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The effect of ion charge-mass ratio on adsorption of heavy metals on magnetotactic bacteria

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The magnetotactic bacteria have the properties of both capturing heavy metal ions and being quickly separated out from the wastewater, which makes them high quality adsorbents. The adsorption of ions usually shows selectivity in the multi component aqueous solutions. This paper investigated the mechanism of adsorption selectivity using the molecular dynamics method on the basis of periodic law of elements. A universal equation with respect to the mass, volume and charge of ions was deduced. Based on the analysis of the surficial properties, a model was built to describe the structure of magnetotactic bacteria using the organic groups. Then, the interface system of bacterium surface, aqueous solutions and heavy metal ions was developed and dynamics simulation was performed. It was found that the ion having smaller charge-mass ratio according to the periodic system of elements might be easier to be adsorbed. The ionic thermal motion could depress the adsorption of ions and might be one of the reasons which cause adsorption selectivity. Furthermore, the larger charge-mass ions were more inclined to be drifting away from the bacteria in the simulation.

Key words: Magnetotactic bacteria, heavy metal, adsorption, charge-mass ratio, periodic law of elements, molecular simulation.

INTRODUCTION

The wastewater containing heavy metals has always been a troublesome problem in the fields of chemical, petrochemical and metallurgical industry. Many separation methods have been applied to the treatment of wastewater, such as the mechanical, pyrometallurgical and hydrometallurgical recycling. As a novel wastewater treatment technology in recent years, the biosorption-magnetic separation process has been used to extract the metals from aqueous solutions. Magnetotactic bacteria were used in this process to adsorb metals and external magnetic field was subsequently used to quickly draw the metal loaded microorganism out of the wastewater. However, the utili-

zation of such a technology is still restricted by the vague understanding of adsorption selectivity in the multi-component aqueous system. For instance, it has been found that Cu (II), Ni (II) or Au (III) showed perfect adsorption behavior in their own solutions (Song et al., 2008). However, Cu (II) and Ni (II) would be depressed in adsorption when they co-exist with Au (III) (Song et al., 2007). That is, the magnetotactic bacteria are inclined to adsorb only one metal ion in the water system containing several cations. The industrial application of biosorption - magnetic separation needs the knowledge of which metal would be extracted and which one would be depressed in the water treatment process.

Recent years, many studies reported on the biosorption mechanism. It was found that the surface complexation, ion exchange, electrostatic attraction, redox and enzymatic promotion were all play roles in the adsorption process. With the extensive study of the biosorption of

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heavy metals, there are types of biosorbents. In recent studies, the biosorbents were grouped into three categories. The first is the bacteria (Lioyd et al., 1997; Merroun et al., 1998), including *Bacillus subtilis*, *Bacillus licheniformis*, *Pseudomonas*, colon bacillus, etc. The second is the fungi such as the yeast, white rot fungi, bread mold and *Penicillium chrysogenum*. The third is the algae such as brown algae, green algae. The reason for the interest of magnetotactic bacteria in the recycling of heavy metals lies in the bacterial paramagnetism properties. The magnetotactic bacteria contain a chain-like arrangement of magnetosomes (Hakho et al., 2004), which can make them attracted, moved and separated out from the water by a magnetic field. After the magnetotactic bacteria were first reported, they were widely studied in microbiology, bionics, geochemistry, magnetic materials, bio-pharmaceutical engineering and other fields. Great progress has been made.

It is well known that many microorganisms have the affinity to metal ions, which is derives from the requirements of the microbial metabolism. However, the affinity of the microorganisms to metal ions usually shows selectivity. A lot of metal ions can be perfectly adsorbed in their own single-component solution. However, when these metal ions co-exist in a multi-component solution, the adsorption selectivity appeared. This seems to imply the influence of the nature of ions on the adsorption process. It is interesting which ions will be adsorbed more easily on the surface of magnetotactic bacteria.

The objective of this paper was to examine the common regularity in the biosorption of different ions based on the periodic law of elements theory and then determine which elements will be easily adsorbed. This selective adsorption mechanism is of importance for the treatment of multi - component wastewater using magnetotactic bacteria as the biosorbent.

MATERIALS AND METHODS

The experimental analysis of the surficial groups was carried out to determine the structure of the magnetotactic bacteria. The acid-base titration (Fourest and Volesky, 1995) was used to determine the bacterial surface groups. The pH of the suspension containing 0.25 g/L biomass was adjusted to 2 with HNO_3 solution. After conditioning for 1 h, the suspension was titrated with NaOH solutions in the nitrogen gas flow. The pH value was monitored by a digital pH meter. The surface complexation model was used to fit the titration curve and determine the types of bacterial groups. Due to each functional group corresponding to a specific dissociation constant, the groups could be decided by contrasting experimental dissociation values with those in literatures. Therefore, the magnetotactic bacteria structure could be determined.

The adsorption process was studied using molecular dynamics method (Mackerell et al., 2004; MacKerell et al., 1998; Khavrutskii et al., 2009; Heinz et al., 2008). The Not (just) Another Molecular Dynamics program (NAMD) (Phillips et al., 2005; Humphrey et al., 1996) package was applied. NAMD was developed by the Theoretical and Computational Biophysics Group in the Beckman Institute for Advanced Science and Technology at the University of Illinois at Urbana-Champaign.

These groups determined experimentally were assembled together to create a sphere style in a virtual environment, which was used to describe the bacterial cell. Then, the simulated cell was placed into an aqueous cubic system containing a cation. Dynamics simulation was performed and the displacements of ions were calculated and compared with each other. By adjusting the molecular weight and electric charge, various cations were tested using this method. Thus, the relationship between the bacterial adsorption tendency and the charge-mass properties of various cations could be found.

RESULTS AND DISCUSSION

The work built a model comprising of water, magneto-tactic bacteria and ions. Then dynamics simulations were carried out using different ions. Comparing the displacements of various ions, the tendency of adsorption of the ions was evaluated. However, before those procedures, the model of ions must be first established. It was necessary to develop a universal or easy method to characterize the different ions. In this paper, the periodic law of elements was selected as a breakthrough point.

Periodic properties of ions

The bacterial surface was filled with charged groups. These groups can promote the adsorption of metal ions using the electrostatic attraction. Therefore, it can be speculated that the electronic activity of a metal ion determines its tendency to be adsorbed. The atomic absorption spectrophotometer was used to test and verify the electronic energy levels of some of the metal elements. According to the principle of atomic absorption spectrometry, electrons in atoms show many different energy levels. The lowest energy level is named the ground state and the remaining energy levels the excited states. The atoms will absorb a certain wavelength light and the outer electron moves from the ground state to the excited state generating the atomic absorption spectroscopy when the external energy such as a light provides energy to the ground state atoms. Thus, the atomic absorption spectroscopy reflects the atomic energy, which can be used to analyze the electronic activities of the metal atoms. Accordingly, the absorption wavelengths of the atoms of each element were measured, as shown in Figure 1.

Figure 1 demonstrates the regular changes in the adsorption wavelength as the increase of atom weight. Compared with the periodic table of elements (period 2 to 7 in Figure 1), it could be seen that the atomic absorption wavelength became shorter when the atomic number in each cycle (atomic mass, that is, outermost electrons) was increased, which revealed a certain decrease in the electronic activity. Thus, the influence of the micro-electrostatic field on the movement of ions of large atomic number should be relatively weak due to the decline of the electronic activity. Such ions will exhibit the
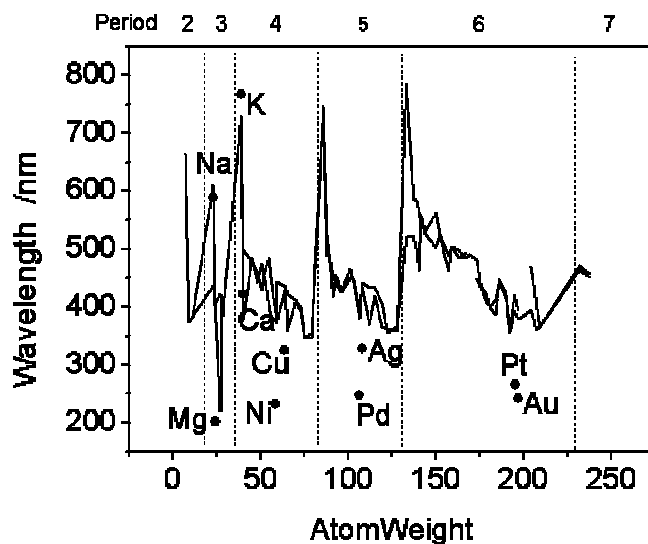
Figure 1. The atomic absorption wavelength. − ,Theoretical Data; ●, measured data.
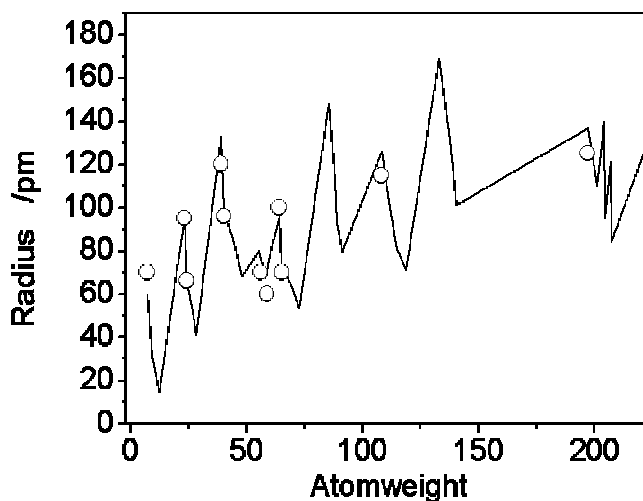
Figure 2. The ionic radii having different atomic numbers. − ,Pauling radius of ion; ●, calculated radius of ion

slow movement and displacement during the process of being captured by the bacteria.

Figure 2 shows the ionic radii having different atomic numbers, that is, the relative masses. The data sources included the Pauling radii of ions (Cotton and Wilkinson 1980) and the ionic radii calculated using the molecular simulation of R-Cl bond (R is the ion to be measured) while simulation was carried out in a vacuum environment. The ions were considered as charge hard balls with reference to the Pauling radii. Comparing the energy of

the R-Cl compounds of different bond length with each other, the optimum bond length was used to determine the final ionic radii after the energy minimization.

According to the similarities between the calculated ionic radii and Pauling's ones, it could be considered to be correct that an ion was regarded as a hard-sphere, which provided the foundation for the follow-up study of the simulation. The hard balls could be characterized by three variables including mass, volume and charge. In the subsequent modeling studies, the mass and charge of   a
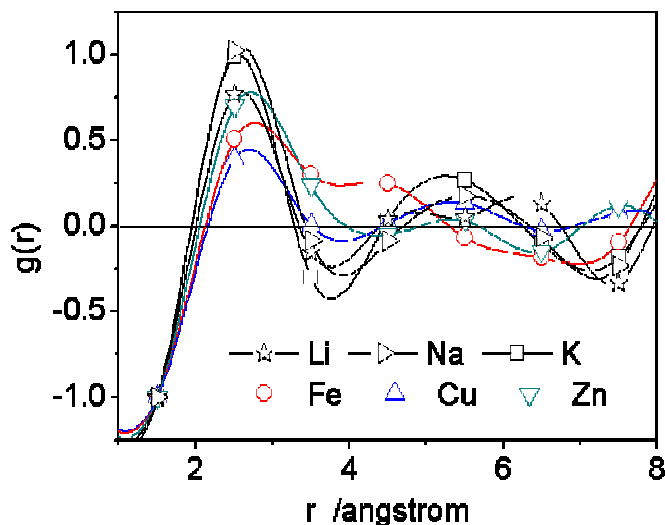
Figure 3. The radial distribution of ions in aqueous solutions.

hard ball could be adjusted in accordance with the simulation requirements, but the volume was still an uncertain variable. On the one hand, similar to Figure 1, the ionic radii in Figure 2 also shows the cyclical changes which would make the modeling more complicated. On the other hand, the surrounding water molecules might exhibit some binding force when a single ion was placed in an aqueous environment. Thus, the gathering of the water molecules would make the effective volume of ion increase. Figure 3 shows the radial distribution function of some ions of alkaline and transition elements in the aqueous solution.

It could be seen in Figure 3 that the gathering of water molecules around a Cu ion was the weakest among these ions. The number of water molecules surrounding Cu was less than those surrounding other ions, which meant the movement of Cu would be less restricted due to the less drag of Coulomb force and van der Waals force. Further, Figure 3 shows that there was little obvious difference in the radial distribution curves of the ions of transition elements. However, in any case, each ion attracted a circle of water molecules. Thus, the prediction of the ionic radius was fraught with uncertainty.

Hard sphere model of ions based on periodic law of elements

Through the above analysis, it seemed that the real radius of the ions in the process of movement in aqueous solutions should be regarded as the combination of Pauling radius and hydrated size. According to the results of both Figures 2 and 3, the radius size of an ion drifting in solutions could be recalculated by adding a layer of water molecules surrounding the ion on the basis of the Pauling

radius. Since Figure 1 has confirmed that the activity of electrons in an atom was periodically changing, the ions could not be modeled only based on the radius sizes but need to consider the electronic activity. The modeling of ions should be in accordance with the mode of $f(m,r,q)$, where, m is the ion mass, R is the size of the re-identified by the simulation radius, and q is the charge amount. m might be regarded as a fixed value for each ion. r and q actually influenced and depended on each other. It was necessary to find their relations in the calculation. Based on the simulation results of Figures 2 and 3, referencing the concept of charge-mass ratio, the radii of the ions of different atomic numbers were calculated, as shown in Figure 4. It could be seen that the data points in Figure 4 have the regularity which was conducive to the following modeling of ions.

Fitting the data in Figure 4, the below equation could be obtained,

$$r = 19.772 \times (\frac{q}{m})^{-0.4127} \tag{1}$$

Where the ionic radius, r, was characterized by picometer (pm). m, r and q were linked together in the above equation, which could indicate the occurrence of each ion in the aqueous solution circumstance. Accordingly, in the subsequent modeling studies, each of the ions of the element in the periodic table was to be characterized using this equation.

Aqueous system of bacterial cell and ions

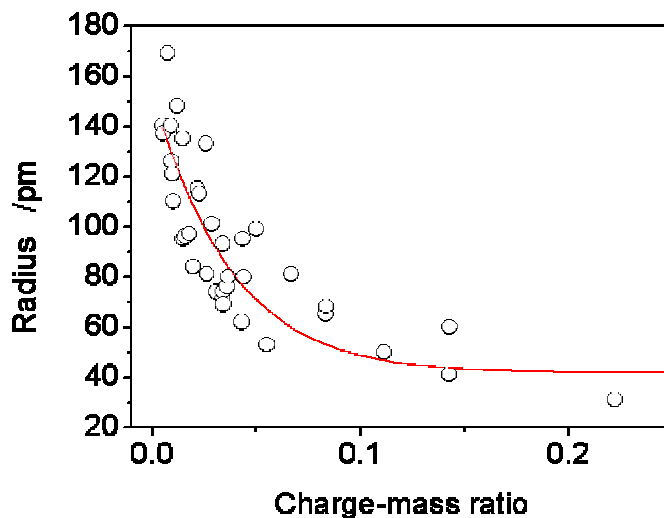Based on the titration, the structure of the bacterial   cell

Figure 4. The variation of ion radius with the charge-mass ratio.
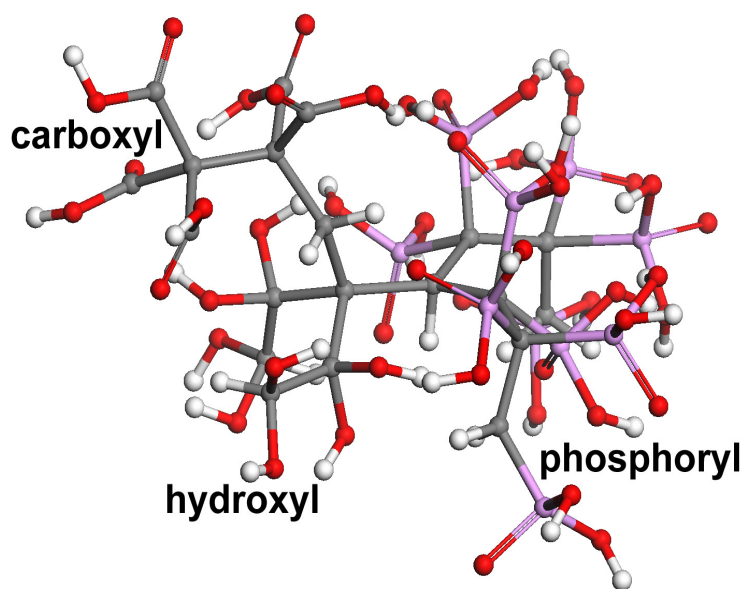

Figure 5. The virtual cell surface of magnetotactic bacterium.

could be decided as an assemblage of three organic groups including carboxyl, phosphoryl and hydroxyl (Cheng et al., 2012). The ratio of groups' quantity was 22% carboxyl, 35% phosphoryl and 43% hydroxyl. According to the amount of groups, a cell structure could be drawn as shown in Figure 5. The aqueous system containing the bacterial cell is shown in Figure 6.

The bacteria's selective capture to an ion was mainly attributed to the attraction of microscopic forces. That is, the attracting forces would lead to the bias of adsorption. At the same time, it could be conceivable that there was also a great influence on the interaction and movement

between the bacteria and ions due to the ionic random drift and moving away from the bacteria as a result of thermal motion. This means that the strength of promoting the ions away from the bacterial cells might also be one of the reasons for the adsorption selectivity. This phenomenon could be observed by the molecular dynamics simulation. Under the same conditions, the ion with higher thermal motion was more likely to drift away from the bacteria. Conversely, an ion with weaker thermal motion was slow in its displacement and relatively appeared to be more close to and likely to be captured by the bacteria if other ions exhibited more violent   random
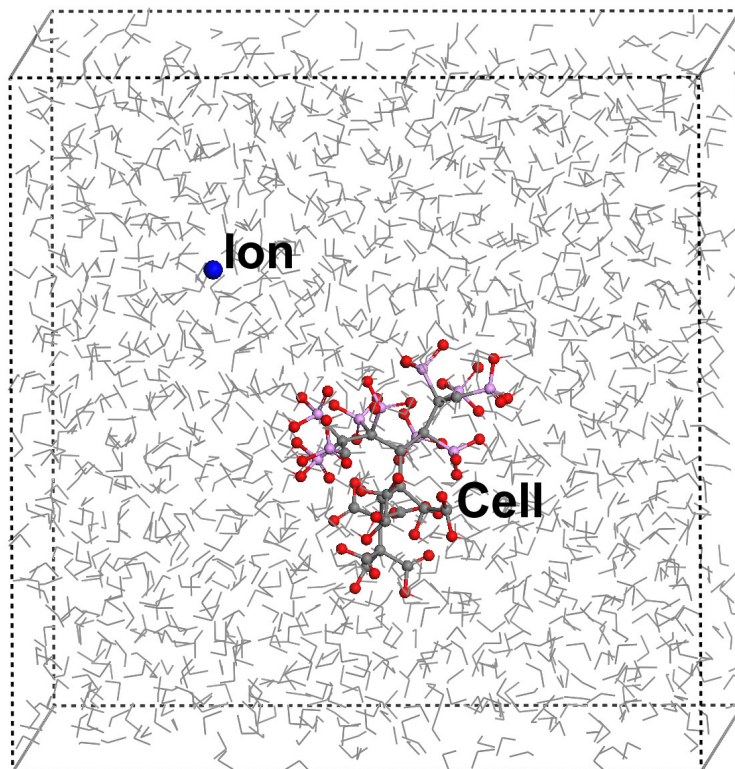
Figure 6. The aqueous cell-ion system.

motion during the adsorption process.

The tendency of selective adsorption of ions

According to Equation 1, two ions of different charge-mass ratios were selected to investigate the hypothesis that the adsorption was affected by ionic thermal motion. As shown in Figure 7, a cation of low molecular weight (Ion_{LW}) and one of high weight (Ion_{HW}) were placed into an aqueous system containing a cell of magnetotactic bacterium. The charge-mass ratio of Ion_{LW} was as twice as that of Ion_{Hw}. As shown in Figure 7a, in the aqueous solution without bacterial cell, there was little difference between the displacements of the two ions. In the aqueous solution containing a bacterial cell in Figure 7b, the displacement of Ion_{HW} was still not obvious but the amount of displacement of Ion_{LW} was large and Ion_{LW} greatly drifted away from the cell. It seemed that the ion of smaller charge - mass ratio was more easily to be captured by magnetotactic bacteria.

The phenomenon of the easy drift of Ion_{LW} was considered to be due to the electrostatic field in the system. There was no significant difference between the displacement of Ion_{HW} and that of Ion_{LW} in the aqueous solutions without bacterial cell because the electrostatic field of the system was relatively uniform. The electrostatic field became inhomogeneous when the bacterial cell was added into the system, which made the ion of small atomic weight and large charge-mass ratio drift more violently and irregularly. In contrast, Ion_{HW} could be maintained at the current position relatively close to the bacterial cell.

By adjusting the charge - mass ratio, many metal ions could be tested using this above simulation procedure. It could be found that the phenomenon of ion's tendency to leave the bacteria existed in many systems, for example, an aqueous solution of Cu^{2+}, Ni^{2+}, Zn^{2+}, etc, indicating a common nature of ions' leave from the sorbent caused by thermal movement. It could also be understood that the thermal motion could depress the adsorption of ions and be also one of the reasons that causes adsorption selectivity. These assumptions implied that the ion of smaller charge-mass ratio according to the periodic law of elements might be easier adsorbed by the magnetotactic bacteria.

Conclusion

A model cell of magnetotactic bacterium used in the wastewater treatment process was developed. The ions in the aqueous solutions were modeled on the basis of the periodic law of elements, which was used to simulate the process of adsorption of heavy metal ions on magnetotactic bacteria.
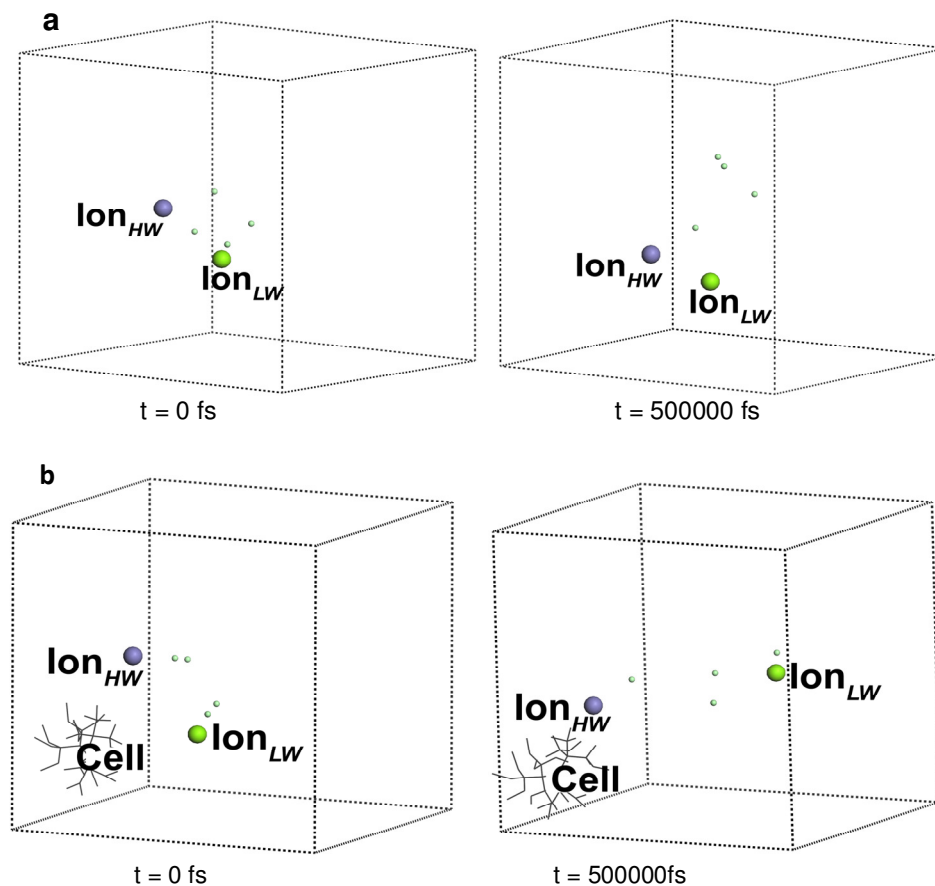
Figure 7. Ions' movement in the aqueous system. **(a)** Aqueous system containing ions. **(b)** Aqueous system containing ions and a bacterial cell.

Through the simulation studies, it was found that the balance of thermal motion and intermolecular forces was one of the important factors to affect bacteria's capturing bias to ions. The thermal movement prompted ion to drift more freely, so that the ions might be randomly moved away from the bacteria. In contrast, the ions of weaker thermal motion maintained a relatively closer position near the bacterial cell and then exhibited a larger tendency to be selectively adsorbed.

It could be considered that the small charge and large mass ions might be easily captured by the bacterial cell because they would move slowly and tend to stay near the biosorbent in the dynamic process of adsorption. A hypothesis was proposed that the ions having smaller charge-mass ratio in the periodic system of elements might be easier to be adsorbed.

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