



## Static Adsorption of $\text{Sr}^{2+}$ with Low Concentration by Granulated Ca-Alginate

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The adsorption of  $\text{Sr}^{2+}$  from solution with low concentration onto dried Ca-alginate was investigated in batch system. The adsorption dynamics, thermodynamics and effects of pH on  $\text{Sr}^{2+}$  sorption capacity were carried out and the energy parameters of adsorption were computed. The results show that the adsorption of  $\text{Sr}^{2+}$  onto dried Ca-alginate was rapid and low temperature was in favour of adsorption. The adsorption was considered a spontaneous exothermic process. The capacity of adsorption reaches the maximum when pH was 7. The energy parameters and electronic property of system have discovered that the MM block has the best adsorptive effect of  $\text{Sr}^{2+}$  in all three kinds of blocks.

**Key Words:** Ca-Alginate, Adsorption,  $\text{Sr}^{2+}$ , Kinetics, Thermodynamics.

### INTRODUCTION

As an important composition part of the environmental monitoring work, the determination of  $^{90}\text{Sr}$  generated by nuclear fission in the nuclear industry is performed through measuring  $\beta$ -ray from the water containing  $^{90}\text{Sr}$  via low background. Nevertheless, a lot of preparation, especially separation and purification of  $^{90}\text{Sr}$  in the aqueous solution, leads to low efficiency. Thus, researchers dedicate to seeking some new materials possessing to achieve separate aim. Wang *et al.*<sup>1</sup>, have found that maximum adsorption capacity of  $\text{Sr}^{2+}$  into carboxymethylated cellulose at 25 °C were 108.7 mg/g. Nevertheless,  $\text{Sr}^{2+}$  ionic strength was high in adsorbate of strontium solution. In order to obtain an accurate result of  $^{90}\text{Sr}$  through the Cerenkov radiation measurement, one of the extractors is *bis*(2-ethylehexyl) hydrogen phosphate acid (HDEHP), employed to separate  $^{90}\text{Sr}$  by Mosqueda *et al.*<sup>2</sup>. But the separate process of  $^{90}\text{Sr}$  was not clear; the efficiency of Cerenkov counting was sensitive. In a word, study on a new material with low cost and high efficient has important meaning for determining  $^{90}\text{Sr}$  in the solution.

Alginate, a kind of natural polysaccharide separated from brown algae, is a common term used for a family of segmented copolymers composed of  $\beta$ -D-mannuronic (M) and its epimer,  $\alpha$ -L-guluronic acid (G) residues in varying proportions<sup>3,4</sup>. Alginate molecule contains a large number of carboxyl and hydroxyl, which causing gel form by the static electric force between negatively charged electrons attached to theirs own and metal ions and the mechanism of the cooperation can be

interpreted by so-called 'egg-box'<sup>5</sup>. Zhang *et al.*<sup>6</sup> have investigated the absorbing  $\text{Cu}^{2+}$  in the aqueous solution using adsorbent prepared by bacteria alginate and made a discussion on chelating mechanism of the interaction of  $\text{Cu}^{2+}$  and MG block.

In this work, the adsorption kinetics and thermodynamic properties were discussed, as well as the dependence of pH value on adsorption. Meanwhile, the adsorption mechanism was proposed after having completed calculation of energy and electronic properties of cage-like compounds, produced by the reaction of  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$  with block of alginate molecule, using Materials Studio 5.0.

### EXPERIMENTAL

Alginate, strontium nitrate, barium chloride, hydrochloric acid and sodium hydroxide used in this experiment were all analytical reagents and they were purchased from Aladdin Co. Ltd., China.

**Preparation of Ca-alginate:** In first step, 10 g/dm<sup>3</sup> sodium alginate solution was added dropwise into a  $\text{CaCl}_2$  solution in the same concentration under constant stirring with the speed of 400 r/min. The calcium alginate gelatum micro balloons were washed three times with deionized water. All glassware were washed with ultrasonic in advance and thereafter dried under 120 °C (Fig. 1).

**Adsorption kinetics and isotherms:** 0.2 g of treated Ca-alginate particles was added into 20 mL known solution of  $\text{Sr}(\text{NO}_3)_2$  (10 g/dm<sup>3</sup>). Amount of adsorbed  $\text{Sr}^{2+}$  was determined in the obtained suspension at different time intervals. The value of capacity (q) can be calculated using the following equation:



(a) Ca-alginate gelatin



(b) Dried Ca-alginate granule

Fig. 1. Ca-Alginate

$$\text{Adsorbed amount (g/g)} = \frac{(Q_i - Q_f)V}{m} \quad (1)$$

where  $Q_i$  and  $Q_f$  being the initial and final concentrations of  $\text{Sr}(\text{NO}_3)_2$  solutions ( $\text{g/dm}^3$ ),  $V$  being the volume of adsorbate solution and  $m$  is the weight of particles, *i.e.*, adsorbent. The above suspensions was settled for 24 h at different levels of 20, 30 and 40 °C.

**Influence of pH:** The effect of solution pH was studied in the range 2–12. Initial pH values were adjusted using KOH and  $\text{HNO}_3$  solutions. Initial concentrations of  $\text{Sr}(\text{NO}_3)_2$  solutions were  $10 \text{ g/dm}^3$  and equilibration time was 24 h.

**Structure optimization of alginate molecule:** Four models of random copolymers and alternative copolymers, denoted as 8G, 8M, 4G and 4 M, respectively, were built by  $\beta$ -D-mannuronic (M) residues and  $\alpha$ -L-guluronic acid (G) residues and polymerization degrees of the copolymers was set to 4. All polymers were capped with H. Dynamics (MD) simulations were performed to investigate adsorption behaviour at 298 K. The first *ab initio*-based force fields, COMPASS, canonical ensemble NVT and Nose thermostat were adopted to simulate. The time step was set to 1 fs. And the frame output yielded every 2000 step.

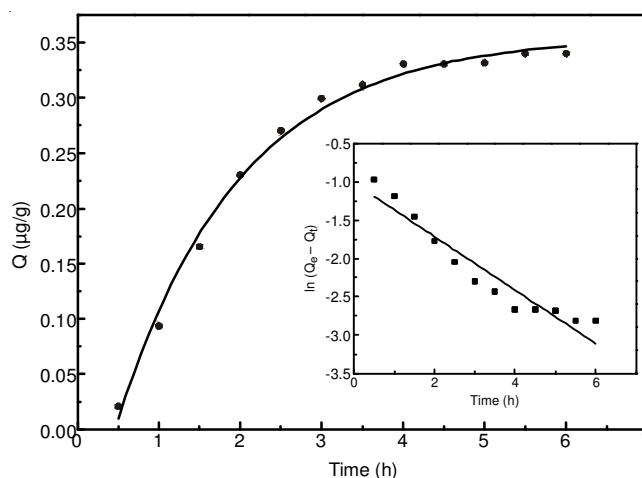
**Interaction between alginate block copolymers and  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ :** In this paper, modeling for the interaction of  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$  and alginate was performed using the adsorption module. This module employs the Monte Carlo simulated annealing method to search for interaction sites with lower energy. Hybrid QM/MM<sup>7</sup> was employed to study the electronic properties and energy of adsorption, afterwards the possible adsorption mechanism of  $\text{Sr}^{2+}$  onto Ca-alginate involved was discussed. In order to investigate all possible reactions of metal ions and oxygen atoms, all electron density functional theory

implemented the generalized gradient approximation method (GGA), the PW91 functional and the double-numeric quality basis with polarization functions (DNP) in Accelrys' code Dmol<sup>3</sup>. All convergence accuracy of calculations was specified to fine.

All the calculations of structures and molecular adsorption were run with the commercial molecular modeling software package Materials Studio 5.0, implemented on an Intel Core2 Duo CPU, E8400 and 3.00 GHz computer.

## RESULTS AND DISCUSSION

**Kinetics model:** The progress of the adsorption process monitored at different time intervals is shown in Fig. 2 which clearly reveals that the adsorbed amount of  $\text{Sr}^{2+}$  constantly increases with increasing time and then levels off after 5 h.

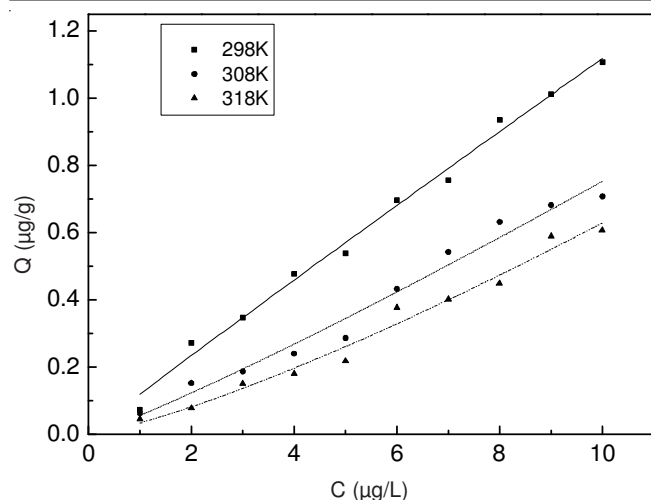
Fig. 2. Kinetic curve for  $\text{Sr}^{2+}$  on Ca-alginate

Assuming that the adsorption process was in conformity with the first-order dynamic equation, according to Langmuir, the reversible sorption-desorption process can be described by the following equation<sup>8</sup>:

$$\ln(Q_e - Q_t) = \ln Q_e - kt \quad (2)$$

where  $k$  is the equilibrium constant and  $Q_t$ ,  $Q_e$  represent the adsorption capacity of at time  $t$  and at equilibrium. The results of Fig. 2 can be calculated into the plots of  $\ln(Q_e - Q_t)$  versus  $t$  (Fig. 2) and the values of  $k$  is 0.662. The fitted straight of inset of Fig. 2 indicate that the adsorption data could be satisfactorily described with the first-order equation. It is also shows that  $\text{Sr}^{2+}$  with low concentration may have higher probability of diffusing to surface of Ca-alginate through water film, which make diffusion in particle easier. Moreover, secondary diffusion to the inner surface of particles and adsorption on reactive sites of Ca-alginate is relatively slow.

**Thermodynamics model:** Fig. 3 shows the experimental equilibrium isotherm of the adsorption of  $\text{Sr}(\text{II})$  ions on Ca-alginate at different temperatures (298, 308 and 318 K). The adsorption capacity of  $\text{Sr}(\text{II})$  ions increases as its initial concentration in the solution, whereas, the adsorption capacity keeping negative correlation with the temperature, which indicates the adsorption of  $\text{Sr}^{2+}$  using Ca-alginate at lower temperature has more advantages over other temperatures.

Fig. 3. Isotherms adsorption curve for  $\text{Sr}^{2+}$  on Ca-alginate

The semi-empirical Freundlich equation, which often used to describe the isotherms of equilibrium adsorption, was employed to fit the experimental data. The Freundlich adsorption isotherm is mathematically expressed as

$$Q_e = K_f \cdot C_e^{1/n} \quad (3)$$

where  $Q$  (mg/g) denote the adsorption amount of  $\text{Sr}(\text{II})$  ions per unit weight of adsorbent at equilibrium,  $C_e$  ( $\mu\text{g/L}$ ) is the equilibrium concentration of  $\text{Sr}(\text{II})$  ions and  $K_f$ ,  $n$  are constants for a given adsorbate and adsorbent at a particular temperature.

Table-1 shows the fitting equations and parameters, from which  $K_f$  and  $n$  reach a maximum when temperature was 298 K. The larger value of  $K_f$  and  $n$  are, the bigger adsorption amount of  $\text{Sr}(\text{II})$  is, thus,  $K_f$  and  $n$  can be treated as reflex of adsorptive capacity.

TABLE-1 FREUNDLICH EQUATION AND PARAMETER				
T (K)	Freundlich equation	$K_f$	$n$	$R^2$
298	$\ln Q_e = 0.972; \ln C_e - 2.129$	0.12	1.03	0.9927
308	$\ln Q_e = 1.125; \ln C_e - 2.865$	0.06	0.89	0.9782
318	$\ln Q_e = 1.269; \ln C_e - 3.381$	0.03	0.79	0.9803

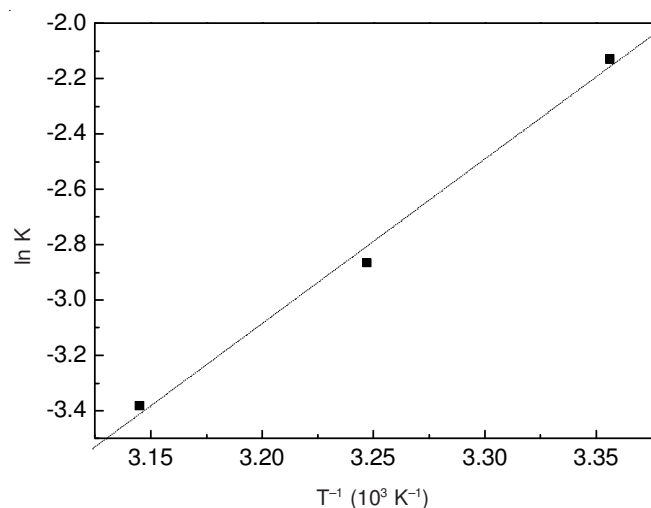


Fig. 4. van't Hoff linear relation of adsorption

According to the van't Hoff equation,  $d \ln K/dT = \Delta H/RT^2$ ,  $\Delta H$  of the adsorption of  $\text{Sr}(\text{II})$  ions on Ca-alginate can be calculated into the plots of  $\ln K$  versus  $1/T$  (Fig. 4).  $\Delta G$  and  $\Delta S$  are also obtained by solving eqns. 2 and 3 simultaneous are list below.

$$\Delta G = -RT \int_0^C \left( \frac{q_e}{c_e} \right) dc_e \quad (4)$$

$$\Delta S = \frac{(\Delta H - \Delta G)}{T} \quad (5)$$

$\Delta G$  and  $\Delta S$  of the adsorption of  $\text{Sr}(\text{II})$  ions on Ca-alginate at different temperature are shown in Table-2.

TABLE-2 THERMODYNAMICS DATA OF Ca-ALGINATE			
T (K)	$\Delta H$ (KJ/mol)	$\Delta G$ (KJ/mol)	$\Delta S$ (J/mol K)
298	49.44	-2.549	8.719
308		-2.276	7.551
318		-2.083	6.707

It can be seen from the Table-2, the adsorption was an endothermal process with the system's enthalpy increasing and the value of  $\Delta H$  exceeds 30 KJ/mol, which suggests adsorption process has the characteristic of chemical adsorption. Also, calculation results show that the value of  $\Delta G$  is less than 0 at different temperatures which indicated the spontaneity of  $\text{Sr}^{2+}$  adsorption. In addition, the entropy production results from the decreasing of order degree and increasing of the randomness of the adsorption which owing to the fact that the movement of  $\text{Sr}^{2+}$  inside the Ca-alginate particles is more vigorous than it in solvent.

**pH effect on adsorption:** Based on egg-box model<sup>5</sup>, the interaction of  $\text{Ca}^{2+}$  and alginate lead to the formation of gels containing water, which come into being solid granule after processing of stoving and dehydration. When  $\text{Sr}^{2+}$  in the solution of different pH values was allowed to come into contact with the gels, it can be adsorbed to the hollow blocks. Adsorption amount is influenced by remaining hollow blocks, deformation of spatial structure, electric negative of carboxyl and  $\text{Sr}^{2+}$  radius<sup>9</sup>.

The capacity-pH curves of adsorption are shown in Fig. 5. As it can be seen from the figure, the adsorption capacity of  $\text{Sr}^{2+}$  increases when the pH increases from 1 to 7. According to the Acid-Base Proton Theory, hydrated ions of alkaline earth metal are weak acid while the corresponding hydrated oxides are strong alkali. When pH is low ( $\text{pH} \leq 4$ ) is less than 4, absorption sites are occupied by  $\text{H}^+$  existing in solution in large quantity. The plentiful  $\text{H}^+$  in the solution will compete with  $\text{Sr}^{2+}$  to combine with  $-\text{COOH}-$  groups. The adsorbents almost have not enough affinity to  $\text{Sr}^{2+}$  so that little  $\text{Sr}^{2+}$  ions are adsorbed. While the pH value is 4-7, carboxyl is in dissociation state (dissociation constants of carboxylic acid is 3.38), which provide more possibilities of the bond formation between  $\text{Sr}^{2+}$  and carboxyl. With the increase in pH, the adsorption capacity increases rapidly and reach the maximum of ca. 1.09 g/g at  $\text{pH} = 7$ . The sharp decrease in the adsorption at  $\text{pH} = 7$  may be caused by the adsorption of  $\text{Sr}^{2+}$  and  $\text{Sr}(\text{OH})^+$  on  $\text{OH}^-$  surface groups and by lesser competition from  $\text{H}^+$  ions for adsorption



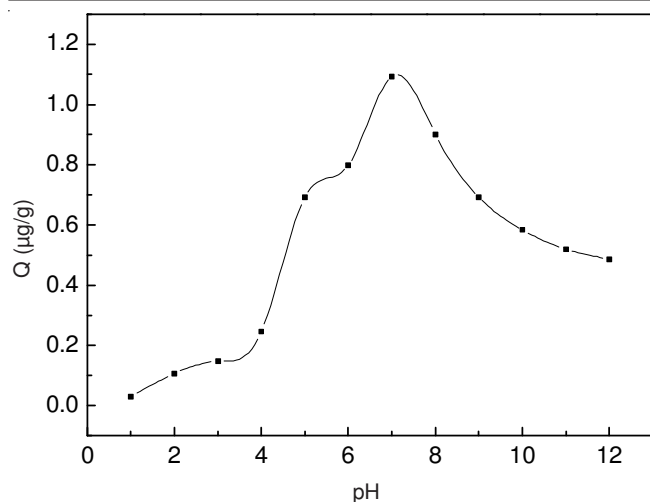


Fig. 5. Adsorption effect of pH

sites. This is due to the fact that lower competition between  $H^+$  and  $Na^+$  ion at high pH exist.

**Adsorption mechanism:** Fig. 6 shows that interactions of  $Ca^{2+}$ ,  $Sr^{2+}$  and alginate result in the formation of gel and the reactive sites lie nearby the GG blocks hollow since electrostatic force between metal ions and carboxyls was influenced by distance. Adsorption sites of  $Sr^{2+}$  in the 8GCa are moved to the molecular surface excursion for the center of hollow has occupied by  $Ca^{2+}$ , which can be illustrated by the fact that total energy of 8GCaSr is higher than those of 8GCa and 8GSr.

The highest occupied molecular orbital (HOMO) level increases while the lowest unoccupied molecular orbital (LUMO) level decreases after  $Sr^{2+}$  are adsorbed. High chemical activity adsorbing  $Sr^{2+}$  to the GG block of alginate bring about the increase of energy gap and electron appearance in LUMO. Interaction sites of  $Ca^{2+}$ ,  $Sr^{2+}$  and MM block lie almost above the hollow center and hence relative total energy of GG block

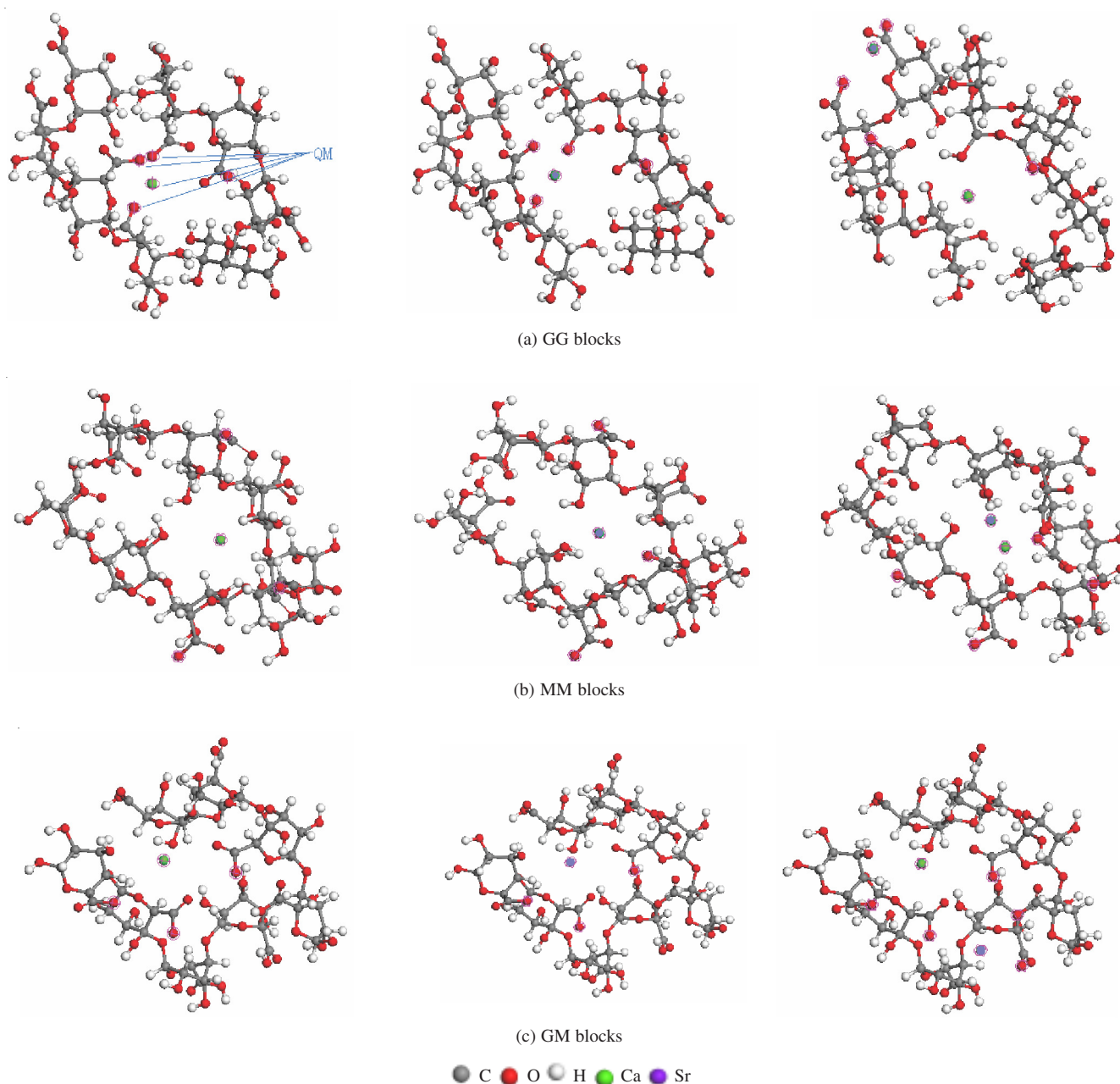
Fig. 6. Reaction of GG, MM and GM blocks in dried alginate with  $Ca^{2+}$  and  $Sr^{2+}$

TABLE-3  
ENERGY PARAMETERS OF SYSTEM

System	QM (eV)	MM (eV)	Total energy (eV)	HOMO (eV)	LOMO (eV)	$E_{\text{gap}}$ (eV)	Occupation of HOMO	Occupation of LOMO
8GCa	-8.275	22.408	14.133	-15.909	0.000	-15.909	1.313	0.000
8GSr	-6.854	21.150	14.297	-16.014	-10.029	-5.985	1.107	0.000
8GCaSr	-6.710	108.661	101.651	-10.925	-10.666	-0.259	1.502	0.621
8MCA	3.368	113.509	116.878	-13.942	-13.511	-0.431	1.404	0.181
8MSr	2.200	71.804	74.003	-13.598	-12.991	-0.607	1.426	0.056
8MCAr	-5.369	52.287	46.918	-11.976	-11.084	-0.892	1.501	0.008
4G4MCA	3.649	75.570	79.218	-15.081	-14.317	-0.764	1.393	0.017
4G4MSr	2.274	78.206	80.480	-14.886	-13.381	-28.267	1.398	0.000
4G4MCAr	-15.532	76.154	60.622	-12.035	-11.693	-0.342	1.171	0.206

is high while its stability decreases. Adsorption sites of  $\text{Sr}^{2+}$  in 8MCA lie in the one side and those of  $\text{Ca}^{2+}$  lie in the other side. HOMO level increases with the appearing probability of electronics getting larger while the probability of decreased with the increase of LUMO level. These all explain that MM block of calcium alginate have higher stability after adsorbing  $\text{Sr}^{2+}$ . Interaction sites of  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$  and GM block are located above the hollow excursion. The interaction energy of GM block and  $\text{Ca}^{2+}$  is less than that of GM block and  $\text{Sr}^{2+}$ . Interaction sites of  $\text{Sr}^{2+}$  in 4G4MCA lie in the same side with those of  $\text{Ca}^{2+}$ . The HOMO level and the LUMO level both increase and the energy gaps decrease, consequently the stability of Ca-alginate with  $\text{Sr}^{2+}$  adsorbing on the GG blocks is improved.

Through a comprehensive comparison, GG blocks of Ca-alginate take priority of the formation of gel with  $\text{Ca}^{2+}$ , which are in agreement with reference<sup>5</sup>. Nevertheless, adsorption of  $\text{Sr}^{2+}$  on the MM blocks is easier than that of  $\text{Ca}^{2+}$ . The result shows that there existed competition between  $\text{Sr}^{2+}$  and  $\text{Ca}^{2+}$  during the adsorption with Ca-alginate, namely the difference of configuration and position of carboxyls in the blocks lead to the effects of selective.

Nucleophilicity or electrophilicity of active areas in a molecule can be characterized by Fukui index *via* determination of chemical prime sites. Fukui index<sup>10</sup> is defined as first-order partial derivative of electron density  $\rho(r)$  on the electron numbers  $N$  in case of the certain applied potential field  $V(r)$ :

$$f(r) = \left( \frac{\partial \rho(r)}{\partial N} \right)_{V(r)} \quad (6)$$

Convergent Fukui function  $f(r)$  can be deduced based on the finite difference approximation of eqn. 6:

$$f(r)^+ = q_i(N+1) - q_i(N) \quad (7)$$

$$f(r)^- = q_i(N) - q_i(N-1) \quad (8)$$

where  $q_i(N)$ ,  $q_i(N+1)$  and  $q_i(N-1)$  are electric quantity of the atom  $i$  for a neutral molecular, anion molecular and cation molecular, respectively.  $f(r)^+$  and  $f(r)^-$  are nucleophilic attack index and electrophilic attack index, which can indicate ability of the atom  $i$  of receiving and losing electrons, the larger values are, the stronger ability of receiving and losing electrons are.

Fukui indexes of Ca and Sr in the 8GCaSr, 8MCAr and 4G4MCAr are given in Table-4. It can be perceived that the two metal atoms have the same ability of receiving and losing electrons in the 8GCaSr while the ability of Ca is stronger

TABLE-4  
FUKUI INDICES OF SYSTEM

System	Atom	$f(r)^+$	$f(r)^-$
8GCaSr	Ca	0.315	0.315
	Sr	0.319	0.318
8MCAr	Ca	0.244	0.246
	Sr	0.210	0.209
4G4MCAr	Ca	0.352	0.350
	Sr	0.090	0.090

than that of Sr in the 8MCAr and much stronger than that of Sr in the 4G4MCAr. By comparison of values of the indices, the chemical activity of MM block is the lowest of all while the adsorption stability of it is the strongest when absorbing Sr after the existence of Ca. These results are consistent with the analysis of aforementioned energy parameters.

Mulliken charge population analysis has been employed to investigate of the changes of charge distribution in the process of adsorption. O1, O2, O3 and O4 are presetting QM atoms from Fig. 6 in the Table-5. Before  $\text{Sr}^{2+}$  was absorbed to the GG blocks, carboxyl charges close to metal of O3 were most. Charges of Ca and O3 decrease after absorption while those of O2 and O4 increase.

TABLE-5  
MULLIKEN CHARGE POPULATION ANALYSIS OF SYSTEM

System	O1	O2	O3	O4	Ca	Sr
8GCa	-0.400	0.043	-0.661	-0.078	1.732	—
8GCaSr	-0.431	-0.497	-0.448	-0.274	1.141	1.414
8MCA	-0.177	-0.319	-0.106	—	1.675	—
8MCAr	-0.320	-0.287	-0.289	-0.432	0.927	1.270
4G4MCA	-0.238	-0.176	-0.300	—	1.807	—
4G4MCAr	-0.470	-0.527	-0.624	-0.437	1.400	1.679

Negative charges taken by O band increase after  $\text{Ca}^{2+}$  absorbed to the MM block, but the disparity of charges among O atoms is not big and which caused by the fact that adsorption sites is near the cavity center. Positive charges of Ca reduce by 0.748 while the charge's decrease of Sr is 0.730.

Negative charges taken by O atoms obviously increase after  $\text{Sr}^{2+}$  absorbed to the GM blocks and the charges decrease of Ca and Sr are 0.407 and 0.321. Through a comparison of charge transfers, value of charge transfer caused by absorbing  $\text{Sr}^{2+}$  to the MM block is largest in all processes of adsorption and the stability of adsorption is the best of all. In a word, once again the results show that the MM block has the best adsorptive effect of  $\text{Sr}^{2+}$ .

## Conclusion

In summary, we have applied a method of reactions between sodium alginate and  $\text{CaCl}_2$  to access a Ca-alginate gel and further obtain the Ca-alginate particles *via* dehydrating. Adsorbing  $\text{Sr}^{2+}$  in solution with low concentration by use of dried Ca-alginate can be described quantitatively by the first-degree reaction dynamic equation. We have found that low temperature tend to favours adsorption on the basis of study of thermodynamics and the absorption process is a spontaneous endothermic reaction because  $\Delta G < 0$  and  $\Delta H > 0$ . The capacity to adsorb depends on the pH value. The adsorption capacity increases rapidly with the pH value increasing from 4-7 and reach the maximum at  $\text{pH} = 7$ , while the sharp decrease in the adsorption capacity at  $\text{pH} > 7$ . The energy parameters and electronic property of system total energy, HOMO, LOMO, energy gaps, Fukui index and Mulliken charge population analysis have indicated that  $\text{Sr}^{2+}$  is more easily adsorbed on the MM blocks in Ca-alginate compared with GG blocks and GM blocks. In short, Ca-alginate can be treated as a adsorbing material to separating or determining  $^{90}\text{Sr}$ .

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