calcium alginate beads. Their results showed that the metal uptake capacities were significantly affected by the solution pH, and the FTIR analysis indicated that both carboxylic and hydroxylic functional groups in alginate beads were involved in the metal binding process. Papageorgiou et al. [23] investigated the sequestration of Cu^{2+} and Cd^{2+} by means of biosorption onto calcium alginate beads and reported that the sorption followed a competitive mechanism in multi-metal solutions. However, for most of the studies, the removal of heavy metals was achieved mainly by adsorption onto alginate beads, which is subject to a limited surface area and a slow mass transport process. The adsorption capacity of used biosobents actually can be hardly recovered by regeneration [24–26]. More importantly, the subsequent heavy metal recovery has scarcely been reported.

In this research work, we developed a more effective method in using alginate for both heavy metal removal and recovery from wastewater. During the process, the aqueous alginate solution was dosed into the wastewater, inducing its direct and rapid gelation with the heavy metals. The metal-laden gels were then treated by simple calcination for effective metal recovery. The experimental study was conducted on Pb^{2+}, Cu^{2+}, and Cd^{2+} as the model heavy metals. The kinetics of metal gelation, the effects of the alginate dosing ratio and pH on the metal removal efficiency, and the metal products recovered after the thermal treatment were investigated. Additionally, the metal–alginate gels were analyzed, the gelation mechanisms were revealed, and the metal oxide nanopowders obtained were characterized.

2. Materials and methods

2.1. Chemicals

Sodium alginate was purchased from Sigma–Aldrich (St. Louis, MO). Its stock solution was prepared to have an alginate concentration of 10 g/L by dissolving sodium alginate in hot water (75 °C) with constant stirring until forming a homogeneous and clear solution.

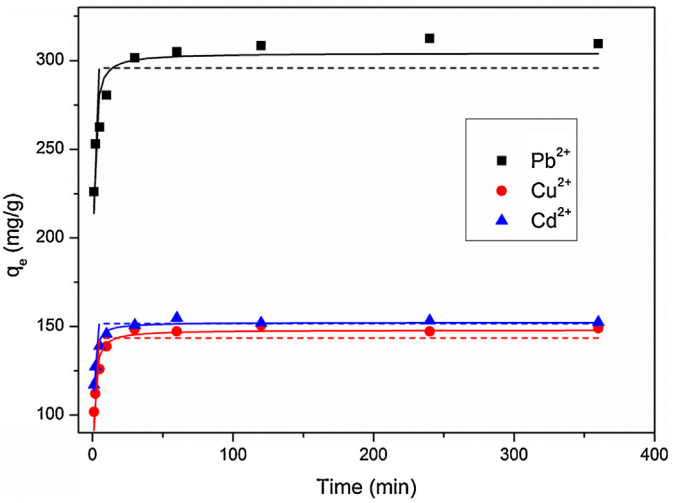

Fig. 1. The amount of the heavy metals (Pb^{2+}, Cu^{2+}, and Cd^{2+}) immobilized by gel formation with alginate during the gelation process. The data can be well fitted with the pseudo second-order kinetic equations (solid lines).

Table 1
Rate constants of the pseudo first-order and pseudo second-order kinetic equations fitted for the gelation process of Pb^{2+}, Cu^{2+}, and Cd^{2+} with the aqueous sodium alginate. (Test condition: 200 mg/L sodium alginate with 100 mg/L metal ions at pH = 4.5 ± 0.1).

Metal type	Pseudo first-order			Pseudo second-order		
	k_1 (min^{-1})	q_e (mg/g)	R^2	k_2 (g/mg min)	q_e (mg/g)	R^2
Pb^{2+}	1.38	295.8	0.608	0.0194	304.2	0.962
Cu^{2+}	1.28	151.6	0.897	0.0123	152.3	0.942
Cd^{2+}	1.01	143.5	0.699	0.0085	148.0	0.887

Table 2
Constants of the Langmuir and Freundlich equations for gelation of Pb^{2+}, Cu^{2+}, and Cd^{2+} with alginate (test condition: 500 mg sodium alginate in 50 mL at pH = 4.5 ± 0.1).

Metal Type	Langmuir constants			Freundlich constants		
	K_L (L/mg)	q_m (mg/g)	R^2	K_F [(mg/g)(mg/L)-n)]	n	R^2
Pb^{2+}	0.046	435.3	0.977	126.0	5.22	0.902
Cu^{2+}	0.011	167.1	0.983	24.7	3.69	0.882
Cd^{2+}	0.018	179.0	0.990	42.9	4.85	0.908

Three types of heavy metals, Cu, Cd, and Pb, were selected as the model metals in the experimental study. $CuSO_4{\cdot}5H_2O$, $CdSO_4{\cdot}8H_2O$, and $Pb(NO_3)_2$ were purchased from BDH (Poole, Dorset, UK). Their respective stock solutions were prepared by dissolving the chemicals in water to have the metal ion concentrations at 10 g/L.

2.2. Gelation for the removal of heavy metals from wastewater

Synthetic wastewaters were made by diluting the heavy metal stock solutions in water to pre-determined concentrations for the experimental study. All gelation experiments were conducted in 50 mL polypropylene (PP) centrifuge tubes. For tests on the metal gelation and removal kinetics, a metal concentration of 100 mg/L and an alginate concentration of 200 mg/L in the final solution were adopted. For the isotherm studies, the heavy metal concentrations varied from 100 to 1000 mg/L, and the dry weight of sodium alginate in the gelation system was 500 mg in 50 mL liquid. For the experiments on heavy metal removals from wastewater by gelation, a low metal concentration of 50 mg/L and a high metal