Praise Worthy Prize

International Review of Chemical Engineering (I.RE.CH.E.), Vol. 4, N. 3
ISSN 2035-1755 *May 2012*
Special Section on Open Door Initiative (ODI) - 2nd edition

Molecular Simulation on Magnetotactic Bacteria's Adsorption in Aqueous Cu^{2+} Solution

Huaigang Cheng[1,2], Huiping Song[1], Fangqin Cheng[1]

Abstract – *Magnetotactic bacteria is one of the biosorbents for heavy metal elimination from industrial effluents. In order to investigate the effects of microscopic intermolecular forces on the adsorption of Cu^{2+}, molecular dynamics simulation was performed. The acid-base titration experiments were carried out to determine the functional adsorption groups on magnetotactic bacteria surfaces, and then a bacterium cell model consisting of $-PO_3H$, -OH, -COOH and magnetosome was established. The contributions of the functional groups to the adsorption of Cu^{2+} were simulated and analyzed from the aspects of electrostatic interaction and thermal motion. The simulation showed that the adsorption of Cu^{2+} was the combined results of both the electrostatic attraction and the particle's thermal motion. There was the different attraction strength for each of the functional groups. The simulation results also indicated that the diffusion tendency of Cu^{2+} towards $-PO_3H$ was the greatest, followed by that towards -OH, and that towards-COOH weakest. These conclusions may provide a new theoretical reference to the development and application of bio-magnetic separation process.* ***Copyright © 2012 Praise Worthy Prize S.r.l. - All rights reserved.***

Keywords*: Magnetotactic Bacterium, Molecular Dynamics Simulation, Adsorption, Diffusion*

I. Introduction

In recent years, the research of biosorption have received more attention because of their potential applications in environmental protection and recycling precious metals from waste water. Among the bio-absorbents, magnetotactic bacterium (MTB) [1], [2] has the characteristics of not only the selective adsorption of heavy metals but also the unique magnetotaxis presented by the magnetic Fe_3O_4 particles existed in its body. The heavy metal loaded MTB could be rapidly removed from the waste water with the help of high-gradient magnetic field, which artfully avoided the problem that ions were easily adsorbed but hard to separate from waste water in the conventional water treatment processes. A series of researches showed that the technology combining MTB with high gradient magnetic field [3] could effectively process the waste water containing Cu^{2+}, Ni^{2+} or other heavy metal ions, having the characteristics of fast adsorption rate and large adsorption capacity [4],[5],[6]. At the same time, many other researches also demonstrated the potential applications of these bacteria in wastewater treatment. Microbes have a certain affinity for capturing ions, which comes from the microbial metabolism. Therefore, many microbes can be used to adsorb metal ions.

While the magnetotactic bacteria showed a strong adsorption bias for heavy metal ions. However, besides the biochemical properties of the bacteria themselves, the intermolecular forces between bacteria and heavy metal particles and the particles' thermal motion should also be the important factors in promoting the adsorption of heavy metal ions. The promotion mechanism was not clear as far. For the practical application of MTB in the waste water treatment, the mechanism of the adsorption selectivity is of great importance, whereby this paper will carry out research in this area.

With the help of molecular simulation methods, the micro-level analysis of the interaction between ions and MTB surface groups was carried out from the perspective of the ionic motion. The objective of this work was to provide a new theoretical reference for the in-depth study of the waste water treatment process using MTB.

II. Experimental and Simulation Details

II.1. Determination of MTB Groups

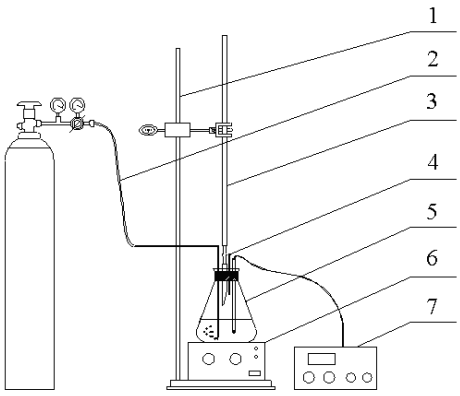
The bacterial surface groups were determined by titration measurements, and then the molecular dynamics simulation was executed to examine the adsorption tendency of ion on the bacterial surface.

The common method for the analysis of bacterial surface groups is the acid-base titration [7],[8]. The experimental setup was shown in Fig. 1. 10mL biomass (2.5g/L in bacteria concentration) and 90mL deionized water were added into a conical beaker, adjusting pH at 2 with drops of HNO_3 solutions. After the continuous stirring with a magnetic stirrer at the temperature of 25

Manuscript received and revised April 2012, accepted May 2012

°C for 1 hour, the titration using a standard solution of NaOH (0.1 mol/L) was performed in the N_2 atmosphere. During the titration process, a digital pH meter was used to monitor and record the solutions' pH value.

The fitting analysis of acid-base titration curve using the surface complexation model was done to obtain the dissociation constant *Ka* of group. Generally, each functional group corresponded to a specific *Ka*, thus the types of bacterial groups could be found out on the basis of dissociation constants in literatures. Thus, the structure of MTB can be determined accordingly.



1-bracket; 2-nitrogen; 3-base burette; 4-exhaust pipe; 5- conical beaker; 6-electromagnetic stirrer; 7-pH meter

Fig. 1. Equipment Drawing of Acid-base Titration

II.2. Simulation Methods

In the simulation, the Coulomb force and the van der Waals force were calculated to examine the intermolecular attractions between the ion and the bacterial groups, with the consideration of the ionic thermal motion. The ion was imagined to be a charged hard-sphere, ignoring its hydration. A single group was placed into the system containing a Cu^{2+} and 1000 H_2O molecules. A structured programming language was used for this simulation using NVT ensemble.

The molecular dynamics simulation for 50×10^{-12}s was executed after 5000 steps of energy minimization and 20×10^{-12}s of relaxation at 298K. Then the Cu^{2+} moving trajectory and its equilibrium position away from the groups were analyzed to determine the tendency of ion adsorption.

III. Results and Discussion

III.1. Effects of Groups on the Ionic Diffusion

According to the fitting of acid-base titration curve, three logarithm values of *Ka*, 3.5, 6.2 and 9.6, were obtained. The literatures showed that these *pKa* values should represent -COOH, -PO_3H and -OH groups at the values of 1.7~4.7 [9],[10], 6.1~6.8 [11],[12] and 9.5~13 [13], respectively. Furthermore, the amounts of these groups could also be got from the titration experiments [14], i.e., 0.3mmol/g for -COOH, 0.5mmol/g for -PO_3H and 0.6mmol/g for -OH. The conclusion that -COOH, -PO_3H and -OH were the main groups on MTB surface was in agreement with the literatures [15],[16].

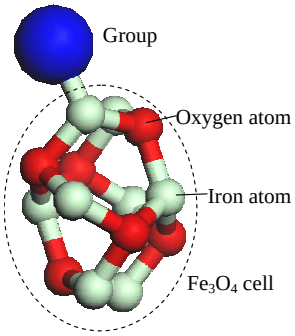


Fig. 2. The structure of MTB unit cell

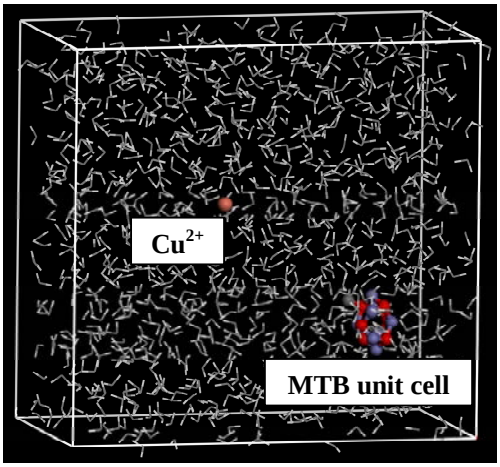
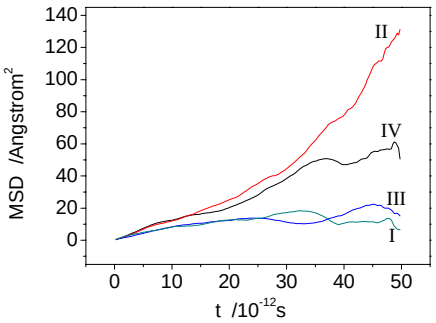


Fig. 3. The simulation system of MTB adsorption

Therefore, the above groups were fixed at the surface of Fe_3O_4 cell to represent a MTB unit, as shown in Fig. 2. Then in the simulated aqueous system as shown in Fig. 3, a Cu^{2+} and 1000 H_2O molecules was added and the molecular dynamics simulation was performed. The mean square displacements of Cu^{2+} under the action of these groups were calculated, as shown in Fig. 4.



Functional group in the aqueous system:
I, Fe_3O_4-PO_3H; II, Fe_3O_4-OH;
III, Fe_3O_4-COOH; IV, Fe_3O_4

Fig. 4. Mean Square Displacement(MSD) of Cu^{2+}

From Figure 4, the displacements of Cu^{2+} could be seen in the Cu^{2+}-Fe_3O_4 system. Generally, one of the reasons for Cu^{2+} diffusion should be the thermal motion of ion itself. The thermal motion existed in any system, but the displacements of the ions in each system were not the same, which should be the results of the different micro-forces derived from each of the functional groups.

Furthermore, there were not the same moving intensifies in these systems, indicating the different strength of electrostatic attraction by these groups. In the system containing -OH, the moving intensifies of Cu^{2+} were obviously larger than those in other systems, which showed that the group's electrostatic attraction could make an impact on the ions movement. -OH was an electron-donating group, which could strengthen the electronegativity of MTB unit cell and thus its attracting force to ion. In contrast, -PO_3H and -COOH were electron-withdrawing groups, so that Cu^{2+} tended to move slightly under their influences. This rule was exactly reflected in Figure 4.

III.2. Effects of Groups on the Capture of Ion

In Figure 4, the mean square displacements demonstrated the Cu^{2+} diffusions, but not characterized the diffusion directions. No information could be got whether Cu^{2+} was attracted to or repeled away from the MTB unit cell, or just moving around MTB.

The capture possibility of Cu^{2+} by the groups could be calculated from the diffusion trajectories. Figure 5 showed the probabilities of ions at different locations around the MTB unit cell. The electrostatic attraction of Cu^{2+} suffered prompted its movement towards the MTB unit cell, while thermal motion prompted it to get rid of the gravitational constraints and move away. The balance of these two forces would result in the particle's fluctuation near the equilibrium position. The distances of the equilibrium positions to MTB and the range of fluctuation region indicated the strength of the combined effects of these two forces.

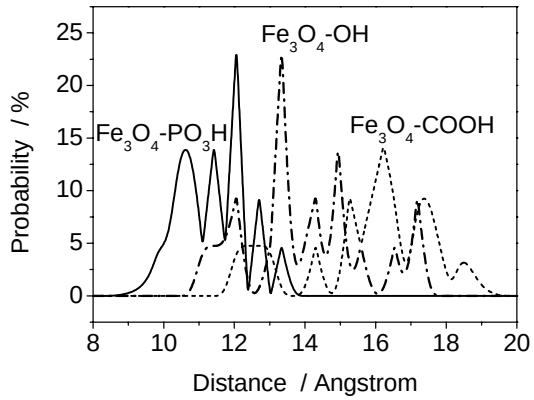


Fig. 5. Probability distribution of Cu^{2+} diffusion

It can be seen from Figure 5, -PO_3H was of biggest attraction to Cu^{2+} in those groups. The fluctuation distance of Cu^{2+} around Fe_3O_4-PO_3H ($9.0\sim14.0\times10^{-10}$m) is the shortest, that around Fe_3O_4-OH the moderate and that around Fe_3O_4-COOH the longest.

The same conclusion could be drawed from the location at the maximum probability of Cu^{2+} trajectory. Around Fe_3O_4-PO_3H, Cu^{2+} was most likely to occur at a distance of 12.0×10^{-10}m away, where the probability of appearing was 23%.

In the same simulation conditions, around Fe_3O_4-OH and Fe_3O_4-COOH, the maximum probability points of Cu^{2+} occurrence were located at 13.5×10^{-10}m and 16.3×10^{-10}m, respectively, which were longer than that around Fe_3O_4-PO_3H.

Thus, the conclusion was that the diffusion tendency of Cu^{2+} towards Fe_3O_4-PO_3H was the strongest, followed by that towards Fe_3O_4-OH, and that towards Fe_3O_4-COOH the weakest.

III.3. Verification Using Experiments

The simulation indicated that there were different abilities for each groups to capture ions. Such a conclusion could be verified by adsorption experiments. To do this, the chemical treatment was carried out to inactivate one of the functional groups (-COOH, -OH and -PO_3H) on MTB in the adsorption process. Methanol and hydrochloric acid were added in the biomass to turn -COOH on MTB surface into ester, which made the -COOH blocked. Esterification was also executed by adding acetic anhydride to inactivate -OH. Triethyl phosphite and nitromethane were used to dispose of -PO_3H.

The MTB adsorption capacity was changed after the chemical treatment, as shown in Fig. 6. The group-blocked MTB lost a large proportion of adsorption capacity, thus it could be conjectured that all the three groups, i.e., -COOH, -OH and -PO_3H, had the function to adsorb Cu^{2+}. The adsorption capacity of -COOH blocked MTB changed most among these systems, indicating that -COOH was the major functional group in the adsorption process.

This phenomenon seemed conflict with the simulation results that -PO_3H was the main group for adsorption. The explanation was that there was chemical adsorption happened in the real adsorption experiments. In this paper, the simulation was used to evaluate the diffusion of ions. Comparing the time for reaching adsorption equilibrium, it could be found that the speed for ion's adsorption on -PO_3H blocked MTB was the slowest, i.e., 10 minutes were needed to reach equilibrium.

This revealed that the diffusion velocity of Cu^{2+} towards -PO_3H should be faster than those towards other groups; which meant that as for an individual group, -PO_3H had the strongest capture ability to Cu^{2+} by the influence of ionic diffusion.

From Figure 6, the capture abilities (i.e., adsorption speed of Cu^{2+}) of -OH and -COOH were weakened in turn, which was in agreement with the simulation results.

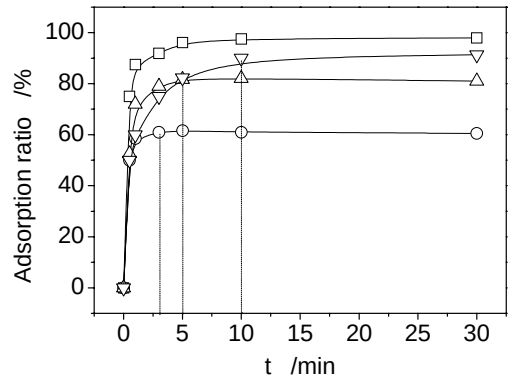


Fig. 6. Adsoption kinetics for Cu^{2+} on MTB in different systems

IV. Conclusion

The functional groups on MTB surface were determined by titration method, and then the model of MTB unit cell was established as an assemblage of -PO_3H, -OH, -COOH and Fe_3O_4. By calculating the probability profile of Cu^{2+} diffusion, the adsorption tendency of Cu^{2+} on MTB surfacial groups was estimated. The trajectory of Cu^{2+} showed that both the electrostatic attraction of groups and the thermal motion of ion itself exerted influences on the ionic diffusion and the adsorption bias. Furthermore, the strength of groups electrostatic forces were not the same for each other. The capture ability of groups to Cu^{2+} is -PO_3H, -OH and -COOH in strength order, respectively.

Acknowledgements

This work was financially supported by National Natural Science Foundation of China (No. 20906053) and (No. 51104097), Shandong Province Natural Science Foundation (No. ZR2009BQ002) and the Program of International Science and Technology Cooperation (No. 2012DFA91500).

References

[1] A.S. Bahaj, P.A.B. James, F.D. Moeschler, Low magnetic-field separation system for metal-loaded magnetotactic bacteria, *Journal of Magnetism and Magnetic Materials*, 177-181(1998)1453-1454.

[2] M.S. Marius, P.A.B. James, A.S. Bahaj, et al., Development of a highly magnetic iron sulphide for metal uptake and magnetic separation, *Journal of Magnetism and Magnetic Materials*, 293(2005)567-571.

[3] T.M. Petrova, L. Fachikov, J. Hristov, The magnetite as adsorbent for some hazardous species from aqueous solutions: A review, *International Review of Chemical Engineering (IRECHE)*, 3(2011)134-152.

[4] H.P Song, X.G. Li, J.S. Sun, et al., Application of a magnetotactic bacterium, Stenotrophomonas sp. to the removal of Au(III) from contaminated wastewater with a magnetic separator, *Chemosphere*, 72(2008)616-621.

[5] C.J. Sun, X.H. Yin, W. Ma, J.S. Sun, D.Z. Lu, Cultivation of magnetotactic bacteria and use for biosorption of heavy and precious metal ions, *Microbiology*, 37(2010)394-400.

[6] H.P Song, X.G. Li, J.S. Sun, Equilibrium and kinetic modelling of biosorption of Au(III) and Cu(II) on magnetotactic bacteria (MTB) *Chinese Journal of Chemical Engineering*, 15(2007) 847-854.

[7] H.P. Song, Selective biosorption behavior of precious metal ions on magnetotactic bacteria and gold recovery from Gold(III) contained solution, PhD Thesis, *China Tianjin University*, 2008. (In Chinese)

[8] Fourest E, Volesky B, Contribution of sulfonate groups and alginate to of Sargssum fluitans *Environmental Science and Technology*, 30(1996)277-282.

[9] B.Volesky, *Sorption and Biosorption*, Quebec, BV-Sorbex Inc., St. Lambert, Canada, 2003, pp. 41.

[10] N. Yee, L.G. Benning, V.R. Phoenix, et al., Characterization of infrared spectroscopic investigation, *Environmental Science and Technology*, 38(2004)775-782.

[11] T.J. Beveridge, R.G.E. Murray, Sites of metal deposition in the cell wall of Bacillus subtilis, *Journal of Bacteriology*, 141(1980)876-887.

[12] Xu Han, Yuk Shan Wong, Nora Fung Yee Tama. Surface complexation mechanism and modeling in Cr(III) biosorption by a microalgal isolate, Chlorella miniata. *Journal of Colloid and Interface Science*, 303(2006)365-371.

[13] J.Y. Wang, S.G. Zhu, C.F. Xu, Biological *Chemistry (3rd Edition)*, Higher Education Press, Beijing, 2002, pp. 131.(In Chinese)

[14] H.P. Song, H.G. Cheng, F.Q. Cheng, Simulation on biosorption of Ni^{2+} by magnetotactic microorganism in aqueous solution, *Ion Exchange and Adsorption*, 27(2011) 392-399. (In Chinese)

[15] H. Seki, A. Suzuki, S.I. Mitsueda, Biosorption of heavy metal ions on Rhodobacter sphaeroides and Alcaligenes eutr. phush16, *Journal of Colloid and Interface Science*, 197(1994)185-190.

[16] Y.S. Yun, B. Volesky, Modeling of lithium interference in cadmium biosorption. *Environmental Science and Technology*, 37(2003) 3601-3608.

Authors' information

[1]Institute of Resources and Environment Engineering, State Environment Protection Key Laboratory of Efficient Utilization of Coal Waste Resources, Shanxi University, Taiyuan 030006, China.

[2]Taiyuan National High-tech Industrial Development Zone, Taiyuan 030006, China.
Tel.: +86 351 7016893
Fax: +86 351 7016893
E-mail: chenghg@sxu.edu.cn (Fangqin Cheng)