Absorptive Removal of Copper from Aqueous Solution by Biosorbents

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Abstract. Four bacteria were isolated from soil polluted by copper solution. They were purified, cultured, prepared to biosorbents. They were used to adsorptive removal of copper ions from aqueous solution. The bacterial 1 has best ability. The parameters that affected the adsorption of copper ions on bacterial 1, such as initial pH of copper solution, contact time and initial concentration of copper solution, were studied. Under optimal conditions, the maximum adsorption capacity was 16.27 mg g^{-1} and the recovery ratio was 16.7%. The adsorption experimental equilibrium data correlate well with Langmuir isotherm and Freundlich isotherm.

Keywords: copper, removal, biosorption, isotherm.

1. Introduction

Heavy metal pollution is a world environment problem because of their undegradability [1]. As a heavy metal, copper causes diseases in humans and animals [2, 3] while it is absolutely necessary to humans and animals. But the copper is widely used in fields including mining, materials process, paper making, printing, and so on. The Word Health Organization (WHO) requires the copper in drinking water not to exceed 2.0 mg L^{-1}. So the removal of copper from aqueous solution is important to these fields.

The conventional methods for copper removal from aqueous solution include oxidation [4], reduction [5], precipitation [6], ion-exchange [7], ultrafiltration [8] and so on. Compared with these conventional techniques, adsorption is a simple, economical and efficient method for the removal of copper from very dilute solutions [9, 10]. With the rapid development of adsorbents and microbiology, more and more researchers [11, 12] have focused on the use of biosorbents such as yeast, bacterial and fungi since the biosorptive removal procedure does not produce chemical sludge.

Soil is a dynamic and multi-component system, natural nutrient for microbe and abundant culture collection storage for humans. Recent studies [13, 14] indicated that the microbial strains isolated from contaminated soils have excellent removal capacity to heavy metals.

In this paper, four strains of bacteria were isolated from soil polluted by copper and were produced as biosorbents to remove copper from aqueous solution. The bacterium having maximum absorption ability to copper ions was selected and its biosorptive removal performance was also studied.

2. Experimental

2.1. Reagents and Solutions

GBW 08615 (1 000 mg/L) was a produce of Chemistry Department of National Institute of Metrology. Copper standard solutions were prepared from GBW 08615. Copper stock solutions were produced by

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dissolving its high purity compounds in deionized water. Copper solutions for polluting soil were produced by dissolving $CuSO_4$ $5H_2O$ (analytical regent) in distilled water. Other chemicals were analytical regents. Soil sample was collected from natural environment locally. Nutrient agar and nutrient broth were prepared in our laboratory.

2.2. Instruments

An atomic absorption spectrometer (model WFX-1F2B) equipped with deuterium background corrector was used for the measurement of copper concentration. The measure mode was apex with D lamp correcting baseline. An air-acetylene burner and a copper hollow cathode lamp were used too as parameters 1.5/7.0 combustion-supporting ratio, 4.5 mA lamp current, 324.8 nm wavelengths. The slit width was 1.0 nm. Separation was done by a LDZ5-2 model table-centrifuge. The pH values were measured by a PHS-3CT pH meter. A thermostat water bath shaker (model CHA-S) was used too.

2.3. Bacteria Isolation

200.0 g soil was added to 1000 mL beaker which contains 0.5 g $CuSO_4$ and 500 mL distilled water. The mixture was stirred overnight for three days. Then the soil was separated from mixture by filtration. 1.0 g of this soil was mixed with 10.0 mL 0.85% (w/v) sterile saline solution and plated on nutrient agar. Four colonies with different morphologies were chosen at random and then purified by sub-culturing. All operation were done in an axenic environmental.

2.4. Biosorbents Preparations

The bacterial isolate was incubated in a nutrient broth at 30 ℃, 125 rpm and pH 7.0. The biomass was separated by centrifugation at 4500 rpm for 10 min and washed successfully by distilled water. Then it was dried at 80 ℃ for 24 h. The dried biomass was crushed by mortar and sieved to 150 μm for use as biosorbents for removal of copper from aqueous solution.

2.5. Biosorptive Experiments

Erlenmeyer flask was orderly added 50 mL copper solutions of known concentrations, 1 mol L^{-1} H_2SO_4 for adjusting the pH to study value, 1.0 g biosorbents made early. The flask was settled in thermostat water bath shaker at 125 rpm. Half an hour later, the biosorbents was separated from the reaction mixtures by centrifugation at 1 000 rpm for 10 min and the determination of copper ions in supernatants was done by flame atomic absorption spectrometer. GBW 08615 was used for checking the instrument response for every 10 readings. Blank tests that have not add biosorbents was carried out to avoid the error caused by chemical precipitation and sorption on vessel walls. All experiments were worked three times. The mean value and relative error were calculated and evaluated. According to the average, the adsorption was calculated by substraction method.

3. Results and Discussions

3.1. Selection of Bacteria

For adsorptive removal of copper from aqueous solution, adsorbent is the most important factor that influent the adsorption. The adsorptive ability of four bacteria was investigated separately. The results were shown in Fig. 1. It indicated that the bacterial 1 has maximum biosorption capacity compared with the other bacteria. The bacterial 1 was selected to produce biosorbents used in follows experiments.
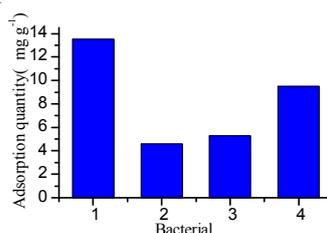

Fig. 1: Adsorption ability of bacteria isolated from soil in this work

3.2. Choice of pH

The pH of adsorption solution is another parameter that influent the adsorption ability evidently. The studies [15, 16] reported that the functional group in biomass chelate with the metal ions in the process of biosorption. So the optimum biosorption pH should be the pH which is suitable for chelating. And the pH should be low enough to avoid the chemical precipitation. In order to investigate the effect of pH of adsorption solution on adsorption, the pH was adjusted to 1.0-6.0 by vitriol solution and then contacted with absorbents. The adsorptions in different pH were calculated and listed in Tab. 1. As can be seen from the Table, the optimum pH value for biosorption of copper was 5.0.

Tab. 1: Effect of pH on adsorption

pH	Blank test	Adsorption (mg g^{-1})
1.0	0.0	0.0
2.0	0.0	0.1
3.0	0.0	5.1
4.0	0.0	9.5
5.0	0.0	13.2
6.0	9.2	16.7

3.3. Effect of Contact Time

In the process of biosorption, the contact time should long enough the biosorbents adsorbed maximum copper ions. But too long contact time makes the method inefficiency. To find the shortest contact time, different contact time from 5-80 min was investigated by picking up 3 mL samples and determination every 5 min. The effect of contact on adsorption was calculated and recorded as Fig. 2. The results showed that the recovery of copper improved with the contact time up to 30 min. Above 30 min, the recovery of copper changed seldom. So 30 min were selected as contact time in sequent works.
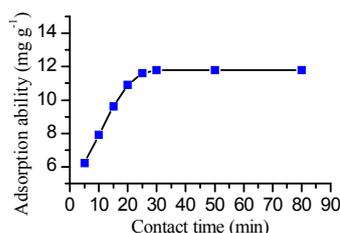

Fig. 2: Effect of contact time on adsorption ability of bacterial 1

3.4. Effect of Initial Copper Concentration

At pH 5.0 and contact time 30 min, 25-300 mg L^{-1} copper aqueous solutions were used to evaluate the effect of initial concentration on the biosorption capacity of bacterial 1. The adsorption at different initial concentration was showed in Fig. 3. The adsorption capacity improved first with the improving of initial concentration. And then the value changed seldom with the initial concentration changing. The results indicated that the bacterial 1 can successfully remove copper ions from 200 mg L^{-1} solution or lower.
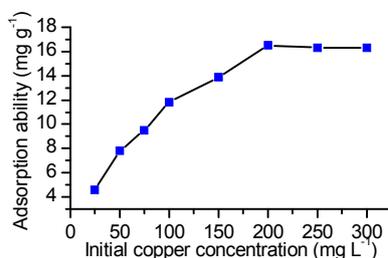

Fig. 3: Effect of initial concentration on adsorption ability of bacterial 1

3.5. Adsorption isotherms

Adsorption isotherm provides a relationship between the concentration of copper ions in solution and the amount of copper ions adsorbed onto the adsorbent when both phases are at equilibrium. There are two widely accepted adsorption isotherm models which are namely Freundlich [17] and Langmuir [18] models. In this study, their constants have been calculated by the data gained from frontal experiments. The results are

shown in Tab. 2. The regression coefficients were near to or more than 0.99. It suggests that the biosorption of copper on bacterial 1 can be successfully described by Langmuir isotherm and Freundlich isotherm. As the regression coefficient of Langmuir is higher than that of Freundlich, Langmuir equation provides a better correlation with the experimental data in studied concentration range.

Tab. 2: Langmuir and Freundlich constants and regression coefficient

Langmuir			Freundlich		
Q_0	b	R	K_f	n	R
19.88	0.0188	0.996	1.53	2.24	0.987

4. Conclusions

The bacterial 1, isolated from soil, can be produced as low-cost and effective biosorbents for the removal of copper from aqueous solutions. The adsorption was affected evidently by factors such as initial pH of copper solution, contact time and initial concentration of copper solution. At 25 ℃, the optimal initial pH was 5.0. Initial concentration of copper solution should lower than 200 mg L^{-1}. After half an hour, the biosorption is near equilibrium. The maximum adsorption of copper on bacterial 1 was 16.27 mg g^{-1} and the recovery ratio was 16.7%. The experimental data correlated well with Langmuir isotherm and Freundlich isotherm. In industrial use, the recovery ratio can be improved by settling adsorbents in series.

5. References

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