

Heavy Metals Removal from Wastewater by Magnetic Field-Magnetotactic Bacteria Technology

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Introduction

Plating, electron devices and other industries frequently generates large quantity of wastewater containing high levels of toxic heavy metal ions, such as copper, cadmium, nickel and lead, which are drastically harmful to aquatic and terrestrial life. Many traditional methods such as chemical precipitation, solvent extraction and ion-exchange had been helpful to relief the harmful situation. All these methods, however, were not effective when the metal ion concentration is lower than 100 mg l^{-1} , and often involve high capital and operational costs and may also be associated with the generation of secondary wastes^[1]. In recent years, several studies suggested that many algae, yeasts, bacteria and other fungi were known to be capable of concentrating metal species from dilute aqueous solutions and accumulating them within their cell structure. Compared with the conventional methods, the biosorption process was more economical, efficient and environmentally friendly^[2]. However, the serious problem of the biosorption technology was difficult to separate the microorganisms which has loading metal ions from the aqueous solution.

Magnetotactic bacteria (MTB), first discovered by Blakemore^[3] in 1975, could be a feasible alternative to resolve the problem. MTB possess a magnetic moment due to the presence of membrane bounded crystals called *magnetosomes* (MS) within their intracellular. The crystals, usually membrane bound crystals of magnetite (Fe_3O_4 or Fe_3S_4) and range in size from 30~60 nm, enable the bacteria to orient and migrate along the local magnetic field lines. Therefore, the special property of MTB could be used in the removal and recovery of heavy metal and precious metal ions from solution. Previous work focused specifically on two aspects: one is the growth condition of MTB and MS^[4, 5], and the other is the magnetic movement of MTB in different magnetic intensity^[6,7] and the effects of various sizes of separators^[8,9]. However, study on the biosorption conditions of precious metals ions on MTB and Equilibrium models of the biosorption system which are crucial to develop a systematic process for removal and recovery metals using MTB as sorbents were very limited.

In this paper, the primary adsorption parameters including the pH value and temperature of the solution, adsorption time, initial metal ion concentration and the biomass concentration were investigated in the biosorption of Cu (II) ions on MTB. And the Langmuir, Freundlich equilibrium models and the pseudo second-order kinetic model were studied for the fundamental knowledge of adsorption

equilibrium and adsorption kinetics of Cu (II) ions.

Theory

Equilibrium adsorption model

Several isotherm models were used to describe the equilibrium between adsorbed metal ions on the cell (q_{eq}) and unadsorbed component remaining in solution (C_{eq}) at constant temperature. The most widely used isotherm equation for models equilibrium is the Langmuir equation, based on the assumption that there is a finite number of binding sites which are homogeneously distributed over the adsorbent surface, these binding sites have the same affinity for adsorption of a single molecular layer and there is no interaction between adsorbed molecules^[10]. The linear form of Langmuir model is:

$$\frac{C_{eq}}{q_{eq}} = \frac{1}{Q^0 b} + \frac{C_{eq}}{Q^0} \quad (1)$$

where Q^0 is the maximum value of q_{eq} , and b is a constant related to the affinity of the binding sites. Then, a plot of C_{eq}/q_{eq} versus C_{eq} should indicate a straight line of slope $1/Q^0$ and an intercept of $1/bQ^0$.

The Freundlich expression is an empirical equation based on sorption on a heterogeneous surface, suggesting that binding sites are not equivalent and/or independent. The the linear form of the Freundlich equation is presented as:

$$\lg q_{eq} = \lg K_F + \frac{1}{n} \lg C_{eq} \quad (2)$$

where K_F is an indication of the adsorption capacity of the adsorbent, and n indicates the effect of concentration on the adsorption capacity and represents the adsorption intensity. K_F and n can be determined from the slope and intercept of the linear plot of $\lg q_{eq}$ versus $\lg C_{eq}$.

Adsorption kinetic model

In order to investigate the mechanism of biosorption and potential rate controlling step such as mass transport and chemical reaction process, kinetic models have been used to test experimental data. Numerous studies reported that the pseudo first-order Lagergren kinetics and the pseudo second-order kinetics were available for the sorption of metals^[11]. Furthermore, in most cases the first-order equation of Lagergren does not fit well for the whole range of contact time and is generally applicable over the initial 20–30 min of the sorption process. On the contrary, the pseudo second order equation predicts the behaviour over the whole range of adsorption and is in agreement with an adsorption mechanism being the rate controlling step^[12]. The integrated and linear form of the pseudo second-order adsorption kinetic rate equation is expressed as:

$$\frac{t}{q_i} = \frac{1}{k_{2i} q_{eqi}^2} + \frac{1}{q_{eqi}} t \quad (3)$$

where, k_{2i} was the rate constant of each component for the second-order biosorption ($\text{g mg}^{-1} \text{min}^{-1}$), q_{eqi} was the metal uptake per unit mass of cells at equilibrium (mg g^{-1}). The plot of t/q_i against t should give a linear relationship, from which q_{eqi} , and $k_{2,i}$ could be determined from the slope and intercept of the plot and there is no need to know any parameter beforehand^[13].

Material and methods

Preparation of the microorganisms for biosorption

Water and sediment samples were taken from an aeration tank of wastewater treatment plant in Tingjin. Bottles filled to approximately two-thirds their volume with sediment and culture medium^[14] in the ratio of 2:1. The loosely covered bottles were left undisturbed in dim light at room temperature (22° C). After the growth period (almost a month), MTB was harvested using the “special-made collecting apparatus” recommended by Matsunaga^[15] and washed twice with deionized water to remove the traces of medium constituents. Then, the biomass was concentrated by centrifugation at 4000rpm from the medium for the following biosorption studies.

Biosorption process

The initial solution of Cu (II) (500 mg l⁻¹) was prepared by dissolving a weighed quantity of Copper Sulphate Pentahydrate (CuSO₄•5H₂O, AR) in deionized double-distilled sterilized water, and the solutions were diluted to different concentration levels using deionized water.

1) In order to determine the optimum conditions for biosorption of Cu (II) metal ions by MTB, the experiments were conducted in 250 ml conical flasks containing 100 ml of metal ion solution adding 0.1~0.5 mg (wet-weight basis) centrifuged MTB at the temperature 15~35°C and pH 1~13 with 0.1M HCl and 0.1M NaOH solution. The flasks were agitated at 130 rev min⁻¹ on a shaker for 1 h, allowing sufficient time for adsorption equilibrium.

2) To determine the biosorption isotherms, initial concentrations of Cu (II) ions were designed as seven typically levels, 20, 40, 80, 200, 300, 400 and 500 mg l⁻¹.

3) In the kinetic experiments, 10 ml samples were taken before mixing MTB solution and metal-bearing solution and at predetermined time intervals (0.5, 1, 3, 5, 10, 30, 60min) for determining the residual metal ion concentration in the solution.

Biosorption with and without cells were conducted in order to investigate the real sorbents in the sorption process. Each experiment above was repeated three times and the following data were given as average.

Measurement of metal ions

At the end of the mixing period, 10 ml of the samples were taken and filtered with millipore filters of 0.22 µm pore size, and the filtrate was collected for Au (III) and Cu (II) analysis. The concentration of Au (III) and Cu (II) in solution was determined using HITACHI 180-80 Atomic Absorption Spectrophotometer.

Results and discussion

The uptake of metal ion q_e (mg g⁻¹) and the adsorption yield Y (%) were selected as the test criteria in this paper. q_e and Y were calculated from Eq. (4) and Eq. (5), respectively.

$$q_e = \frac{C_0 - C_e}{m} \quad (4)$$

$$Y = \frac{C_0 - C_e}{C_0} \times 100\% \quad (5)$$

where C_e (mg l^{-1}) was the free metal-ion concentration in solution at equilibrium, C_0 (mg l^{-1}) was the initial metal-ion concentration, m (g l^{-1}) was the biomass concentration.

The equilibrium studies

1) The effect of initial pH

Cell walls have binding sites that are considered as being part of ionizable groups such as carboxyl, hydroxyl, amino and imino. At highly acidic pH values, cell wall ligands would be closely associated with H_3O^+ which restricts metal ions access to ligands as a result of repulsive forces. It is to be expected that as pH values are increased, more ligands with a negative charge would be exposed with subsequent increase in attraction for positively charged metal ions^[16]. However, high efficiency in adsorption process of Cu (II) ions (Fig.1) had obtained at highly acid solution. Similar pH effect on the adsorption trend had also been obtained by Nasernejad^[17] and Gamez^[18]. Taking into account that the industry effluents and leaching liquid were strong acid, the working adsorption pH was chosen as 5.0 in other experiments.

2) The effect of temperature

The effect of temperature on adsorption of Cu (II) ions on MTB were studied, and shown in Fig. 2, At the temperature in the range of 15~35°C, Cu (II) ions were effectively adsorbed to the biomass at any designed values of temperature. The adsorption yield of Cu (II) ions was obtained 97.8 ~ 98.0 %, and the uptake was 7.82~7.84 mg g^{-1} . A reasonable explanation might be that the actual attachment of the metal ions on the cellular surface was mainly chemisorption and ion exchange, but not physical adsorption, for the latter could be affected easily by thermal movement of the ions with high temperature. Now that temperature of biosorption process was not significant on the uptake and the adsorption yield for the biosorption of Au (III) and Cu (II) ions, room temperature, 25 °C, was selected in the following experiments.

3) The effect of the biomass concentration

As shown in Fig.3, the maximum uptake of Cu (II) ions was found to be 7.9~8.0 mg g^{-1} with the biomass concentrations of 3.0~5.0 mg g^{-1} , and the adsorption yield was 99.99~100%. Therefore, 5.0 mg g^{-1} was as the optimum biomass concentration in the following experiments.

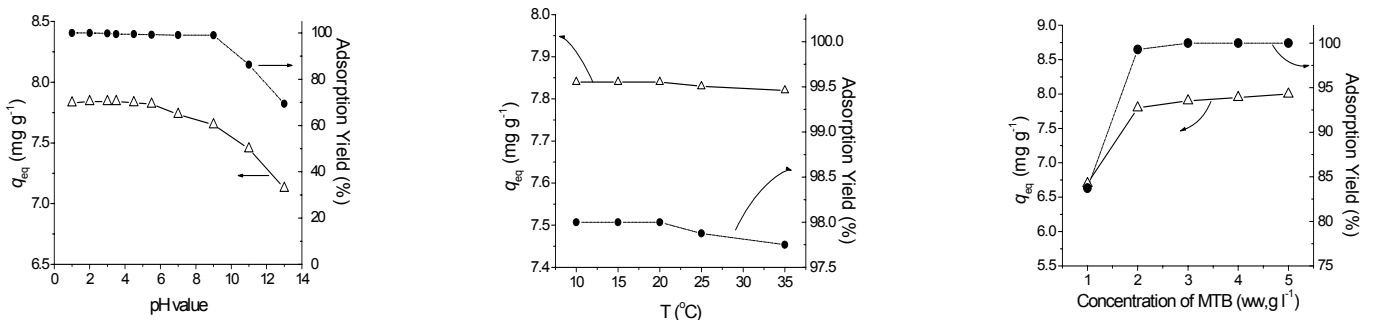


Fig.1 Effect of pH value on adsorption of Cu (II) ions on MTB (T=25°C, MTB 3.0 g l⁻¹, (pH 5.0, MTB 3.0 g l⁻¹, C₀=80 mg l⁻¹, 130 rev min⁻¹, 60 min)

Fig.2 Effect of temperature on adsorption of Cu (II) ions on MTB (T=25°C, pH 5.0, MTB 3.0 g l⁻¹, C₀=80 mg l⁻¹, 130 rev min⁻¹, 60 min)

Fig.3 Effect of biomass concentration on adsorption of Cu (II) ions on MTB (T=25°C, pH 5.0, 130 rev min⁻¹, C₀=80 mg l⁻¹, 60 min)

4) Equilibrium isotherms

The adsorption isotherm of Cu (II) ions was given in Fig.4. To study the biosorption capacity of MTB for Cu (II) ions, the linearized Langmuir and Freundlich adsorption models were used for the mathematical description at the optimum conditions obtained above. The model profiles are presented as solid lines and the experimentally obtained values are given by symbols in Figs.5~6. The individual Langmuir and Freundlich constants evaluated from the isotherms and their correlation coefficients were listed in Table 1. High correlation coefficients(0.9996 and 0.9428) were found in both isotherm models, so both models were suitable for describing the biosorption equilibrium of Cu (II) ions on MTB.

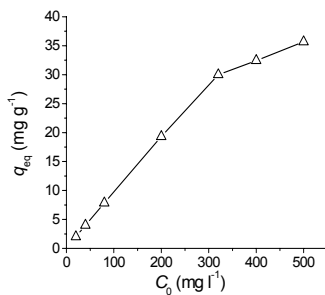


Fig.4 Equilibrium isotherms for Cu (II) ions biosorption on MTB(T=25°C, pH 5.0, MTB 3.0 g l⁻¹, 130 rev min⁻¹, 60 min)

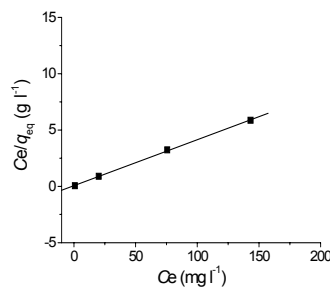


Fig.5 The Langmuir isotherms for Cu (II) ions biosorption on MTB(T=25°C, pH 5.0, MTB 3.0 g l⁻¹, 130 rev min⁻¹, 60 min)

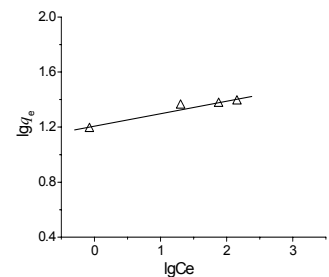


Fig.6 The Freundlich isotherms for Cu (II) ions biosorption on MTB (T=25°C, pH 5.0, MTB 3.0 g l⁻¹, 130 rev min⁻¹, 60 min)

Table 1 The Langmuir and Freundlich constants and their individual correlation coefficients

Langmuir model			Freundlich model		
Q ⁰ (mg g ⁻¹)	b(l mg ⁻¹)	R ²	K _F	n	R ²
24.3013	1.8072	0.9996	16.0901	11.0241	0.9428

Kinetic studies

Microorganism was known to accumulate metals by two distinct stages containing passive physical adsorption and active uptake. Initially, metal ions diffused to the surface of the cell walls where they bind to the active sites on the cell surface formed by the presence of various chemical groups such as the carboxylate, hydroxyl, amino and phosphate which exhibit affinity for the metal ions. Generally, such adsorption was very fast, reversible, and not a limiting factor in biosorption kinetics when dealing with dispersed cells.

Similar results had been obtained in the time dependence experiments (Fig.7), and showed that the adsorption yield of Cu (II) ions on MTB increased rapidly up to 96.13% within the beginning 5 min. However, thereafter the amount of adsorbed metals ions did not significantly change with time, 98.0%

were achieved at the final biosorption equilibrium time. The pseudo second-order kinetic model was applied to the experimental data (Fig.8). High correlation coefficients in Table 2 assumed that the external mass transfer limitations in the system can be neglected and biosorption is sorption controlled.

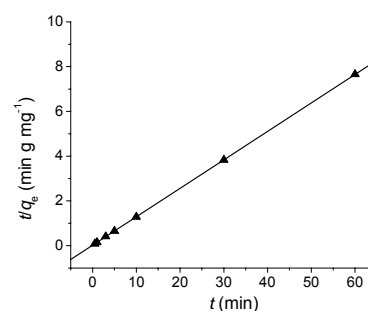
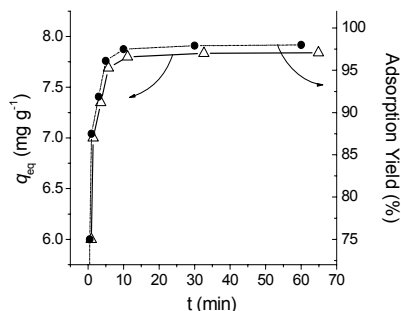


Fig.7 Adsorption kinetics of Cu (II) ions on MTB (T=25°C, pH 5.0, MTB 3.0 g l^{-1} , $C_0=80 \text{ mg l}^{-1}$, 130 rev min^{-1}) Fig.8 Comparison of t/q_e vs. t plots for biosorption of Cu (II) ions on MTB

Table 2 The pseudo second-order rate constants and correlation coefficients

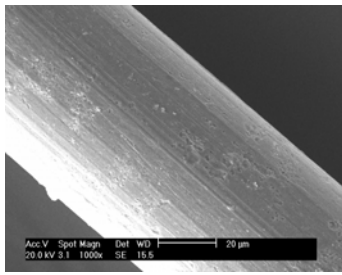
The pseudo second-order model		
q_{eq} (mg g^{-1})	k_2 ($\text{g mg}^{-1} \text{min}^{-1}$)	R^2
8.0006	63.4236	1

Separation of metal-loaded MTB from the solution

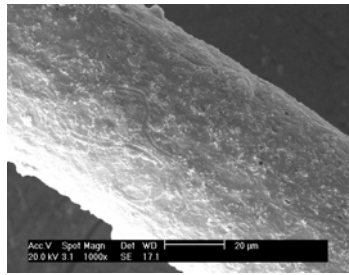
Strings separator with a high gradient magnetic field was used to study separation efficiency of metal-loaded MTB from the solution, and the focusing was the intensity of magnetic field and the place of wire casing. The separation efficiency is very good when magnetic field intensity is 100 Gauss, and no distinct improvement with higher magnetic field intensity. Moreover, the separation efficiency is better when metal wires are perpendicular than parallel to magnetic line. The experiment result shows that Cu (II) ions concentration decrease from 100 mg l^{-1} initially to less than $5 \mu\text{g l}^{-1}$ at optimum conditions (T=25°C, pH 5.0, MTB 3.0 g l^{-1} , $C_0=80 \text{ mg l}^{-1}$, 130 rev min^{-1}).

SEM image of wires

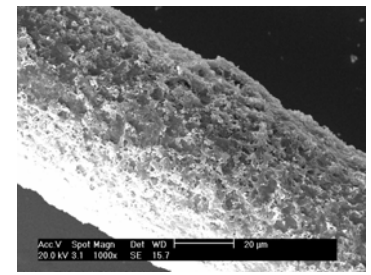
At the same time, the wires unloading and loading MTB are observed by Scanning Electron Microscope (SEM). The SEM image of the wire untouched (Fig.9 (a)) shows the diameter of wire is 67 μm , and the surface layer of wire is smooth. The diameter of the wire parallel to the magnetic line (Fig.9 (b)) increases to 70.3 μm , and the wire surface is rough. The wire perpendicular to the magnetic line (Fig.9 (c)) is 73 μm , and the surface is covered with bacteria layer. This shows the wire perpendicular to the magnetic line has the highest separation efficiency.



(a) the wire untouched



(b) the wire parallel to the magnetic line



(c) the wire perpendicular to the magnetic line

Fig.9 The SEM of the wire (magnify 1000 times)

Conclusion

1) In this work, MTB had been successfully used as the adsorbent for adsorption of Cu (II) ions from artificial wastewaters. The results show that pH and biomass concentration highly affected the uptake capacity of the biosorbent for the biosorption of Au (III) and Cu (II) ions. The optimum pH value for Cu (II) ions is 1.0~9.0, and the optimum biomass concentrations is 3.0 g l⁻¹, respectively. Temperature had no significant effect on adsorption of both metal ions. Time dependence studies showed that the adsorption equilibriums of both metals were achieved within 5 min.

2) The Langmuir and Freundlich adsorption models were used to predict the equilibrium uptake. Both models are suitable to describe the adsorption equilibrium data of Cu (II) ions, and Langmuir model is better. And the second-order kinetic model is very suitable for the experimental kinetic data with a high correlation coefficient of 1.0 at optimum conditions.

3) Separation of metal-loaded MTB from the solution is studied using separators with strings by applying a high gradient magnetic field. The separation efficiency is very good when magnetic field intensity is 100 Gauss, and no distinct improvement with higher magnetic field intensity. Moreover, the separation efficiency is better when metal wires are vertical than parallel with magnetic force line. At the same time, the wires loading MTB are observed by Scanning Electron Microscope (SEM). The diameter of wires after loading MTB increases from 67 to 73 μm.

So the MTB might be proposed as an alternative to more costly traditional methods for the removal and recycling of copper from wastewater or leaching liquid from solid waste containing Cu (II) ions. The equilibrium biosorption and kinetics results are essential for further works, especially for the sorption process evaluation and design, offering the possibility of an effective, simple, and relatively accurate sorption process scale-up.

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