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Effect of trace Ag^+ adsorption on degradation of organic dye wastes

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ABSTRACT

By the introduction of Ag^+, the molecular imprinting technology and photocatalysis technology were associated with each other and the Ag^+-imprinted biosorbent (Ag-IB) was prepared. Ag-IB could first adsorb Ag^+ and then degraded Methyl Orange (MO). Firstly the influences of the ionic strength and pH value in solution on adsorption capacity for Ag^+ were studied, and then the effects of Ag^+ adsorption capacity on degradability for MO were investigated. The maximal degradation ratio of MO reached over 93% at Ag^+ adsorption capacity of 78.0 mg/g after 5.0 h. In contrast to MO, Methylene Blue (MB) and Sunset Yellow (SY) were studied and the degradation ratios could be about 70% and 98% at Ag^+ adsorption capacity of 36.9 mg/g, respectively. And XPS analysis showed that Ag^+ was reduced to Ag on Ag-IB surface. Furthermore, the mechanism for photocatalytic degradation of MO dye was primarily researched.

1. Introduction

Silver is a noble metal that has been widely employed in the photographic and imaging industry for many years. It is known to be released to the environment through its various industrial applications, leading to the possible exposure of aquatic organisms [1]. Then, the silver ions that could be accumulated in organisms (including humans) through the food chain have caused numerous diseases and disorders. Therefore, the effective removal and recovery of Ag^+ has been emphasized recently [2–4]. Although some conventional methods can remove silver ions from their effluents, they are practically not economical [5]. It urgently needs a new technology.

The biological materials, including living and non-living microorganisms, have been widely used in the removal and possibly recovery of toxic or precious metals from industrial wastes in recent years [6]. A molecular-imprinted biosorbent that could selectively adsorb valuable metal ions which was prepared by Su et al. [7–9], showed 30–50% higher uptake to Ni^{2+} compared with the non-imprinted biosorbent (IB).

In addition, the development of new and inexpensive methods for the treatment of industrial dye wastewater is also needed. Dye wastewater usually consists of a number of contaminants including acids, bases, dissolved solids, toxic compounds, and colored materials. These contaminants are noticeable even at very low concentrations and must be removed before the discharge of wastewater [10]. It is reported that about 17 billion tons of dyes were discharged from the textile industry in China every year [11]. For the treatment and control of certain kinds of pollutants, some physical, chemical and biological methods have been successfully used [12–17]. For example, Silver impregnated TiO_2 has also been explored for dye degradation [18,19]. Although they may allow the complete degradation of organic pollutants to CO_2 and inorganic acids, the high cost limit them to be applied widely in actual wastewater treatment. There is a novel method that molecular-imprinted biosorbents could be used in the degradation of dyes. Degradation studies of dyes by ion-imprinted chitosan-TiO_2 biosorbents had been referred in the previous work of our lab [20,21]. And TiO_2 always played an important role in those degradation studies. However, there were no researches reported about the effects of the molecular-imprinted biosorbents that had adsorbed heavy metal ions on degradability of organic pollutants.

In the present work, Ag^+-imprinted biosorbent (Ag-IB) that adsorbed Ag^+ could be used in the degradation of dyes such as MO in UV irradiation. The prime objective of this study is to examine the effect of Ag-IB that has adsorbed Ag^+ on the degradation of MO. Therefore, Ag-IB could be used not only in the removal and recovery of precious metal ions Ag^+, but also in the elimination of dye wastes after adsorption for Ag^+. Simultaneously, Ag^+ was reduced to Ag on the biosorbent surface. Since Ag-IB was prepared mainly using waste mycelium, the cost of silver-bearing and organic dye wastewater treatments could be greatly reduced. Moreover, the use of dead biomass from industries also helps to solve the problem of waste biomass disposal. The actual application of the novel method

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has not proven yet, but compared to those traditional methods, it brings us the new ideas to reduce the pressures of worldwide environmental pollution.

2. Materials and methods

2.1. Chemicals and reagents

Mycelium from waste biomass of *Penicillium chysogenum* was obtained from Dongchen Biochemical Engineering Company in Shandong Province; chitosan with 90.0% degree of deacetylation was extracted from shrimp shells obtained in our laboratory. Aqueous Methyl Orange (MO) and Methylene Blue (MB) solutions were prepared from their respective chloride and sodium salts (Merck), respectively, without further purifications. And Sunset Yellow (SY) (China National Measuring Science Research Inst). Silver nitrate, nitric acid, sodium nitrate, calcium nitrate, magnesium nitrate, potassium nitrates, acetic acid, sodium citrate and epichlorohydrin were of analytical grade and all reagents were prepared with deionized water.

2.2. Preparation of non-imprinted (IB)/Ag^+-imprinted biosorbent (Ag-IB)

The preparation of the biosorbents can be seen from the literature [7–9].

The preparation process of IB was as follows: chitosan (0.1 g dry weight) was dissolved in a 2.0 mL 2.5% (v/v) acetic acid solution. The mixture was stirred until all chitosan was dissolved. Then, 0.5 mL epichlorohydrin as cross-linking agent was added to the mixture and allowed to react for 8.0–10.0 h at room temperature. Then 2.0 g (dry weight) of mycelium was added to the cross-linking mixture and the suspension was stirred for 10 min. Finally, the surface non-imprinted biosorbent was filtered using filter paper and dried at room temperature for 24 h. The dry adsorbent was sized by a 60-mesh sieve and stored at a sealed bottle for further use.

The preparation process of Ag-IB was as follows: $AgNO_3$ was dissolved in 2.0 mL dilute acetic acid solution (2.5%, v/v) to give a Ag^+ solution of 2.0 mg/L. Then 0.1 g chitosan (dry weight) was dissolved in this solution. 2.0 g mycelium (dry weight) and enough deionized water were added into the above solution, and the mixture was stirred. Then, 0.5 mL epichlorohydrin as cross-linking agent was added into the mixture and allowed to carry out for 8.0–10.0 h at room temperature. Finally, the Ag^+ imprinted in the biosorbent was removed by treating with EDTA solution containing 0.2 g/L for 8.0–10.0 h. Regeneration was carried out by washing the adsorbent with 0.2 M NaOH for 2.0 h by resuspension at shaking bath. The biosorbent Ag-IB was filtered using filter paper and dried at room temperature for 24.0 h. The dry biosorbent was sized by a 60-mesh sieve and stored for further use.

2.3. Biosorption and degradation experiment

0.15 g adsorbent (dry) was added into a 100 mL beaker containing Ag^+ (0–1000 mg/L), and the total solution volume was 50 mL. The mixtures were agitated in a reciprocal shaker (agitation rate, 80 rpm) for 12.0 h at constant temperature (25–27 °C). The adsorption capacity of the biosorbent for Ag^+ (mg/g) was computed using the following equation:

$$Q\ \ (\text{mg/g}) = \frac{(C_M - C_e)V}{W} \qquad (1)$$

where Q is the adsorbed concentration (mg/g), C_M and C_e are the initial and equilibrated concentrations of metal ion (mg/L), respectively. V is the volume of added solution (L) and W is the weight of the adsorbent (dry).

pH was adjusted by NaOH and HCl solutions. Ionic strength was changed by addition of $NaNO_3$, KNO_3, $Ca(NO_3)_2$ and $Mg(NO_3)_2$ solution in the range of 0–400 mg/L.

For the degradation study, 0.15 g biosorbent was contacted with 50 ml Ag^+ solution (0–1000 mg/L). After adsorption experiment, the biosorbent was collected by filtration. Then it was transferred to 50 ml organic dye (10 mg/L) solutions. The mixtures were shaken in a reciprocal shaker (80 rpm) at room temperature (25–27 °C) for 5.0 h. An ultraviolet lamp (20 W, and the lamp is 0.5 m long and have a diameter of 0.02 m) was available in the shaker which is placed at a distance of 10 cm above from the beaker. Degradation rate was calculated from the amount of organic dyes in the degradation medium, as the following:

$$D\ \ (\%) = 100 \times \frac{C_m - C_d}{C_m} \qquad (2)$$

where D is the degradation ratio (%), C_m and C_d are the initial and equilibrated concentrations of dyes (mg/L).

2.4. Analytical methods [3]

The amount of metal ion Ag^+ was determined by an Atomic Spectroscopy (SpectrAA 55-B, Varian Company, USA). And the optimum work range of Ag^+ was 0.02–10 μg/mL. The MO, MB and SY were analyzed by an adsorption spectrophotometer under 464 nm, 664 nm and 482 nm.

All experiments were repeated three times and the results given are the average values.

3. Results and discussion

3.1. Adsorption characteristics studies

3.1.1. Effect of pH on adsorption

pH is termed as a key factor in most processes governed by adsorptive separation. The pH dependence of adsorbed concentration for Ag^+ is shown in Fig. 1. The adsorption capacity increased with an increase of pH value of the solution in the range 1.0–6.0. As pH value was over than 6.0–7.0, the adsorbed concentration decreased. A pH value of about 6.0–7.0 was found to be optimum for Ag^+ adsorption. This could be explained that at low pH value (acidic

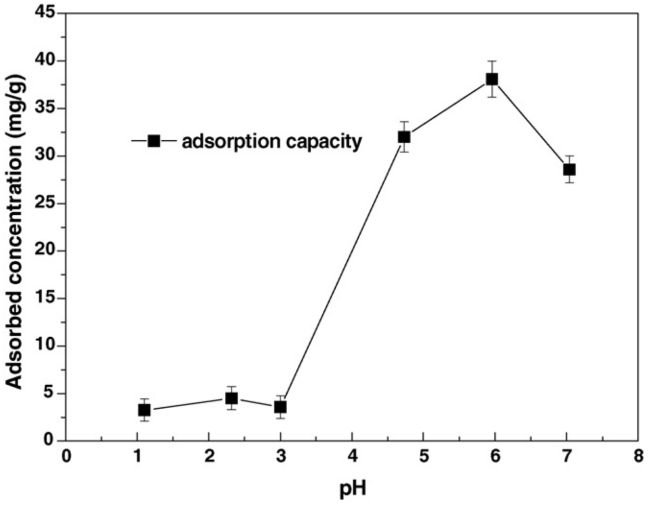

Fig. 1. Effect of pH on adsorbed concentration (the initial Ag^+ concentration in the solution was 200.0 mg/L (Ag^+-imprinted biosorbent of 3.0 g/L, and agitate rate of 170 rpm, stirred at room temperature (25–27 °C) for 1.5 h).