Korean J. Chem. Eng., 39(1), 121-133 (2022)
DOI: 10.1007/s11814-021-0949-3

pISSN: 0256-1115
eISSN: 1975-7220

Assessment of sulfonation in cornstalk for adsorption of metal-ions from seawater

Hee-Jeong Choi†

Department of Biomedical Science, Catholic Kwandong University, 24, Beomil-ro, 579beon-gil, Gangneung-si 25601, Korea

(*Received 18 January 2021 • Revised 26 July 2021 • Accepted 5 September 2021*)

Abstract−The aim of this study was to adsorb Ca, K, Mg and Na from seawater using sulfonated cornstalk. Cornstalk, a ligno-cellulose derived agricultural waste, was selected as an adsorbent. It was separated into the inside and outside and then sulfonated to be used as an adsorbent. Sulfonated cornstalk has higher ion exchange capacity than natural cornstalk, and the largest ion exchange capacity was 4.35 meq/g of sulfonated outside cornstalk. In addition, according to the FT-IR analysis, the surface of cornstalk was converted to negative charge after sulfonation, so that it was very easy to adsorb cationic ions in seawater. The adsorption efficiency of the sulfonated cornstalk increased by 27.96-41.58% for Ca, 22.61-26.78% for K, 27.96-44.14% for Mg and 18.47-27.16% for Na compared to the non-sulfonated cornstalk. Surface modified cornstalk with sulfuric acid can efficiently adsorb Ca, K, Mg and Na from seawater. This is meaningful not only in terms of recycling ligno-cellulose based waste, but also adsorbing useful resources from seawater.

Keywords: Adsorption, Cornstalk, Sulfonation, Ion Exchange, Seawater

INTRODUCTION

Seawater consists of about 96.5% pure water and about 3.5% dissolved matter. Dissolved substances in seawater are classified into main component elements (over 100 ppm), minor component elements (over 1 ppm) and trace elements (less than 1 ppm), depending on the amount dissolved [1]. The main constituent elements of seawater contain six components, including chlorine, sodium, magnesium, sulfur, calcium and potassium, and they constitute more than 99% of the total dissolved components [2]. Besides very valuable elements such as lithium, uranium, platinum, gold, silver, cobalt, nickel, bromine, molybdenum and boron are contained in low concentrations [3]. Potassium, magnesium and calcium are essential elements of all living organisms. Among the many plant nutrients, potassium, mgnesium and calcium play a particularly important role in the growth of all crops [4,5]. Potassium, calcium and magnesium are abundant and evenly distributed in sea water. In particular, magnesium is as strong as steel, 40% lighter than aluminum, and is used for various purposes due to its high strength characteristics, durability, impact resistance, and structural characteristics compared to its weight [5,6]. The world's land reserves of magnesium are estimated to be about 3.6 billion tons, and mainly exist as minerals such as magnesite, dolomite, serpentine, and brucite [7,8]. Magnesium concentration of seawater is about 1,300 mg/L, and considering the total amount of seawater, the total amount of magnesium in seawater is about 1.84×1,015 tons, which is about 500,000 times that of land resources [6,7].

For the recovery of these resources from seawater, it is very important to develop a material having a high degree of separation and recovery technology, a high selectivity for specific ions, a fast adsorption rate, and excellent physical and chemical stability and durability [4]. Currently used separation/recovery techniques include coprecipitation, flotation, solvent extraction, bioconcentration, and ion exchange adsorption [5]. To recover valuable metals from seawater, separation/recovery using an ion exchange resin is attracting attention. Relatively, ion exchange absorption is widely adopted because it can selectively extract metal ions (Ca, Mg, K, Na etc.), which are present in trace concentrations in complex seawater solutions, at relatively low cost, and easy to operate for practical industrial applications [6]. In particular, since sulfonated biomaterials modify the surface charge to negative charge, cationic metal ions can be extensively recovered from seawater [7]. In addition, the separation/recovery method using an ion exchange resin has the advantage of easy separation, easy selective adsorption for specific ions and regeneration [5]. On the other hand, there is a problem that secondary pollutants are generated due to separation by chemical substances [4]. Therefore, it is considered to be the most advantageous for commercialization as a process that is easy to separate by separating the adsorbed valuable metal ions from the adsorbent and does not generate a secondary waste liquid. Lignocellulose derived agricultural waste has a loose porous structure and contains carboxyl, hydroxyl and other reactive groups and can be used as biomass adsorbents in pollution control applications [8]. In addition, this is very useful not only to reduce the environmental burden, but also to adsorb metal ions using waste. Moreover, bioadsorbents produced by low-cost agricultural waste can be effectively used to adsorb metal ions.

Cornstalk is a lignocellulosic material consisting of lignin (5-18%), cellulose (30-44%) and hemicellulose (20-30%) as structural components [8,9]. Lignin is an aromatic polymer composed of carbonyl, hydroxyl, methyl and other functional groups [10,11]. Both hemicellulose and cellulose contain oxygen functional groups, including carbonyl groups, hydroxyl groups and ethers [11,12]. These functional groups can bind to metal ions and small organic con-

---

†To whom correspondence should be addressed.
E-mail: hjchoi@cku.ac.kr

taminants through chelating, completion, coordination, and hydrogen bonding, which play an important role in the adsorption process [12,13]. In general, cornstalk can directly act as an adsorbent to adsorb metal ions or pollutants, but researchers are paying much attention to increase the adsorption capacity through chemical or physical modification of cornstalk [9,11]. The modified cornstalk can improve the adsorption capacity of metal ions. Many researchers have conducted heavy metal removal experiments using untreated agricultural waste and reported many positive results [9,10]. However, the application of unmodified agricultural waste has significant disadvantages, such as low adsorption capacity in aqueous solutions and high emission of soluble organic compounds [14]. Accordingly, in recent years, there has been an increasing tendency of modifying agricultural waste to improve the removal efficiency of heavy metals, the removal of soluble organic compounds and dyes in aqueous solutions. The efficiency of different inorganic acids in the modification of agricultural waste has been confirmed by many researchers. According to the previous study, among various chemical methods by which ligno-cellulose derived agricultural waste can be modified, sulfonation is very effective in improving the adsorption capacity of metal ions [15]. Authors suggested that pretreatment by sulfonating agricultural waste increased the negative charge on the surface and the porosity of the biomass [10]. Similarly, Elangovan et al. [16] reported that pretreatment of mangrove leaves and water lily leaves with sulfuric acid substantially improved the Cr(VI) adsorption capacity.

Sulfonation is an electrophilic substitution reaction, its applicability largely depends on the aromatic ring reactivity, which is influenced by the electronic properties of the substituents attached to the ring [17]. The sulfonation reaction proceeds easily in the presence of an electron donating group that activates the aromatic ring by increasing the electron density by induction and/or resonance effects [10,18]. In addition, the sulfonic acid substituent is preferably introduced at the activation position of the aromatic ring and only one -SO_3H group per repeating unit may be incorporated [15, 19]. Sulfonation using sulfuric acid is completed in a short time at a low temperature compared to other concentrated sulfuric acids (sulfur trioxide, chlorosulfonic acid, silica sulfuric acid), and sulfonation can be performed with a small amount of chemicals [17]. It is also known to increase the tendency of crosslinking through sulfone formation and to cause decomposition of polymers by oxidation or chain cleavage [19,20]. Therefore, we attempted to sulfonate ligno-cellulose derived cornstalk and use it to adsorb Ca, K, Mg and Na, which are the most widely used cationic metals in seawater.

MATERIALS AND METHODS

1. Materials

1-1. Characteristics of Seawater

Seawater used in the experiment was collected from East sea of Korea, where it was pumped from a depth of 30 m and 200 m away from land. The collected seawater was filtered through a <70 mm sand filter to remove suspended solids, and then stored in a refrigerator (2-4 °C) without pretreatment. The characteristics of the sea water are presented in Table 1. Among inorganic ions contained in the seawater, major cations were Na, Mg, Ca, K and Li, while major anions were Cl^-, SO_4^{2-}, NO_3^-, Br^- and F^-. In particular, among the cations, Na content was the highest at 10,189.2±4.21 mg/L, followed by Mg>Ca>K. The pH of seawater was about 8, the turbidity was 0.32 NTU, the conductivity was 31.9 mS/cm and the alkanity was 1.69 mM $CaCO_3$.

Table 1. Characteristics of sea water

Parameters		Value
pH		8.0±0.1
Turbidity (NTU)		0.32±0.1
Conductivity (mS/cm)		31.9±2.3
Alkanity (mM $CaCO_3$)		1.69±0.5
Inorganic ions (mg/L)	Na	10,189.17±4.21
	Mg	1,127.62±2.86
	Ca	391.87±1.62
	K	359.26±1.87
	Cl^-	19,216±5.26
	SO_4^{2-}	2,670±2.89
	NO_3^-	143±3.21
	Br^-	62±2.16
	F^-	1.2±0.03
	Li	0.19±0.05
	Sr	7.62±0.69
	Rb	0.16±0.02

1-2. Sulfonation of Cornstalk

After leaves and contaminants were removed, cornstalk was dried in a drying oven at 105 °C for 24 h to completely evaporate the moisture. The outside and the inside of the dried cornstalk were separated and the outside of dried cornstalk (OCS) was finely cut into 2 mm sizes, and then pulverized in a ball mill at 120 rpm for 5 h. It was collected as a sample of the outside of crushed cornstalk, separated into 40-60 mesh (0.25-0.4 mm) in an automatic sieve machine, and used as a raw material for adsorbent. Inside of dried cornstalk (ICS) was also prepared in the same way as the OCS. The sulfonation process of OCS and ICS was performed as explained below. 20 g of prepared OCS and ICS was added to 60 mL of ethyl alcohol cooled to −10 °C and mixed well, then added to 200 mL of cooled sulfuric acid. The sulfonation reaction was carried out while stirring at 100-150 rpm for 3 h so as not to exceed 10 °C using a reaction device (Yhana, Model SS-200, 50W). Then, sulfonation-undergoing samples were allowed to stand at room temperature for 3 h to induce the complete occurrence of the reaction, washed well with distilled water until neutral, put in a dryer, and then dried for 48 h. The prepared outer part of the sulfonated cornstalk (SOCS) had a dark brown color, while the inner part of the sulfonated cornstalk (SICS) was a light ivory color (Fig. S1).

2. Methods

2-1. Parameteric Study

A batch test method was used to carry out this experiment. To find optimum conditions for the adsorption process, the experiment was performed by controlling various parameters such as temperature, pH, adsorption time and amount of the adsorbent. The adsorption efficiency experiment on the amount of adsorbent is closely related to the economic evaluation of the adsorbent. To find the influence of the amount of adsorbent on adsorption efficiency, the amount of adsorbent was differentiated from 1 to 10 g without adjusting the pH and temperature. The adsorption efficiency experiment with time was based on the results of the amount of adsorbent, and the most efficient amount of adsorbent was used for a reaction time of 180 min without controlling the pH and temperature. To investigate the effect of pH and temperature on adsorption efficiency, pH was adjusted within the range of 3 to 10 and the temperature was adjusted in the range of 25-40 °C for 180 min. To investigate the effect of temperature, amount of adsorbent and pH on the adsorption efficiency, used raw seawater and the other parameters were fixed to test one parameter.

To optimize the adsorption efficiency of Ca, K, Mg and Na from seawater, the effect of various seawater concentrations on the reaction medium was studied. The dilution ratios of distilled water and seawater were 1 : 3 (125 mL : 375 mL), 1 : 1 (250 mL : 250 mL) and 3 : 1 (375 mL : 125 mL). 5 g of an adsorbent was added to this diluted each sample and then the solution was mixed for 180 min at 298 K and 120 rpm. This dilution effect of seawater can confirm various reactions taking place between the reaction medium and seawater. The experiment on the dilution effect of seawater was carried out without adjusting the pH. This was selected to minimize related costs such as NaOH or HCl use and maximize adsorption efficiency because the pH of seawater was around 8.

2-2. Equilibrium and Kinetics Studies

SOCS and SICS adsorbents were selected as representative samples for isothermal adsorption and adsorption kinetics analysis. For the adsorption kinetics experiment, SOCS and SICS were mixed with seawater and placed in a shaking Erlenmeyer flask and then shaken until equilibrium was sufficiently reached. The adsorption amount at time t (Eq. (1)) and removal percentage (Eq. (2)) of metal ions were calculated by the following equations:

$$q_t=\frac{(C_0-C_t)V}{m} \tag{1}$$

$$R\%=\frac{(C_0-C_t)}{C_0}\times 100 \tag{2}$$

where q_t (mg/g) is the adsorption capacity at time t, C_0 (mg/L) and C_t (mg/L) are the Ca, K, Mg and Na concentrations at initial time and at time t, respectively. V is the volume of the solution (L) and m is the mass of dry adsorbent (g). Isothermal adsorption was analyzed using Langmuir, Freundlich, Temkin and Dubinin Raduskevih (D-R), and adsorption kinetics was interpreted using pseudo-first-order (PFO) and pseudo-second-order (PSO). Thermodynamic analysis was performed using Gibbs free energy. The various models used in the interpretation of the experimental results are summarized in Table 2.

To select appropriate kinetic and isotherm models for Ca, K, Mg

Table 2. Adsorptin kinetic, isotherm and thermodynamic models

Model	Equation	Parameters
PFO	$\ln(q_e-q_t)=\ln q_e-k_1t$	q_t: amount of adsorbate adsorbed at time (mg/L) q_e: equilibrium adsorption capacity (mg/g) k_1: pesudo-first-order rate constant (1/min) t: time (min)
PSO	$\frac{t}{q_t}=\frac{1}{k_2\cdot q_e^2}+\frac{t}{q_e}$	k_2: pseudo-second-order-rate constant (L/mg·min)
Langmuir	$\frac{1}{q_e}=\frac{1}{q_mK_L}\frac{1}{C_e}+\frac{1}{q_m}$ $R_L=\frac{1}{1+K_LC_0}$	q_m: maximum adsorption capacity (mg/g) K_L: Langmuir constant (L/mg) C_e: equilibrium adsorbate conceration in solution (mg/L) C_0: initial adsorbate concetration in solution (mg/L) R_L: separation factor
Freundlich	$\ln q_e=\ln K_F+\left(\frac{1}{n}\right)\ln C_e$	K_F: Freundlich constant (mg/g(L/mg)$^{1/n}$) n: heterogeneity factor
Temkin	$q_e=B\ \ln K_T+B\ \ln C_e$	K_T: Temkin equilibrium binding constant (L/mg) B: Temkin constant (J/mol)
D-R	$\ln q_e=\ln q_m-\beta\cdot\varepsilon^2$ $\varepsilon=RT\ln\left[1+\frac{1}{C_e}\right]$ $E=\frac{1}{\sqrt{2\beta}}$	q_D: theoretical maximum capacity (mg/g) β: Dubinin-Radushkevich constant (mol^2/kJ^2) ε: polanyi potential E: mean energy of adsorption (kJ/mol) R: universal gas constant (8.314 J/mol·K) T: absolute temperature (K)
Gibbs free energy	$\Delta G^o=\Delta H^o-T\Delta S^o$	ΔG^o: Gibbs free energy change (kJ/mol) ΔH^o: enthalpy change (kJ/mol) ΔS^o: entropy change (kJ/mol·K)

Table 3. Characteristic of outside and inside cornstalks (unit: %)

	Cell-wall materials			Protein	Fat	Ash	Other
	Cellulose	Hemi-cellulose	Lignin				
ICS	29.6±0.8	27.1±0.9	5.1±0.2	9.3±0.3	1.4±0.05	9.8±0.2	17.7±0.5
OCS	36.9±1.2	25.1±0.7	9.4±0.3	6.9±0.2	1.0±0.02	6.9±0.1	13.8±0.4
				OCS	ICS	SOCS	SICS
Ion exchange capacity (meq/g)				2.50	1.15	4.35	3.15

and Na adsorption process, Chi-squre (χ^2) was calculated using Eq. (3).

$$\chi^2 = \Sigma_{i=1}^{n} \frac{(q_{e,\,exp} - q_{e,\,cal})^2}{q_{e,\,cal}} \tag{3}$$

where $q_{e,exp}$ and $q_{e,cal}$ are equilibrium adsorption capacity obtained from experiments and models, respectively.

2-3. Desorption and Regeneration

The reusability of SOCS and SICS was tested with multiple adsorption and desorption cycles in batch mode. The SOCS and SICS used for adsorption were filtered from the working solution and then dried for 12 h at 75 °C in an oven. Desorption tests were performed for the dried SOCS and SICS using HCl based on the exchange mechanism of Ca, K, Mg, Na and HCl. Specifically, 1 g of saturated SOCS and SICS adsorbed with Ca, K, Mg, and Na was put in a 500 mL beaker with 50 mL of HCl of different concentration (0.05 M or 1.0 M) and maintained in a suspended state while stirring at 120 rpm for 5 h. Subsequently, as soon as the optimal HCl concentration was identified, multiple cycles of adsorption and desorption were performed. After desorption of metal ions, they were adsorbed onto adsorbent by reacting with HCl and it was possible to check which ions were adsorbed through sample concentration analysis.

3. Analysis Methods

Samples were taken at a predetermined time for concentration analysis and the residual concentration of metal ions in seawater was measured using ion exchange chromatography (IC Vario, 940, Metrohm) with an autosampler. The pH was controlled using 1 M NaOH and HCl between 3-10; it was measured using a pH meter (SevenGO pro, Mettler Toledo). The point of zero charge (pH_{pzc}) of CS, SOCS and SICS was determined by the solid addition method [21]. The temperature was adjusted to 25-45 °C using a thermostat of a Shaking Incubator. Fourier-transform infrared (FT-IR) spectroscopy was performed with an FT-IR spectrometer (Perkin Elmer, FT-IR 1760X, USA) in the range from 100 to 400 cm^{-1}. In addition, the composition analysis of the OCS and ICS was performed using the most commonly used Van Soest method [22]. To measure the ion exchange capacity (IEC), chemically treated OCS and ICS should be hydrogenated. Generally, a conventional acid-base titration method is used to determine the IEC [23]. The ion exchange capacity (IEC) was calculated according to the general Eq. (4):

$$\text{IEC (meq/g)} = \frac{V_{NaOH}N_{NaOH} - V_{HCl}N_{HCl}}{\text{Weight of dried sample}} \tag{4}$$

where V_{HCl} was the volume of HCl entered during quantification in mL, V_{NaOH} was the volume of NaOH used, N_{HCl} and N_{NaOH} are the normal concentration values of HCl and NaOH used, respectively. Resin weight refers to the total weight and 0.2 g of ion exchange resin was obtained by measuring the weight of the resin dried at 110 °C for one day.

RESULTS AND DISCUSSION

1. Properties of Cornstalk

1-1. Physical Characteristics

The main ingredients of cornstalk are protein, fat, sugar, starch and pectin. Cell wall materials are cellulose, hemicellulose and lignin, and their content accounts for 40-80% of woody plants. Table 3 summarizes the results of component analysis of OCS and ICS. Lignin was 9.4% in OCS and 5.1% in ICS, so OCS had about 1.8 times more lignin content than ICS. Among components of OCS, the content of cellulose was 36.9%, which was more than 25.1% of hemicellulose, indicating that the cell wall material was present more than the cell content. In ICS, the content of cellulose was the highest, but it was not significantly different from hemicellulose, with 29.6% and 27.1%, respectively. The total amount of cellulose and hemicellulose in OCS and ICS was 62.0% and 56.7%, respectively, accounting for superior proportions. In particular, OCS showed higher cellulose and hemicellulose content than ICS. Lignin contains carbonyl, hydroxyl and methyl, while cellulose and hemicellulose contains carboxyl, hydroxyl, aldehyde, carbonyl, polysaccharide and amino functional groups, which have strong affinity for metal ions [10,19]. Metal ions can be adsorbed by ion exchange and complexation. The high content of cellulose and hemicellulose in OCS can have a great influence on the adsorption of metal ions such as Ca, K, Mg and Na. This is because these functional groups can bind to metal ions and small organic contaminants through chelating, completion, coordination and hydrogen bond.

1-2. FT-IR Analysis

FT-IR results of ICS, OCS, SOCS and SICS provide important information to help understand the adsorption mechanism. ICS and OCS showed similar peaks because constituent materials are similar. In both ICS and OCS, the cellulose ester peak (1,067 cm^{-1}), the aliphatic CH-stretching characteristic peak (2,917 cm^{-1}) and the bonded OH peak (3,392 cm^{-1}) were very broad. Note that vibrations were severe between 1,300-1,740 cm^{-1} in both OCS and ICS, which corresponds to C=O cabonyl groups, carboxylic groups and C-O stretch. In addition, at 650 cm^{-1} a peak of N-containing bioligands also appears, though not as strong as the bonded OH peak (Fig. 1(a)). Therefore, it can be said that ICS and OCS have structures suitable for adsorbing metals.

Fig. 1(b) shows the FT-IR of sulfonated SICS and SOCS. Like

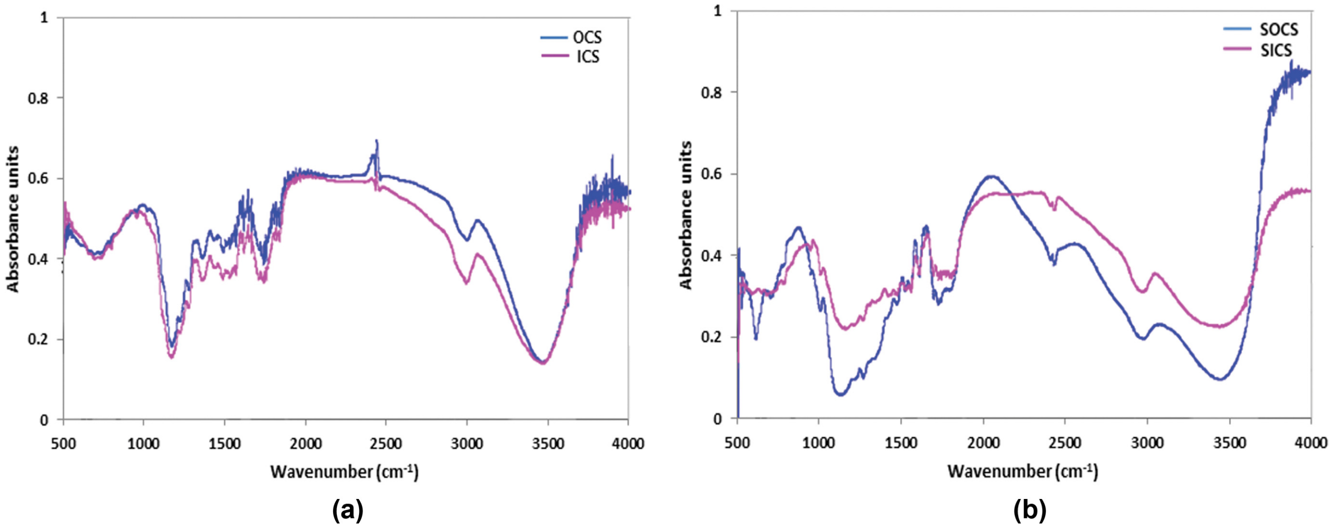


Fig. 1. FT-IR spectra of (a) ICS and OCS, (b) SICS and SOCS.

non-sulfonated OCS and ICS in sulfonated SOCS and SICS, bonded OH-group (3,000-3,500 cm^{-1}), CH stretching (2,900-2,800 cm^{-1}), C=O cabonyl groups (1,740-1,680 cm^{-1}), carboxylic groups (1,670-1,640 cm^{-1}), and C-O stretch (1,450-1,300 cm^{-1}) peaks appeared, but the absorption of the bonded OH-group peak was decreased in the sulfonated cornstalk due to the introduction of sulfone groups. In addition, it was confirmed that the absorption peak of R-SO_3H of 1,232 cm^{-1}, and ketone peaks of 1,642 cm^{-1} and 1,477 cm^{-1} were sulfonated. In particular, N-containing bioligands of SOCS (650 cm^{-1}), the R-SO_3H absorption peak of 1,232 cm^{-1}, carboxylic groups of 1,642 cm^{-1} and peaks of 3,458 cm^{-1} bonded OH-group were larger than that of SICS. This indicates that SOCS has a structure that is easier to ion-adsorb metals than SICS. Significant improvement in the adsorption capacity of OCS and ICS can be achieved by modifying their functional groups. The previous study reported that the metal absorption capacity is proportional to the number of functional groups in the adsorbent [9,14,24]. The transformation of functional groups through sulfonation was predicted to affect the adsorption efficiency of Ca, K, Mg and Na in seawater.

1-3. Ion Exchange Capacity

Ion exchange capacity is one of the most important characteristics of an adsorbent. A large ion exchange capacity means that there are many functional groups [3,10]. When comparing the ion exchange capacity between the outside and inside of cornstalk, the outside was slightly larger than the inside in both chemically treated and untreated cornstalk. In addition, the ion exchange capacity of the sulfonated ones measured 2-3 times higher than that of the unsulfonated ones. Among them, the ion exchange capacity of SOCS, which showed the largest value, was 4.35 meq/g, and the smallest value was 1.15 meq/g of ICS (Table 3). In general, as the ion exchange capacity increases, the amount of metal adsorbed increases too.

2. Adsorption of Metal Ion

2-1. Effect of Adsorbent Dosage and Adsorption Amount

An optimization experiment of the amount of adsorbent was performed to minimize the amount of adsorbent and increase adsorption efficiency. In the study on the effect of the amount of adsorbent on adsorption efficiency, the adsorption efficiency increased significantly from 1 to 5 g/L as the amount of adsorbent increased (Fig. 2). However, the difference between 5 and 10 g/L showed little change in adsorption efficiency in Ca, K, Mg and Na metal ions. This is because the concentration of metal ions in the aqueous solution is fixed, and as the amount of the adsorbent increases, the surface of the adsorbent that cannot be adsorbed increases. Therefore, when the critical value is reached, there is little change in the amount adsorbed to the adsorbent. Therefore, when adsorbing cations such as Ca, K, Mg and Na using OCS, ICS, SOCS and SICS in seawater, 5 g/L of adsorbent is recommended.

The adsorption efficiency of Ca, Mg, K and Na was studied onto OCS, ICS, SOCS and SICS according to results of the above-described adsorbent amount experiment. Based on those results, the average adsorption ratio of all ions decreased in the order of SOCS>SICS>OCS>ICS and the adsorption efficiency of each ion decreased in the order of Ca>Mg>K>Na (Table 4). The adsorption reaction has a difference in selectivity depending on the metal species in solution [10,25]. For example, the selectivity or affinity according to the metal species of the sulfonic acid type ion exchange group, which was a strong acidic cation exchange group, was Na>K>Mg>Ca in order of low affinity. It is known that the arrangement was determined from the positive number of positive ions, the ion radius and the magnitude of the electrostatic force acting between the sulfonic acid. In the case of a transition metal, it was impossible to simply display it because it forms various metal complexes, and Mg dissolved in an aqueous solution has an affinity of about the same size as Ca.

In this experiment, the amount of adsorption of divalent cations (Ca and Mg), which are alkaline earth metals, was higher than that of monovalent cations (Na and K), which are alkali metals. In particular, Na ions showed relatively little adsorption capacity compared to other ions, which is thought to be due to the relatively low selectivity of Na ions compared to K, Mg and Ca. As a result of adsorbing Ca, K, Mg, and Na from seawater with 5 g/L of adsorbent, SOCS showed the highest adsorption rates of 78.9%, 59.4%,

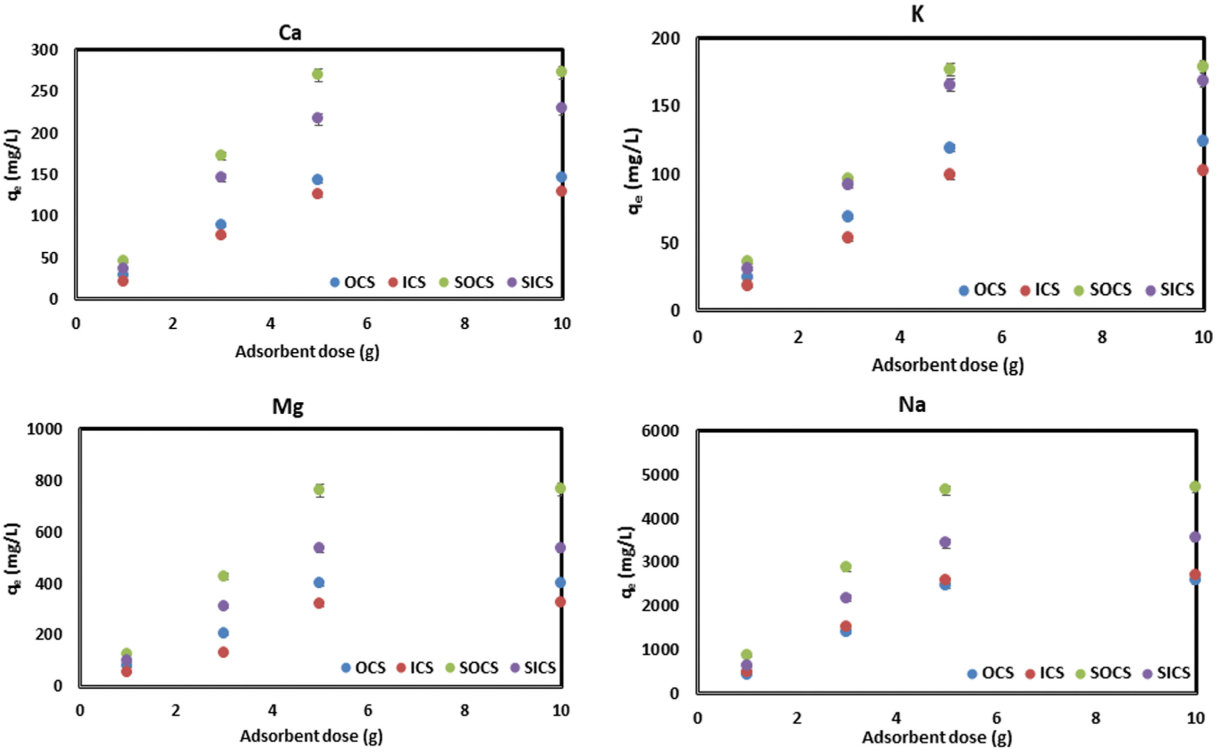


Fig. 2. Recovery amount of Ca, K, Mg and Na onto OCS, ICS, SOCS and SICS by various doses.

Table 4. Maximum removal efficiency of metal ion on various materials (25 °C, pH: 8.0, dosage: 5 g/L)

	Ca [mg/L]	K [mg/L]	Mg [mg/L]	Na [mg/L]
Initial concentration of sea water	391.87±1.62	359.26±1.87	1,127.62±2.86	10,198.17±4.21
OCS	161.45 (41.20%)	126.49 (35.21%)	420.60 (37.30%)	2,756.57 (27.03%)
ICS	146.21 (37.31%)	117.08 (32.59%)	375.61 (33.31%)	2,559.74 (25.10%)
SOCS	309.15 (78.89%)	213.26 (59.37%)	873.34 (77.45%)	5,329.56 (52.26%)
SICS	255.77 (65.27%)	198.31 (55.20%)	690.89 (61.27%)	4,443.34 (43.57%)

77.5% and 52.3%, respectively. On the other hand, ICS showed the lowest adsorption efficiency of Ca, K, Mg and Na of 37.3%, 32.6%, 33.3% and 25.1%, respectively. This is related to the ion exchange capacity, as shown in Table 3. Since the ion exchange capacity is closely related to the adsorption amount of metals, many researchers are modifying various adsorbents to increase the ion exchange capacity [3,10]. The adsorption efficiency of the sulfonated adsorbent increased by 27.96-41.58% for Ca, 22.61-26.78% for K, 27.96-44.14% for Mg and 18.47-27.16% for Na compared to the non-sulfonated adsorbent. This is consistent with the research results of many researchers, who adsorbed heavy metals in aqueous solutions by modifying agricultural waste as already mentioned in the introduction. The adsorption reaction of Ca, K, Mg and Na onto OCS, ICS, SOCS and SICS took place very rapidly until the initial 30 min but slowly slowed after 30 min and almost no change was observed after 60 min. It was found that adsorption equilibrium was reached after 1 h of reaction (Fig. S2).

2-2. Effect of pH

The point of zero charge (pH_{pzc}) represents the pH value when the zeta potential of the adsorbent reaches zero [26]. If the pH value is lower than the pH_{pzc} value, more hydrogen ions can be exchanged for heavy metal cations, but the high concentration of hydrogen ions protonates the surface functional groups (e.g., -OH) of the lignocellulose-based adsorbent, increasing the number of surface positive charges. Then, the adsorption of cationic ions in the aqueous solution is reduced due to electrostatic repulsion, and the adsorption efficiency of anions is improved [24]. Conversely, when the pH value is higher than pH_{pzc}, deprotonation returns the surface of the functional group to a negative charge, resulting in the opposite effect of cations and anions [27]. Therefore, in the adsorption of cationic substances, the pH_{pzc} of the lignocellulose-based adsorbent should be more acidic for a wider range of pH action, whereas for the adsorption of anionic substances, pH_{pzc} should be more alkaline. To find the pH_{pzc} of SOCS and SICS, the experiment was performed by controlling the pH from 2 to 10, and the results are shown in Fig. S3. The ΔpH is the value obtained by subtracting the initial pH from the final pH. The pH_{pzc} of SOCS and SICS was found to be 4.8 and 4.9, respectively, while CS was measured 7.3. The pH_{pzc}

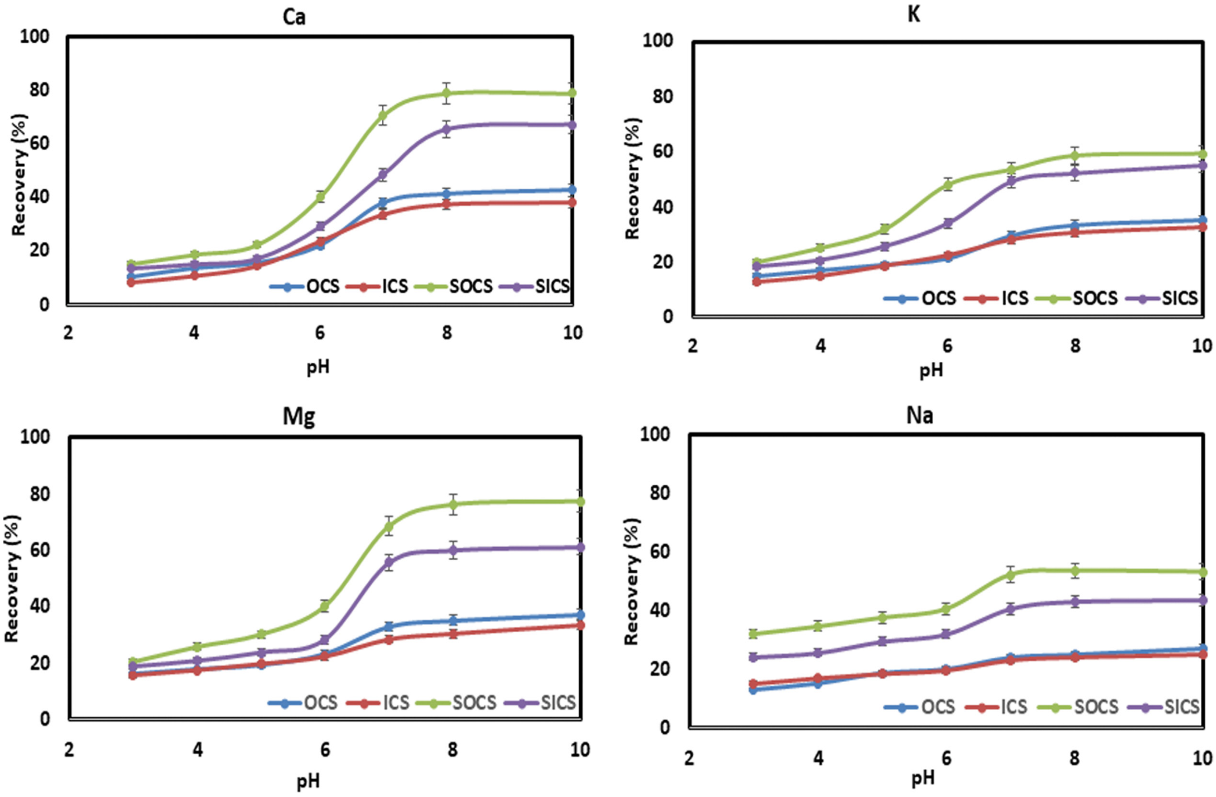


Fig. 3. Recovery amount of Ca, K, Mg and Na onto OCS, ICS, SOCS and SICS by different pH.

was lowered after modification of CS with sulfuric acid and it was confirmed that there is an acidic functional group on the surface of the SOCS and SICS. The negative surface charge of SOCS and SICS can be found in a pH environment above pH_{pzc}, which favors adsorption of cationic ion. In general, cationic ion adsorption may be due to the presence of OH, COO-, and SO_3-groups on the SOCS and SICS surface.

To find the adsorption efficiency of Ca, K, Mg and Na according to the change of pH from sea water, the pH was adjusted from 3 to 10, the experiment was performed using an OCS, ICS, SOCS and SICS of 5 g/L and the results are depicted in Fig. 3. The adsorption efficiency of Ca, K, Mg and Na in seawater onto OCS, ICS, SOCS and SICS was increased as the pH increased. The adsorption efficiency at pH 7 increased around 2.6 times compared to pH 3 in all samples. In particular, the adsorption efficiency of the SOCS and SICS adsorbents increased more than that of the OCS and ICS (Fig. 3).

In general, as the solution pH increases, the adsorption of cationic metals increases, while the removal efficiency of anionic metals decreases [13,28]. The high concentration of H^+ ions will compete with Ca, K, Mg and Na ions for exchangeable cations on the surface of SOCS and SICS adsorbents. Therefore, the electrostatic interaction between Ca, K, Mg and Na ions and SOCS/SICS was weak at low pH, thereby inhibiting the adsorption of Ca, K, Mg and Na ions on the surface of SOCS and SICS, and finally low adsorption efficiency was observed. This opinion is consistent with Li et al. [15] explaining the reason why the adsorption capacity of the adsorbent increased significantly with increasing pH in the experiment of adsorbing cationic dyes using sulfonated lignin. The authors suggested that the increase in adsorption efficiency with increasing pH is not the only improvement in electrostatic interactions caused by pH. As the pH increases, the ionized R-COO$^-$ and R-O- groups perform similar functions to the SO_3^{2-} group [11,20]. Thus, since the ionized R-COO$^-$ and R-O- groups can expand the form of the adsorbent by electrostatic repulsion, it facilitates the formation of π-π stacking with Ca, K, Mg and Na ionic molecules. Then, as the pH increases, the negative group on the surface of the adsorbent not only enhances the electrostatic interaction, but also enhances the π-π stacking in adsorption [19,29]. Therefore, the sulfonated adsorbents reactions are sensitive to pH due to the co-effect of electrostatic interaction and π-π stacking.

2-3. Effect of Dilution

By diluting seawater, various initial concentrations of Ca, K, Mg and Na were studied for adsorption efficiency onto OCS, ICS, SOCS and SICS, and the results are depicted in Fig. 4.

As the initial concentration of each metal ion decreased, the adsorption amount of Ca, K, Mg and Na onto the adsorbent increased. The maximum adsorption efficiency of Ca and Mg was 98% on SOCS at a dilution ratio of 3:1 between distilled water and seawater. It was considered that the lower the concentration of metal ions in the solution, the higher the opportunity to bind with metal ions on the surface of the adsorbent active point, and thus the amount of metal adsorbed on the adsorbent increases. So, it was considered to increase the removal efficiency because the adsorption active point on the surface of the adsorbent is relatively sufficient at a low concentration. The findings of this study are in

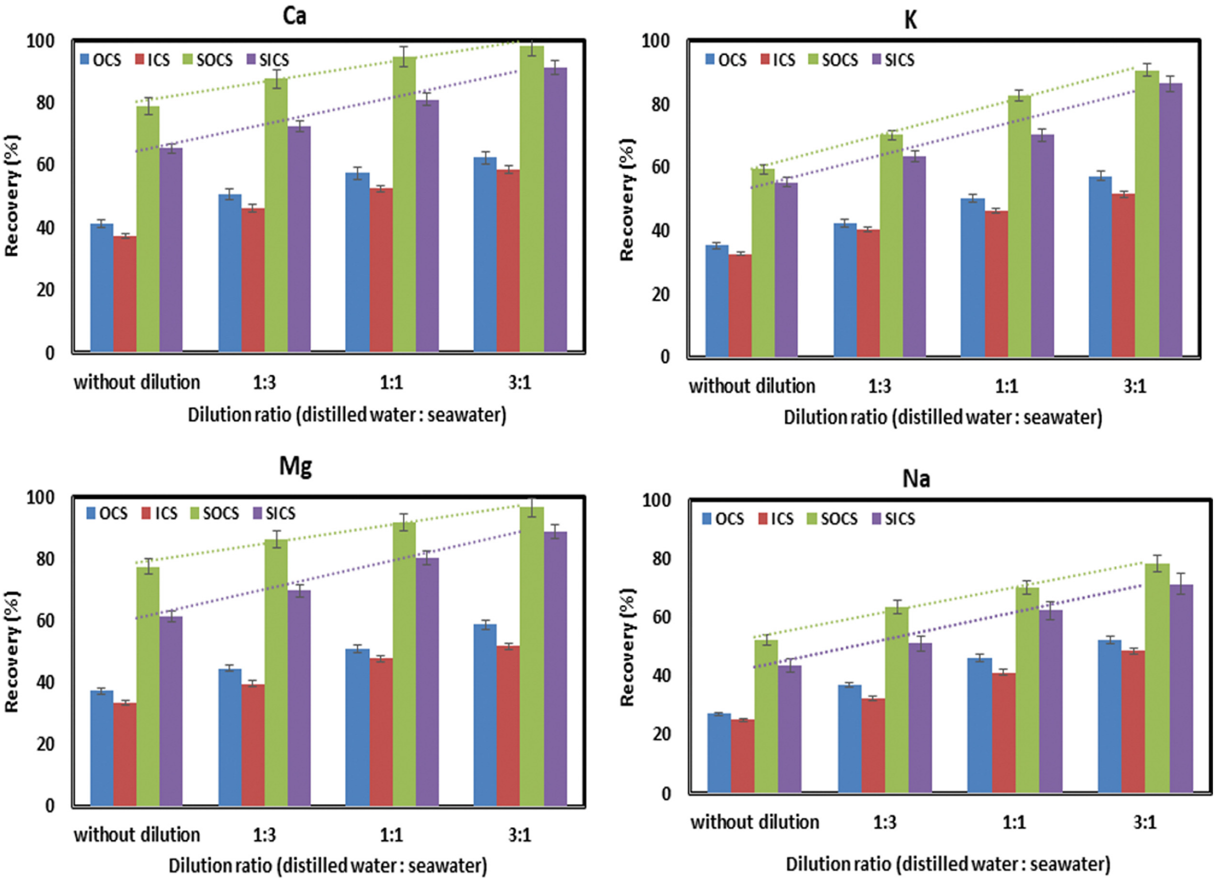


Fig. 4. Effect of dilution ratio for recovery of Ca, K, Mg and Na onto OCS, ICS, SOCS and SICS.

agreement with those of Shaddel et al. [6].

3. Adsorption Kinetics and Adsorption Isotherms

The adsorption amounts of Ca, Mg, K and Na adsorbed onto SOCS and SICS were more than twice than that of the OCS and ICS. Therefore, the adsorption kinetics and adsorption isotherms were to be studied focusing on adsorption efficiency of SOCS and SICS.

3-1. Adsorption Kinetics

To compare the adsorption rate of the SOCS nd SICS, a kinetics experiment was conducted, and the analysis results of the main parameters are summarized in Table 5. To design an efficient model for the adsorption process, it is necessary to understand the kinetics analysis. As representative models for the adsorption rate to analyze adsorption kinetics, there are PFO and PSO. The PFO equation was presented by Lagergren, and is one of the rate equations widely applied to the adsorption process of solutes from aqueous solutions [16,30]. Based on the adsorption equilibrium capacity of the solid phase, k_2 is the PSO constant (g/mg·min), and q_e is the adsorption amount of adsorbent (mg/g) at equilibrium. The plot of PFO and PSO for SOCS and SICS is depicted in Fig. S4. The values of k_2 and q_e can be obtained from the slope and intercept of the equation. As a result of the analysis of the kinetics experiment, when metal ions were adsorbed using SOCS and SICS, the adsorption reaction was almost completed within 60 min.

The k_1 of pseudo-1st-order of SOCS was higher than that of SICS. This indicates that cations of Ca, K, Mg and Na in seawater had a faster adsorption reaction onto SOCS than SICS. In addition, the divalent cations of Ca and Mg had higher k_1 values than the monovalent cations of K and Na, indicating that the divalent cations had a faster adsorption rate to SOCS or SICS than the monovalent cations. The correlation coefficient (R^2) of the kinetic model was higher in PSO (0.9859-0.9991) than PFO (0.8951-0.9971). Therefore, the process of adsorbing Ca, K, Mg and Na in seawater using SOCS and SICS was more suitable for the PSO than that of PFO.

3-2. Adsorption Isotherms

An isothermal adsorption experiment was performed to evaluate the adsorption of Ca, K, Mg and Na for SOCS and SICS, and to obtain information on the adsorption properties. The obtained results are analyzed and summarized in Table 5. In general, the isothermal adsorption equation is represented by two models, Langmuir and Freundlich isotherm. In the Langmuir isothermal adsorption, the bonding site on the surface of the adsorbent reacts stoichiometrically 1 : 1 with the adsorbate and each reaction site is uniform [11,31]. The Freundlich isotherm is an adsorption model based on the assumption that the adsorption site of the adsorbent is not uniform and the adsorption energy continuously decreases as the adsorption amount increases [12,32]. The Freundlich isotherm is the most widely applied equation for the analysis of liquid phase adsorption in a heterogeneous surface adsorption reaction [14,16].

Table 5. Parameters of kinetics and isothermoal models for Ca, K, Mg and Na sorption onto SOCS and SICS

Isotherm models		SOCS				SICS			
		Ca	K	Mg	Na	Ca	K	Mg	Na
PFO	q_e	112.13	60.67	82.12	60.12	131.16	79.43	113.82	63.38
	k_1	0.0764	0.0316	0.0418	0.0299	0.0300	0.0359	0.0388	0.0311
	χ^2	3.3416	2.0621	3.3812	3.5206	2.4654	2.9861	3.4102	3.1349
	R^2	0.9668	0.9971	0.9546	0.8951	0.9848	0.9826	0.9374	0.9749
PSO	q_e	117.65	71.43	100.08	60.61	194.12	87.27	133.33	52.26
	k_2	2.98×10^{-8}	7.95×10^{-8}	1.33×10^{-9}	0.81×10^{-10}	3.93×10^{-7}	8.50×10^{-8}	1.72×10^{-9}	0.95×10^{-10}
	χ^2	1.2768	1.1615	1.3024	1.3821	1.2064	1.2385	1.3426	1.2572
	R^2	0.9987	0.9991	0.9768	0.9933	0.9954	0.9962	0.9859	0.9984
Langmuir	q_m	158.62	133.33	153.85	125.03	153.85	122.86	150.86	111.11
	K_L	0.057	0.010	0.026	0.006	0.008	0.005	0.008	0.004
	R_L	0.171	0.089	0.038	0.149	0.558	0.161	0.113	0.204
	χ^2	1.5106	1.9012	2.0316	1.8362	2.3162	1.3524	1.6623	1.0963
	R^2	0.9889	0.9875	0.9865	0.9884	0.9808	0.9914	0.9888	0.9983
Freundlich	1/n	0.512	0.467	0.378	0.595	0.548	0.577	0.538	0.593
	K_F	51.59	22.31	20.21	5.01	12.46	14.43	11.35	6.46
	χ^2	5.2013	4.2362	4.2916	5.3695	4.3542	4.4621	4.6325	4.6012
	R^2	0.9456	0.9831	0.9792	0.9428	0.9734	0.9627	0.9603	0.9632
Dubinin Radskevih (D-R)	q_m	143.26	121.87	141.06	108.65	143.34	107.06	138.57	89.85
	E	0.8256	0.2061	0.7345	0.3654	0.7129	0.2761	0.6857	0.2557
	χ^2	43.8967	47.5646	38.6212	87.6592	23.1759	40.6528	34.9518	53.7614
	R^2	0.9781	0.9705	0.9816	0.8651	0.9916	0.9848	0.9887	0.8879
Temkin	B	14.42	5.72	8.46	2.59	11.62	4.16	7.17	2.71
	K_T	1.148	0.6004	0.8290	0.3759	0.9862	0.5716	0.7869	0.4153
	χ^2	21.5923	43.2659	30.6532	76.4138	11.9896	26.5621	18.4632	58.5443
	R^2	0.9145	0.9042	0.9134	0.895	0.9547	0.9126	0.9243	0.8891

K_F and n can be determined from the linear plot of $\ln q_e$ vs. $\ln C_e$. A plot of q_e versus $\ln C_e$ enables the determination of the constants A and B. A plot of lnae vs. ε^2 enables the constants q and E to be determined.

The separation coefficient R_L $(=1/(1+K_LC_o)$ of Ca, K, Mg and Na adsorbed on SOCS and SICS was found to be between 0.038 and 0.558. If the value of R_L is between 0 and 1, the adsorption treatment is favorable [12,24]. The adsorption isotherm of Langmuir and Freundlich of Ca, K, Mg and Na by SOCS and SICS is depicted in Fig. S5. The value of K_F, which is a measure of the adsorption capacity calculated from the Freundlich equation, indicates that the higher the value, the better the adsorption capacity. When the value of 1/n, which represents the adsorption strength, is generally between 0 and 1, adsorption easily occurs, but when it is more than 2, adsorption is difficult [25,28]. In this experiment, 1/n was analyzed in the range of 0.378-0.595, so adsorption of Ca, K, Mg and Na onto SOCS and SICS easily happened in seawater. In addition, the value of K_F was highest in Ca, followed by K and Mg in order. The applicability of the adsorption model is that the lower the value of χ^2 and higher the value of correlation coefficient (R^2), the better fit isothermal model [33]. Therefore, adsorption of Ca, Mg, K and Na using SOCS and SICS was more suitable for the Langmuir model than that of other isotherm model (Table 5).

The mean free energy (E) of D-R can be used to determine whether the adsorption process is physisorption (<8 kJ/mol) or chemisorption (8-16 kJ/mol) [27]. In all samples, E was calculated in the range of 0.2061 to 0.8256, indicating that the adsorption process was a physisorption. The Temkin isotherm indicates that the heat of adsorption of Ca, K, Mg and Na decreases linearly rather than logarithmically with coverage. The Temkin isothermal adsorption constant B was measured to be in a range of 2.71 to 14.40 (J/mol), corresponding to the physical adsorption area (B<20 J/mol). Therefore, adsorption of Ca, K, Mg and Na onto SOCS and SICS is considered to be closer to physical adsorption caused by the action of van der Waals force consisting of dispersing force and electrostatic force rather than chemical adsorption of changing chemical form.

4. Adsorption Mechanisms

The lignocellulose-derived sulfonated cornstalk was a strong acid cation adsorbent (SAC). SAC has adsorption capacity due to the sulfuric acid functional group contained in the adsorbent [19]. According to the literature, SAC adsorbent adsorbs almost all cations contained in raw water and exchanges them for hydrogen ions [17,34]. In addition, since the strong acid cation exchange adsorbent is well applied in all pH ranges, its application range is very wide [29]. Here, compared with the structure of sulfonated and

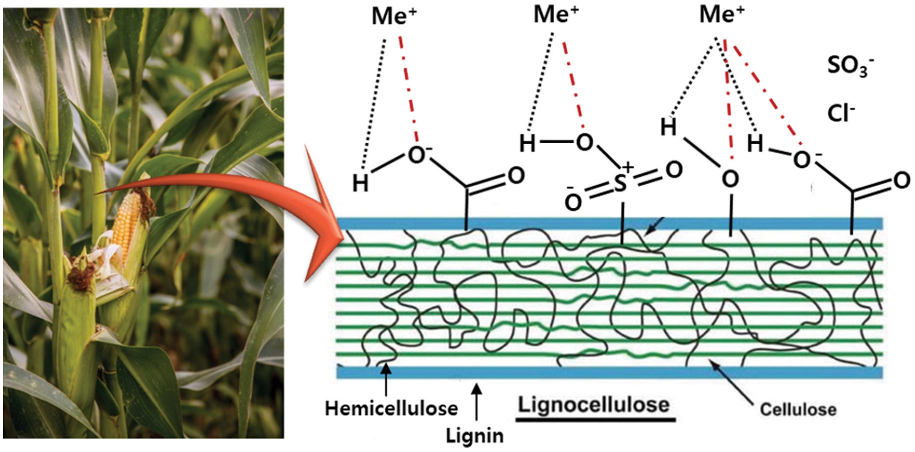


Fig. 5. Possible adsorption mechanism of Ca, Mg, Na and K by SOCS and SICS (Me=Ca, Mg, Na and K).

unsulfonated cornstalk, the sulfonated one has a structure that can easily form a chelating metal complex for large cations. For this reason, it is expected that there will be differences in adsorption capacity between unsulfonated and sulfonated cornstalk. SOCS showed better results for adsorption of Ca, K, Mg and Na in seawater than SICS, and the adsorption efficiency was better than that of the sulfonated adsorbent without treatment. The reason can be seen in Fig. 5.

The adsorbent of SOCS and SICS differs from OCS and ICS in the adsorption mechanism of cations due to the difference in the structural aspect of the functional groups. Thus, the sulfonated adsorbent has a structure that can easily form a chelating metal complex for a cation. The adsorption efficiency of ions may vary depending on the functional group of the adsorbent, the amount of charge of the ions, the difference in ion radius and activity, concentration conditions and pH [10,14]. That is the reason why the adsorption efficiency of ions to the adsorbent was in the order Ca>Mg>K>Na. It can be seen that the effect of the charge amount, activity and functional group of the ions is large. Other factors may be related to the properties of the adsorbent. The smaller the amount of adsorption capacity of the adsorbent, the less the adsorption efficiency can be due to the limitation of the amount that can be adsorbed [17,27]. According to FT-IR analysis, sulfonation grafted the -SO_3 group on the surface of the SOCS and SICS and strengthened the carboxyl group (-COOH) and hydroxyl group. Moreover, after the surface modification of cornstalk with sulfuric acid, the pH_{pzc} was lowered. This indicates that the sulfonyl group is attached to the adsorbent surface, which is consistent with the results of FT-IR analysis. The mechanism of adsorption of SOCS/SICS and Me (Ca, Mg, K and Na) ions in sea water can be explained by the following:

SOCS-OH+MeCl ---> SOCS-O-Me+HCl
SOCS-COOH+MeCl ---> SOCS-COO-Me+HCl
SOCS-SO_3H+MeCl ---> SOCS-SO_3-Me+HCl

As a result, the adsorption efficiency of Ca, K, Mg and Na onto SOCS and SICS was improved. Depending on the functional groups available on the SOCS and SICS surfaces, the adsorption mechanisms for Ca, Mg, K and Na can occur through various interactions. First, the electrostatic attraction between positively charged cations in aqueous solution and negatively charged functional groups on the SOCS and SICS surface. Second, the hydrogen bonding interactions between the surface hydrogen bonding of the functional groups available on the SOCS and SICS surface and Ca, K, Mg and Na ions. Third, the π-π stacking interaction between the cations and the SOCS and SICS adsorbent. The adsorption of Ca, K, Mg and K onto SOCS and SICS is a complex phenomenon due to the various interactions mentioned above.

5. Effect of Temperature

Temperature is an important factor that can affect the adsorption process. The reaction temperature determines all potential ion exchange products as well as the solubility product of the metal ion, which can determine the rate of adsorption [12,35]. The solubility of such metal ions affects adsorption efficiency and can induce adsorption between metal ions contained in seawater and the surface of the adsorbent [19,25]. The thermodynamic parameter was calculated by the following equations:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (5)$$

$$\ln (q_e/C_e) = \Delta S^0/R - \Delta H^0/RT \quad (6)$$

where ΔH^0 is adsorption enthalpy change, ΔS^0 is adsorption entropy change and ΔG^0 is Gibbs free energy. R is the universal gas constant, T (K) is the thermodynamic temperature.

As the temperature increased, the adsorption efficiency of Ca, K, Mg and Na decreased 4.6-12.01% for SOCS and 8.94-22.56% for SICS. These experimental results also mean that there is no need to artificially increase the temperature in order to increase the adsorption efficiency in the process of adsorbing Ca, K, Mg and Na from seawater. The thermodynamic plot is shown in Fig. S6(a) and (b). The range of ΔG^0 for physisorption is –20 to 0 kJ/mol and the range of chemisorption is –400 to –80 kJ/mol. From Table 6, it is clear that the adsorption of Ca, K, Mg, and Na onto SOCS and SICS was close to physisorption. In addition, as the temperature decreases, the value of ΔG^0 gradually decreases, suggesting that the lower the temperature, the more the adsorption of Ca, K, Mg and Na onto SOCS and SICS was favorable. As generally known, increasing temperature accelerates the aggregation of lignocellulose

Table 6. Themodynamic parameters for SOCS and SICS adsorption

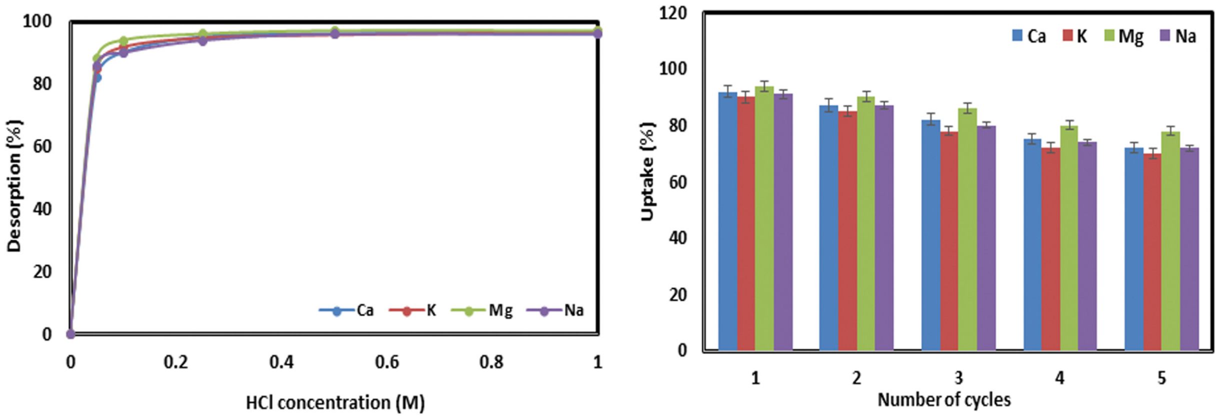
Temperature		SOCS			SICS		
		ΔG^o (KJ/mol)	ΔH^o (KJ/mol)	ΔS^o (J/mol)	ΔG^o (KJ/mol)	ΔH^o (KJ/mol)	ΔS^o (J/mol)
Ca	288	−5.65	−86.24	−279.83	−5.03	−65.23	−209.03
	298	−2.85			−2.94		
	308	−0.05			−0.85		
K	288	−4.25	−78.94	−259.34	−2.59	−43.11	−140.69
	298	−1.66			−1.18		
	308	−0.94			−0.22		
Mg	288	−5.57	−87.38	−284.06	−4.79	−64.29	−206.60
	298	−2.73			−2.72		
	308	−0.11			−0.66		
Na	288	−3.69	−75.69	−250.01	−2.04	−51.33	−171.14
	298	−1.16			−0.33		
	308	1.31			1.38		

molecules in the cornstalk, reducing the amount of various functional groups exposed to the surface [10,19]. Entropy, enthalpy and free energy almost show negative values, indicating that the adsorption of Ca, K, Mg and Na using SOCS and SICS is an exothermic and spontaneous reaction. However, ΔG^0 for Na onto SOCS and SICS at 308 K was found to be positive values, indicating that the reaction was unspontaneous.

Many researchers have reported that the bioadsorption process is exothermic and inversely proportional to temperature [9,12,27]. Kumar et al. [36] reported that the bioadsorption of Cd(II) by the cashew nut shell decreased from 80.13% to 74.32% as the temperature increased from 30 °C to 60 °C, which was due to the decrease in the surface activity of the adsorbent. As a result of adsorbing Zn(II), Cd(II) and Mn(II) using cornstalks with a similar tendency, the bioadsorption efficiency for Zn(II) was decreased from 52% to 28%, for Cd(II) from 34% to 16% and for Mn(II) from 39% to 13% as the temperature increased from 25 °C to 55 °C [7]. However, several researchers have reported the adsorption efficiency increased due to an increase in the number of available active sites or a decrease in the thickness of the boundary layer surrounding the adsorbent with increasing temperature [11,35]. Nevertheless, many researchers agree that high temperatures can lead to physical damage to bioadsorbents. Therefore, most bioadsorption experiments are run at room temperature. This experiment using sulfonated cornstalk was also consistent with the above experimental results. As the temperature increased, the adsorption efficiency decreased and, as mentioned above, the cause can be found in the decrease of the electrostatic attraction of Ca, Mg, K and Na ions onto SOCS and SICS and the decrease of other active sites.

6. Desorption and Regeneration

In this study, SOCS, which has the highest adsorption efficiency, was used in the adsorbent regeneration experiment based on the above experimental results. Ca, K, Mg and Na ions were desorbed using HCl and SOCS was regenerated. Different concentrations of HCl ranging from 0.05 M to 1.00 M were used to desorb Ca, K, Mg and Na ions from SOCS. Desorption close to 92.6±0.6% was achieved above 0.1 M HCl (Fig. 6(a)). Based on the results, 0.1 M HCl was selected to conduct adsorption/desorption experiments



(a) (b)

Fig. 6. SOCS regeneration capacity in terms (a) Ca, K, Mg and Na desorption with HCl at varied concentration (b) adsorption/desorption of Ca, K, Mg and Na with 0.1 M HCl (n=5).

of Ca, K, Mg and Na ions from SOCS. The regeneration and reuse capacity of SOCS was evaluated by adsorbent and desorption through five cycles. In the first cycle, adsorption of Ca, K, Mg and Na onto SOCS was measured to be about 2-3% higher than the desorption value, which may be due to the concentration of Ca, K, Mg and Na already present in SOCS. From the second cycle, desorption and adsorption gradually decreased, and the adsorption of Ca, K, Mg and Na to SOCS decreased by about 20% until the fifth cycle and stabilized in the fifth cycle (Fig. 6(b)). As a result of adsorption/desorption experiments on SOCS, there was little damage to the adsorbent. Therefore, it was confirmed that SOCS was not significantly affected by repeated adsorption and desorption cycles. Nevertheless, regeneration of SOCS in powder form was possible in batch study, but it must be admitted that mass loss is inevitable in the actual field. Therefore, it is considered that proper encapsulation of SOCS is necessary to maintain the mass and be practically applicable to dynamic filter columns. SOCS and SICS, lignocellulose derived adsorbents, can be used to adsorb heavy metal ions in wastewater treatment systems, so they can be seen as having great industrial and economic value.

7. Analysis of Cost

Since the cost required to convert the lignocellulose component of cornstalk into a natural cationic adsorbent is very inexpensive compared to the production cost of the existing synthetic polymer adsorbent (Ambelite IR-124: 50,000 won/50 g, Dowex 50W-X8: 80,000 won/50 g) [10,19], it was confirmed that it is worth using cornstalk, a natural resource, in the seawater desalination industry. In addition, through this study, a sulfonated cornstalk adsorbent will be able to adsorb trace elements in seawater. For example, lithium is a new industrial material that is used as a raw material for alloys, lithium batteries, refrigerants, and chemical products. It accounts for about 170 μg per liter of seawater, and the total amount is about 230 billion tons, which is a huge resource [37].

In the course of this study, the ligno-cellulose derived adsorbent made of sulfonated cornstalk showed high adsorption efficiency for calcium ions. In particular, calcium has a strong reducing power, so it is used to manufacture metals from oxides of hardly reducing metals such as titanium, zirconium, thorium and uranium [38]. It is used as a deoxidizer and desulfurization agent for other metals and alloys [39]. Since it is used in such a variety of ways, the adsorbed calcium can enjoy industrial value and economic effect. In this regard, if the amount of ion adsorbent is increased and mass-produced and a large column of several stages is produced, a large amount of calcium can be adsorbed.

CONCLUSIONS

This study attempted to adsorb Ca, K, Mg and Na from seawater by sulfonating the outer and inner cornstalk. The main components of the outer and inner cornstalk were cellulose, hemicellulose and lignin. In the case of sulfonating cornstalk, it was confirmed that a new adsorbent having a very good cation exchange functional group was made from the reaction mechanism of the adsorbent and the structure confirmation using the FT-IR spectra. The sulfonated cornstalk had higher ion exchange capacity than the natural cornstalk, and the largest ion exchange capacity was 4.35 meq/g of SOCS. Sulfonated cornstalk is a ligno-cellulose derived adsorbent that has excellent stability as an adsorbent material for cations. The adsorption efficiency of Ca, K, Mg and Na from seawater using SOCS was found to be the best under the conditions of pH 7, 1 g/L of SOCS and 3 : 1 (distilled water:seawater). The highest adsorption capacity was found to be in SOCS, where 158.62, 133.33, 153.85 and 125.03 (mg/g) was adsorbed for Ca, K, Mg and Na, respectively. Moreover, the adsorption of Ca, K, Mg and Na onto sulfonated cornstalk was exothermic and was suitable for Langmuir and PSO. Lignocellulose derived sulfonated cornstalk, capable of adsorbing cations such as Ca, K, Mg and Na from seawater, are renewable and can be applied in the field. However, regeneration of SOCS in powder form is possible in batch study, mass loss is inevitable in the actual field. Therefore, it is considered that proper encapsulation of SOCS is necessary to maintain the mass and be applicable to the actual field.

ACKNOWLEDGEMENT

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIT) (No. 2021R111A305924311)

COMPLIANCE WITH ETHICAL STANDARDS

The author(s) confirmed that this article content has no conflict of interest.

DECLARATION OF COMPETING INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CREDIT AUTHORSHIP CONTRIBUTION STATEMENT

Hee-Jeong Choi (Prof. Ph.D): Conceptualization, Methodology, Data curation, Writing - original draft, Visualization, Investigation, Software, Validation, Writing - review & editing.

STATMENT OF INFORMED CONSENT, HUMAN/ ANIMAL RIGHTS

No conflicts, informed consent, human or animal rights applicable.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

SUPPORTING INFORMATION

Additional information as noted in the text. This information is available via the Internet at http://www.springer.com/chemistry/journal/11814.

REFERENCES

1. F. J. Millero, R. Feistel, D. G. Wright and T. J. McDougall, *Deep-sea Res.*, **55**, 50 (2008).
2. K. Ghyselbrecht, B. Sansen, A. Monballiu, Z. L. Ye, L. Pinoy and B. Meesschaert, *Sep. Purif. Technol.*, **221**, 12 (2019).
3. S. Roobavannan, S. Vigneswaran and G. Naidu, *Chem. Eng. J.*, **396**, 125386 (2020).
4. W. Shi, P. Nie, X. Shang, J. Yang, Z. Xie, R. Xu and J. Liu, *Electrochim. Asta*, **310**, 104 (2019).
5. A. S. Bello, N. Zouari, D. A. Da'ana, J. N. Hahladakis and M. A. Al-Ghouti, *J. Environ. Manag.*, **288**, 112358 (2021).
6. S. Shaddel, T. Grini, S. Ucar, K. Azrague, J. P. Andreassen and S. W. Østerhus, *Water Res.*, **173**, 115572 (2020).
7. I. Menshchikov, A. Shiryaev, A. Shkolin, V. vysotskii, E. Khozina and A. Fomkin, *Korean J. Chem. Eng.*, **39**(2), 279 (2021).
8. C. A. Esteves Costa, W. Coleman, M. Dube, A. E. Rodrigues and P. C. Rodrigues Pinto, *Ind. Crop. Prod.*, **92**, 136 (2016).
9. A. O. Ayeni, O. Agboola, M. O. Daramola, B. Grabner, B. A. Oni, D. E. Babatunde and J. Evwodere, *Korean J. Chem. Eng.*, **38**(1), 81 (2021).
10. E. Santoso, R. Ediati, Y. Kusumawati, H. Bahruji, D. O. Sulistiono and D. Prasetyoko, *Mater. Today Chem.*, **16**, 100233 (2020).
11. L. Zhu and Z. Zhong, *Korean J. Chem. Eng.*, **37**(10), 1660 (2020).
12. Y. Dai, Q. Sun, W. Wang, L. Lu, M. Liu, J. Li, S. Yang, Y. Sun, K. Zhang, J. Xu, W. Zheng, Z. Hu, Y. Yang, Y. Gao, Y. Chen, X. Zhang, F. Gao and Y. Zhang, *Chemosphere*, **211**, 235 (2018).
13. Y. Jiang, X. Wang, Z. Wu, J. Xu, L. Hu and L. Lin, *Korean J. Chem. Eng.*, **38**(4), 788 (2021).
14. Q. Chen, J. Zheng, L. Wen, C. Yang and L. Zhang, *Chemosphere*, **224**, 509 (2019).
15. J. Li, H. Li, Z. Yuan, J. Fang, L. Chang, H. Zhang and C. Li, *Int. J. Biol. Macromol.*, **135**, 1171 (2019).
16. R. Elangovan, L. Philip and K. Chandraraj, *J. Hazard. Mater.*, **152**, 100 (2008).
17. J. M. Fonseca, L. Spessato, A. L. Cazetta, K. C. Bedin, S. A. R. Melo, F. L. Souza and V. C. Almeida, *Energy Convers. Manag.*, **217**, 112975 (2020).
18. J. Wolska and J. Walkowiak-Kulikowska, *Eur. Polym. J.*, **129**, 109635 (2020).
19. G. A. O. Weijue, P. John, W. Inwood and F. A. T. E. H. I. Pedram, *J. Bioresour. Bioprod.*, **4**(2), 80 (2019).
20. S. Sabar, H. Abdul Aziz, N. H. Yusof, S. Subramaniam, K. Y. Foo, L. D. Wilson and H. K. Lee, *React. Funct. Polym.*, **151**, 104584 (2020).
21. D. H. Lataye, I. M. Mishra and I. D. Mall, *Ind. Eng. Chem. Res.*, **45**, 3934 (2006).
22. P. J. Van Soest, *JAOAC*, **46**, 829 (1963).
23. K. F. L. Hagesteijn, S. Jiang and B. P. Ladewig, *J. Mater. Sci.*, **53**, 11131 (2018).
24. H. J. Choi, *Water Environ. Res.*, **91**, 1600 (2019).
25. T. A. H. Nguyen, H. H. Ngo, W. S. Guo, J. Zhang, S. Liang, Q. Y. Yue, Q. Li and T. V. Nguyen, *Bioresour. Technol.*, **148**, 574 (2013).
26. H. J. Choi and S. W. Yu, *Korean J. Chem. Eng.*, **35**(11), 2198 (2018).
27. S. Y. Lee and H. J. Choi, *J. Environ. Manag.*, **209**, 382 (2018).
28. H. J. Choi, *Water Sci. Technol.*, **79**(10), 1922 (2019).
29. S. Suganuma, K. Nakajima, M. Kitano, H. Kato, A. Tamura, H. Kondo, S. Yanagawa, S. Hayashi and M. Hara, *Micropor. Mesopor. Mat.*, **143**, 443 (2011).
30. H. J. Choi and S. W. Yu, *Environ. Eng. Res.*, **24**(1), 99 (2019).
31. M. R. Lasheen, N. S. Ammar and H. S. Ibrahim, *Solid State Sci.*, **14**, 202 (2012).
32. S. W. Yu and H. J. Choi, *Water Sci. Technol.*, **78**(4), 837 (2018).
33. J. N. Sahu, R. R. Karri and N. S. Jayakumar, *Ind. Crops Prod.*, **164**, 113333 (2021).
34. A. Ämmälä, O. Laitinen, J. A. Sirviö and H. Liimatainen, *Ind. Crop. Prod.*, **140**, 111664 (2019).
35. H. E. Osman, R. K. Badwy and H. K. Ahmad, *J. Phytol.*, **2**, 51 (2010).
36. P. S. Kumar, S. Ramalingam, V. Sathyaselvabala, S. D. Kirupha, A. Murugesan and S. Sivanesan, *Korean J. Chem. Eng.*, **29**, 756 (2012).
37. C. Liu, B. Tao, Z. Wang, D. Wang, R. Guo and L. Chen, *Chem. Eng. Sci.*, **229**, 115984 (2021).
38. S. J. Giri, P. K. Swart and A. Pourmand, *Earth Planet. Sci.*, **519**, 130 (2019).
39. S. Lin, H. Zhao, L. Zhu, T. He, S. Chen, C. Gao and L. L. Zhang, *Desalination*, **498**, 114728 (2021).

Supporting Information

Assessment of sulfonation in cornstalk for adsorption of metal-ions from seawater

Hee-Jeong Choi[†]

Department of Biomedical Science, Catholic Kwandong University, 24, Beomil-ro, 579beon-gil, Gangneung-si 25601, Korea

(*Received 18 January 2021 • Revised 26 July 2021 • Accepted 5 September 2021*)

(a) (b)

Fig. S1. Sulfornation of outside (a) and inside (b) of cornstalk.

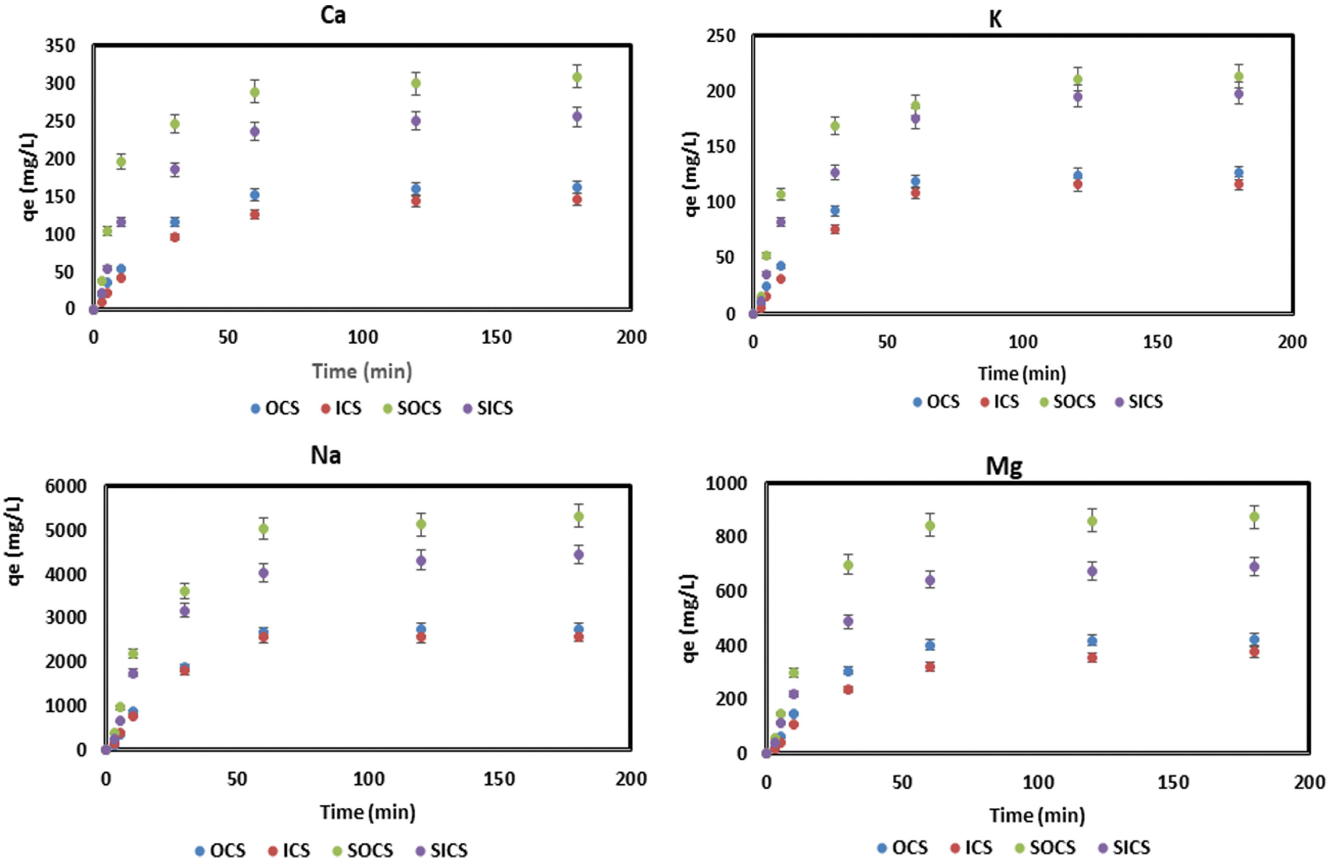


Fig. S2. Change of adsorption efficiency of metal ions onto OCS, ICS, SOCS and SICS.

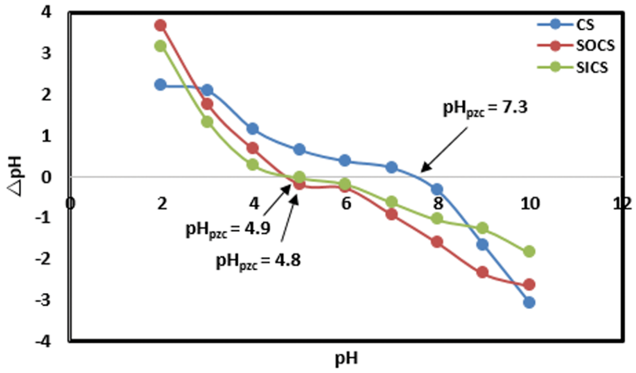
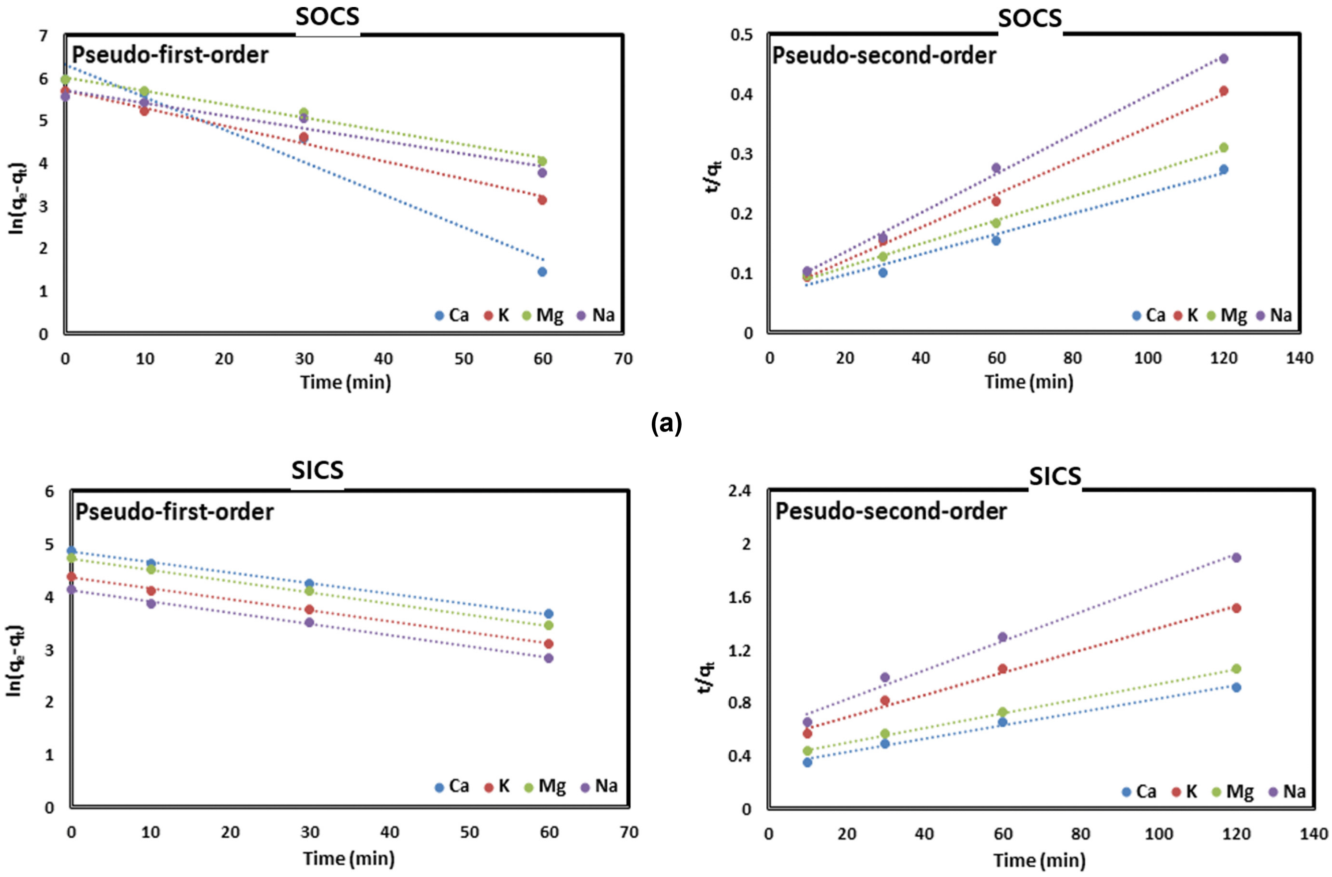


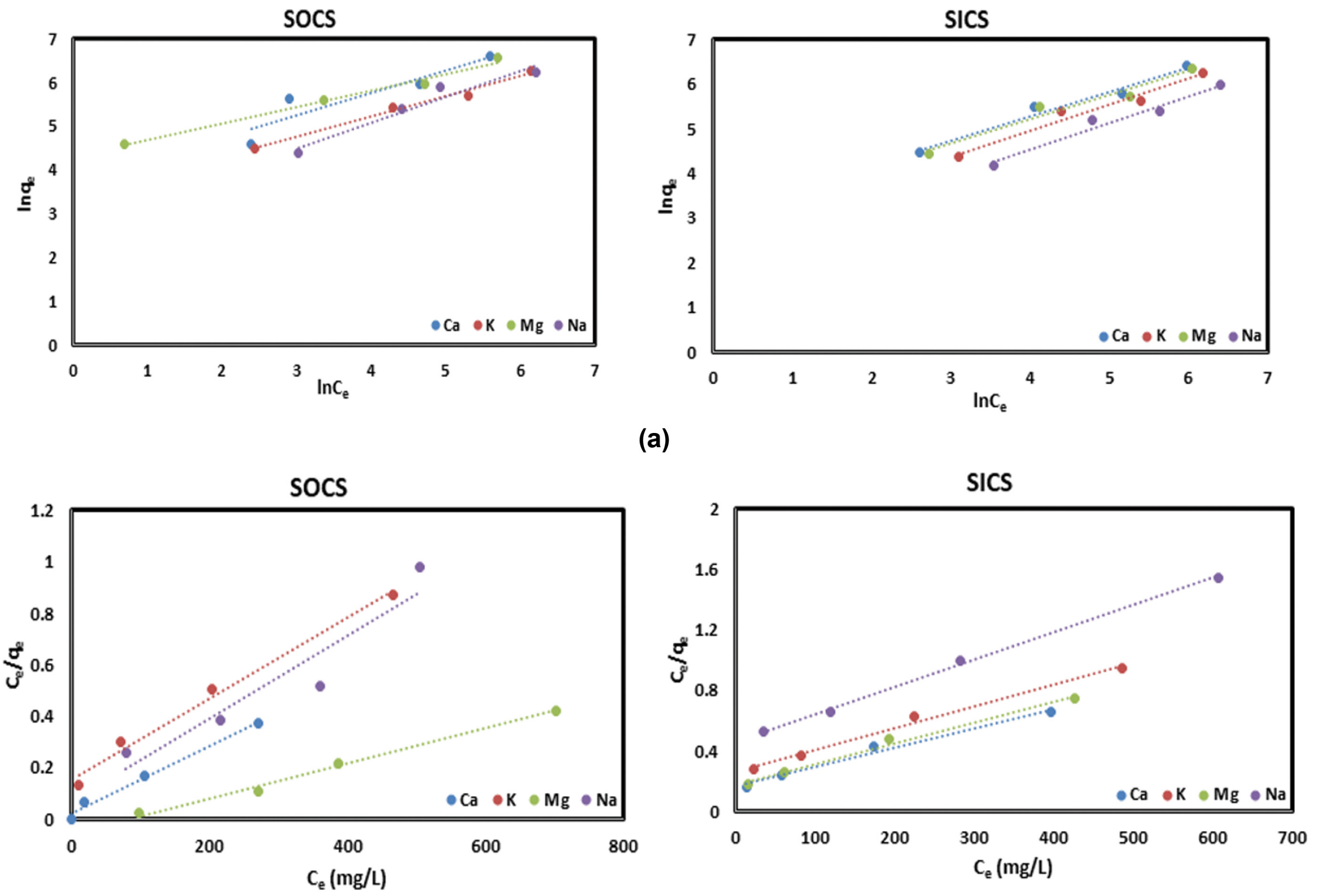
Fig. S3. pH$_{pzc}$ of CS, SOCS and SICS in aqueous solution.



(a)

(b)

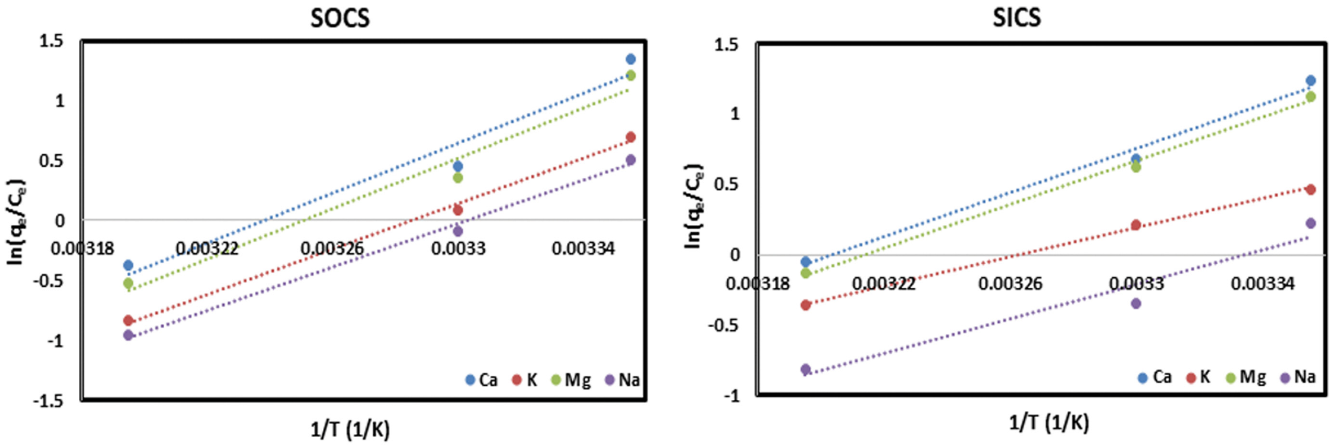
Fig. S4. Plot of pseudo-first-order and pseudo-second-order for SOCS (a) and SICS (b) (T: 298 K, amount of SOCS and SICS: 5 g, time: 180 min).



(a)

(b)

Fig. S5. Adsorption isotherm of Ca, K, Mg and Na by SOCS and SICS at 298 K: (a) Langmuir isotherm, (b) Freundlich isotherm.



(a)

(b)

Fig. S6. Plot of ln(q_e/C_e) vs. 1/T for determining of thermodynamic paeameters for the adsorption of Ca, K, Mg and Na onto (a) SOCS and (b) SICS.