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Surface modification of sulfuric acid-activated lignocellulose-based material for recovery of Ca, K, Mg, and Na from seawater

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ABSTRACT

This study aimed was to recover Ca, K, Mg, and Na from seawater using sulfonated cornstalk. Cornstalk, a lignocellulose-derived agricultural waste, was selected as an adsorbent. It was separated from the inside and outside and then sulfonated to be used as an adsorbent. Sulfonated cornstalk had a higher ion exchange capacity than natural cornstalk and the largest ion exchange capacity was 4.35 meq/g of sulfonated outside cornstalk. Besides according to the FT-IR analysis, the surface of the cornstalk was changed to a negative charge after sulfonation, so that it was very easy to adsorb cationic ions in seawater. The adsorption efficiency of the sulfonated cornstalk 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 cornstalk adsorbent. Sulfonated cornstalk, capable of adsorbing cations such as Ca, K, Mg, and Na from seawater, were renewable and can be applied in the field. However, to be applied to the actual field, it is considered that the encapsulated form, rather than the powder form, is necessary for the ease of use and prevention of mass loss of the adsorbent.

Keywords: Adsorption; Cornstalk; Sulfonation; Ion exchange; Seawater

1. 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 the essential elements of all living organisms. Among the many plant nutrients, potassium, magnesium, 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 seawater. 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]. The 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].

Various methods such as ion exchange, solvent extraction, adsorption, and co-precipitation have been studied to recover enormous amounts of useful metals from seawater [3,9]. Among them, the adsorption method with high removal efficiency and simple operation is most often used. Activated carbon has the advantages of high surface area, microporous structure, uniform pore size distribution, high porosity, high surface reactivity, excellent mechanical strength, and strong adsorption capacity [10]. However, because of the high cost of adsorption using activated carbon, an alternative adsorbent should be found. 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 [11]. Besides 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 [11,12]. Lignin is an aromatic polymer composed of carbonyl, hydroxyl, methyl, and other functional groups [13,14]. Both hemicellulose and cellulose contain oxygen functional groups, including carbonyl groups, hydroxyl groups, and ethers [14]. These functional groups can bind to metal ions and small organic contaminants through chelating, completion, coordination, and hydrogen bonding, which play an important role in the adsorption process [11,15]. 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 [12,14]. 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 [12,13]. 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 [16]. 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 efficacy 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 lignocellulose-derived agricultural waste can be modified, sulfonation is very effective in improving the adsorption capacity of metal ions [17]. Authors suggested that pretreatment by sulfonating agricultural waste increased the negative charge on the surface and the porosity of the biomass [13]. Similarly, Elangovan et al. [18] 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 [19]. 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 [13,20]. 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 [17,21]. Sulfonation using sulfuric acid is completed in a short time at a low temperature compared to other concentrated sulfuric acids (sulfur trioxide, chlorosulfonic acid, and silica sulfuric acid), and sulfonation can be performed with a small number of chemicals [19]. It is also known to increase the tendency of crosslinking through sulfone formation and to cause decomposition of polymers by oxidation or chain cleavage [21,22]. Therefore, this study attempted to sulfonate ligno-cellulose derived cornstalk and use it to adsorb and recover Ca, K, Mg, and Na, which are the most widely used cationic metals in seawater.

2. Materials and methods

2.1. Materials

2.1.1. Characteristics of seawater

Seawater used in the experiment was collected from the East sea of Korea, where it was pumped from a depth of 30 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°C~4°C) without pretreatment. The characteristics of the seawater are represented in Table 1. Among inorganic ions contained in 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 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 alkalinity was 1.69 mM $CaCO_3$.

2.1.2. Sulfonation of cornstalk

After removing leaves and contaminants, cornstalk was dried in a drying oven at 105°C for 24 h to completely

Table 1
Characteristics of sea water

Parameters		Value
pH		8.0 ± 0.1
Turbidity		0.32 ± 0.1 NTU
Conductivity (mS/cm)		31.91 ± 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^-	19,216.13 ± 5.26
	SO_4^{2-}	2,670.03 ± 2.89
	NO_3^-	143.04 ± 3.21
	Br^-	62.01 ± 2.16
	F^-	1.21 ± 0.03
	Li	0.19 ± 0.05
	Sr	7.62 ± 0.69
	Rb	0.16 ± 0.02

evaporate the moisture. The outside and the inside of the dried cornstalk were separated and the outside of the 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 of the adsorbent. The 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. A 20 g of prepared OCS and ICS were 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 to not exceed 10°C using a reaction device (Yhana, Model SS-200, 50 W). 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) has a dark brown color, while the inner part of the sulfonated cornstalk (SICS) has a light ivory color (Fig. S1).

2.2. Methods

2.2.1. 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. In order to find out 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°C–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 recovery 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 were 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.

2.2.2. 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* was calculated by the following equation:

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

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 the 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 and Freundlich, and adsorption kinetics were interpreted using the pseudo-first and pseudo-second-order. Thermodynamic analysis was performed using Gibbs' free energy.

2.2.3. 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 concentrations (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 the sample concentration analysis.

2.3. Analysis methods

Samples were taken at a predetermined time (0, 10, 20, 30, 60, 120, and 180 min) for concentration analysis and the residual concentration of metal ions in seawater was measured using an inductively coupled plasma mass spectrometer (Agilent 7700X, ICP-MS). ICP-MS operating conditions for the analysis of Ca, Mg, K, and Na are given in Table S1. The pH was controlled using NaOH and HCl between 3 and 10, it was measured using a pH meter (SevenGO pro, Mettler Toledo). The temperature was adjusted to 25°C–45°C using a thermostat of a shaking incubator. The Fourier-transform infrared (FT-IR) spectroscopy was performed with a 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 the Van Soest method [23]. In order 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 [24]. The ion exchange capacity (IEC) was calculated according to general Eq. (2):

$$\text{IEC}\left(\text{meq/g}\right)=\frac{V_{\text{NaOH}}\,N_{\text{NaOH}}-V_{\text{HCl}}N_{\text{HCl}}}{\text{Weight of dried sample}} \tag{2}$$

where V_{HCl} was the volume of HCl (0.1 M) entered during quantification in mL, V_{NaOH} was the volume of NaOH (0.1 M) 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 were obtained by measuring the weight of the resin dried at 110°C for one day.

3. Results and discussion

3.1. Properties of cornstalk

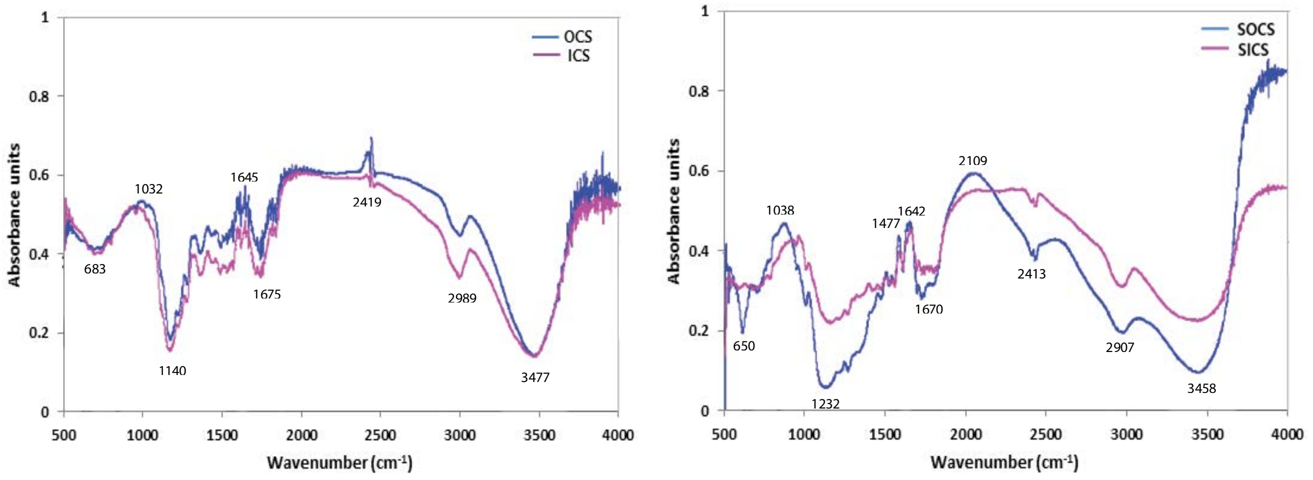
3.1.1. Physical characteristics

The main ingredients of cornstalk were protein, fat, sugar, starch, and pectin. Cell wall materials were cellulose, hemicellulose, and lignin, and their content accounts for 40%~80% of woody plants. Table S2 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 contents. 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 were 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 a strong affinity for metal ions [13,21]. 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 [13,17,19].

3.1.2. FT-IR analysis

FT-IR results of ICS, OCS, SOCS, and SICS provide important information that can help to 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. It should be noted that vibrations were severe between 1,300 and 1,740 cm^{-1} in both OCS and ICS, which corresponds to C=O carbonyl 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. 1a). Therefore, it can be said that ICS and OCS have structures suitable for adsorbing metals.

Fig. 1b shows the FT-IR of sulfonated SICS and SOCS. Like 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 carbonyl 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 sulfonic groups. In addition, it was confirmed that the absorption peak



(a) (b)

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

of R–SO$_3$H of 1,232 cm^{-1}, and ketone peaks of 1,642 and 1,477 cm^{-1} were sulfonated. In particular, N-containing bioligands of SOCS (650 cm^{-1}), the R–SO$_3$H 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 improvements 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 [12,16,25]. The transformation of functional groups through sulfonation was predicted to affect the adsorption efficiency of Ca, K, Mg, and Na in seawater.

3.1.3. Ion exchange capacity

Ion exchange capacity is one of the most important characteristics of an adsorbent. The large ion exchange capacity means that there are many functional groups [3,13]. When comparing the ion exchange capacity between the outside and inside of cornstalk, the outside was slightly larger than the inside of 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 2). In general, as the ion exchange capacity increases, the amount of metal adsorbed increases too [3,24].

Table 2
Ion exchange capacity of samples (unit: %)

	OCS	ICS	SOCS	SICS
Ion exchange capacity (meq/g)	2.50	1.15	4.35	3.15

3.2. Recovery of metal ion

3.2.1. Effect of adsorbent dosage and adsorption amount

The 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. Therefore, when adsorbing cations such as Ca, K, Mg, and Na using OCS, ICS, SOCS, and SICS in seawater, 5 g/L of adsorbent was recommended.

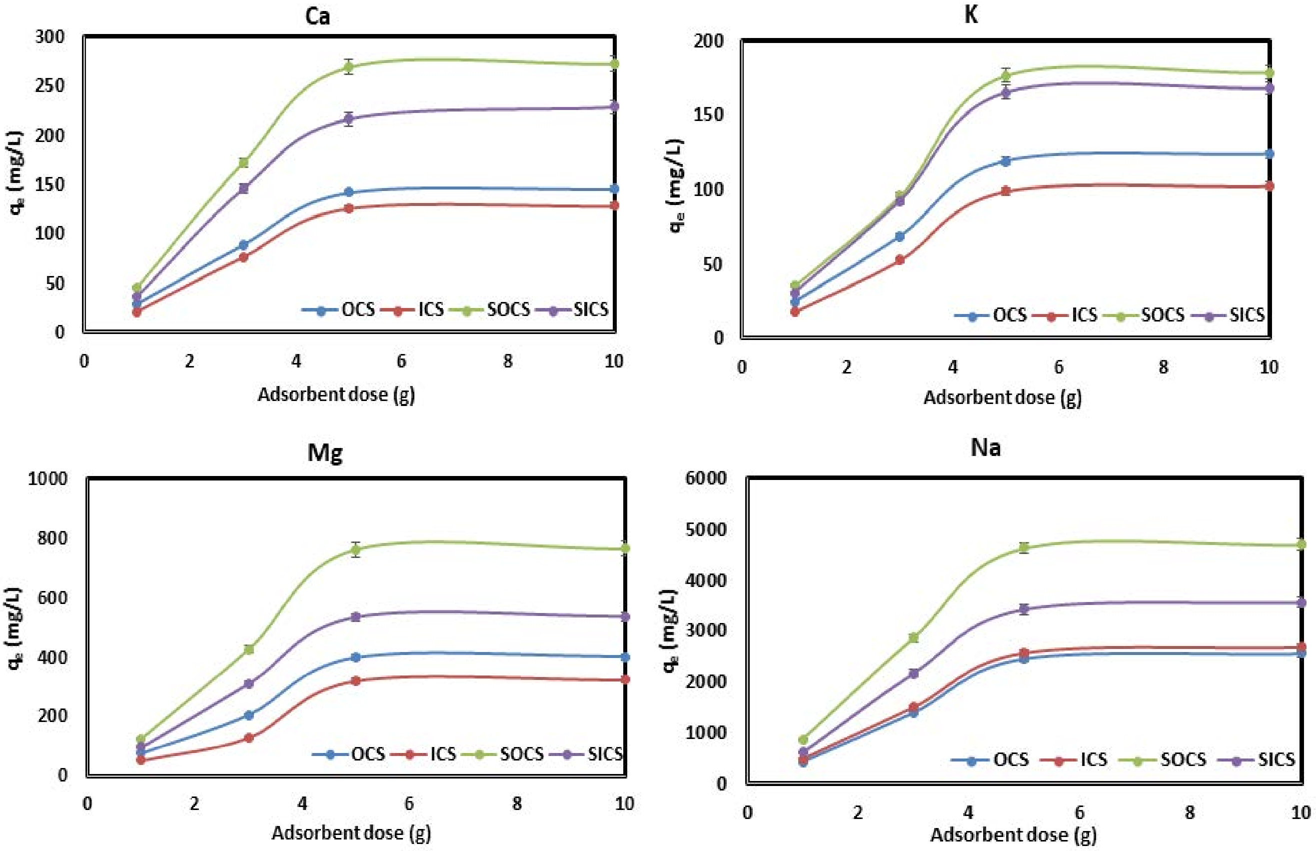


Fig. 2. Recovery amount of Ca, K, Mg, and Na onto OCS, ICS, SOCS, and SICS by various doses.

The adsorption efficiency of Ca, Mg, K, and Na was studied onto OCS, ICS, SOCS, and SICS according to the results of the above-described adsorbent amount experiment. Basing 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 3). The adsorption reaction has a difference in selectivity depending on the metal species in the solution [13,26]. 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%, 77.5%, and 52.3%, respectively. On the other hand, ICS showed the lowest adsorption efficiencies 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 [3,13]. 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 [12,13,16,17,22]. 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 down 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).

3.2.2. Effect of pH

To find out the adsorption efficiency of Ca, K, Mg, and Na according to the change of pH from seawater, 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 efficiencies of Ca, K, Mg, and Na in seawater onto OCS, ICS, SOCS, and SICS were 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). 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 and 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. [17] 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 [14,22,28].

3.2.3. 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 recovery efficiency of Ca and Mg was 98% on SOCS at a dilution ratio of 3:1 between distilled water and seawater (pH: 8 and T: 25°C). 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. In other words, 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 agreement with those of Shaddel et al. [10].

Table 3
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	359.26	1,127.62	10,198.17
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%)

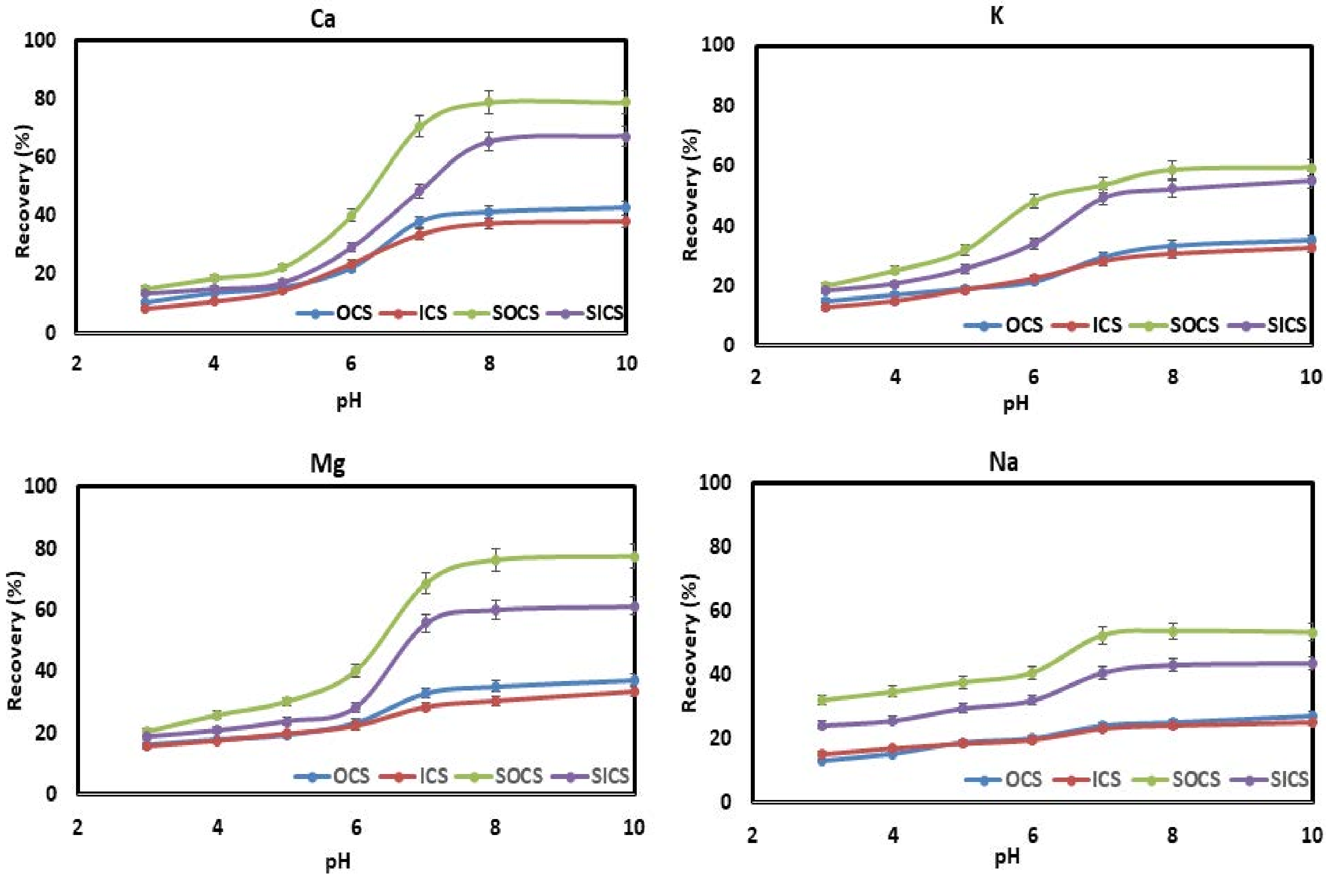


Fig. 3. Recovery amount of Ca, K, Mg, and Na onto OCS, ICS, SOCS, and SICS by different pH.

3.3. Adsorption kinetics and adsorption isotherms

The adsorption amounts of Ca, Mg, K, and Na adsorbed onto SOCS and SICS were more than twice 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.

3.3.1. Adsorption kinetics

To compare the adsorption rate of the SOCS and SICS, a kinetics experiment was conducted, and the analysis results of the main parameters are summarized in Table 4. In order 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 pseudo-first-order and pseudo-second-order models. The pseudo-first-order equation was presented by Lagergren and is one of the rate equations widely applied to the adsorption process of solutes from aqueous solutions [18,29]. Based on the adsorption equilibrium capacity of the solid phase, k_2 is the pseudo-second-order constant (g/mg min), and q_e is the adsorption amount of adsorbent (mg/g) at equilibrium. The plot of pseudo-first-order and pseudo-second-order for SOCS and SICS is depicted in Fig. S3. 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-first-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 pseudo-second-order (0.9859–0.9991) than pseudo-first-order (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 pseudo-second-order model than that of the pseudo-first-order model.

3.3.2. 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 4. In general, the isothermal adsorption equation is represented by two models, Langmuir and Freundlich isotherm. In the Langmuir isothermal adsorption, the binding site on the surface of the adsorbent reacts

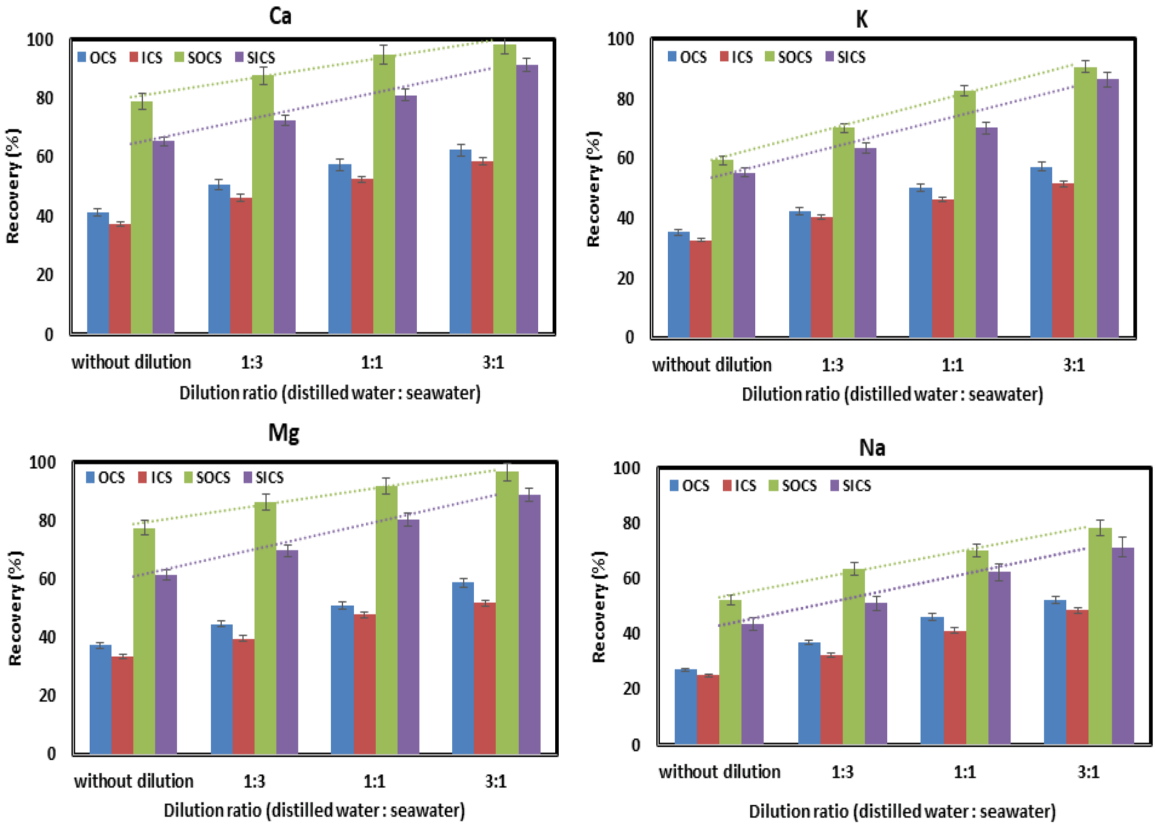


Fig. 4. Effect of dilution ratio for recovery of Ca, K, Mg, and Na onto OCS, ICS, SOCS, and SICS.

Table 4
Parameters of kinetics and isothermal models for Ca, K, Mg, and Na adsorption onto SOCS and SICS

Kinetic models		Pseudo-first-order			Pseudo-second-order		
		q_e (mg/g)	k_1 (1/min)	R^2	q_e (mg/g)	k_2 (g/mg/min)	R^2
SOCS	Ca	112.16	0.0764	0.9668	117.65	2.98×10^{-8}	0.9987
	K	60.67	0.0316	0.9971	71.43	7.95×10^{-8}	0.9991
	Mg	82.12	0.0418	0.9546	100.08	1.33×10^{-9}	0.9768
	Na	60.12	0.0299	0.8951	60.61	0.8×10^{-10}	0.9933
SICS	Ca	131.16	0.0300	0.9848	194.12	3.93×10^{-7}	0.9954
	K	79.43	0.0359	0.9826	87.27	8.5×10^{-8}	0.9962
	Mg	113.82	0.0388	0.9374	133.33	1.72×10^{-9}	0.9859
	Na	63.38	0.0311	0.9749	52.26	0.95×10^{-10}	0.9984

Isotherm models		Langmuir				Freundlich		
		q_m (mg/g)	K_L (L/mg)	R_L	R^2	$1/n$	K_F (mg/g)(L/mg)$^{1/n}$	R^2
SOCS	Ca	158.62	0.057	0.171	0.9888	0.512	51.59	0.8456
	K	133.33	0.010	0.089	0.9875	0.467	22.31	0.9831
	Mg	153.85	0.026	0.038	0.9865	0.378	20.21	0.9792
	Na	125.03	0.006	0.149	0.9884	0.595	5.01	0.9428
SICS	Ca	153.85	0.008	0.558	0.9808	0.548	12.46	0.9734
	K	122.86	0.005	0.161	0.9914	0.577	14.43	0.9627
	Mg	150.86	0.008	0.113	0.9888	0.538	11.35	0.9603
	Na	111.11	0.004	0.204	0.9983	0.593	6.46	0.9632

stoichiometrically 1:1 with the adsorbate and each reaction site is uniform [14,30]. 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 [15,31]. The Freundlich isotherm is the most widely applied equation for the analysis of liquid-phase adsorption in a heterogeneous surface adsorption reaction [16,18].

The separation coefficient R_L (=1/(1 + $K_L C_o$) of Ca, K, Mg, and Na adsorbed on SOCS and SICS was found to be between 0.038 and 0.558 (Table 4). If the value of R_L is between 0 and 1, the adsorption treatment is favorable [15,25]. The adsorption isotherm of Langmuir and Freundlich of Ca, K, Mg, and Na by SOCS and SICS was depicted in Fig. S4. 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 [26,27]. In this experiment, $1/n$ was analyzed in the range 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 correlation coefficient (R^2) of the Langmuir model was higher than that of the Freundlich. Therefore adsorption of Ca, Mg, K, and Na using SOCS and SICS was more suitable for the Langmuir model than that of the Freundlich model.

3.4. 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 [21]. According to the literature, SAC adsorbent adsorbed almost all cations contained in raw water and exchanges them for hydrogen ions [19,32]. In addition, since the strong acid cation exchange adsorbent is well applied in all pH ranges, its application range is very wide [28]. Here, compared with the structure of sulfonated and 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 differ from OCS and ICS in the adsorption mechanism of cations due to the difference in the structural aspect of the functional groups. In other words, 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 [13,16]. That is the reason why the adsorption efficiency of ions to the adsorbent was in the order of 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 [19,33]. According to FT-IR analysis, sulfonation grafted the $-SO_3$ group on the surface of the SOCS and SICS and strengthened the carboxyl (–COOH) and hydroxyl groups. The mechanism of adsorption of SOCS/SICS and Me (Ca, Mg, K, and Na) ions in seawater can be explained by the following equation:

$$\text{SOCS-OH} + \text{MeCl} \rightarrow \text{SOCS-O-Me} + \text{HCl} \tag{A}$$

$$\text{SOCS-COOH} + \text{MeCl} \rightarrow \text{SOCS-COO-Me} + \text{HCl} \tag{B}$$

$$\text{SOCS-SO}_3\text{H} + \text{MeCl} \rightarrow \text{SOCS-SO}_3\text{-Me} + \text{HCl} \tag{C}$$

As a result, the adsorption efficiency of Ca, K, Mg, and Na onto SOCS and SICS was improved. Depending

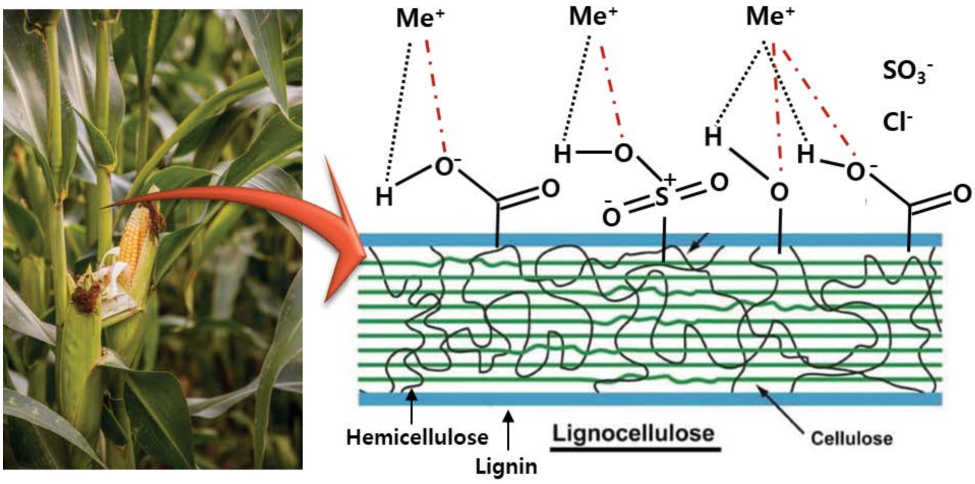


Fig. 5. Possible adsorption mechanism of Ca, Mg, Na, and K by SOCS and SICS (Me = Ca, Mg, Na, and K).

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.

3.5. 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 [15,34]. 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 [22,26]. The thermodynamic parameter was calculated by the following equation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{3}$$

$$\ln\left(\frac{q_e}{C_e}\right) = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{4}$$

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

As the temperature increased, the adsorption efficiencies 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 recovering Ca, K, Mg, and Na from seawater. The thermodynamic plot is shown in Fig. S5. The range of ΔG° for physisorption is −20 to 0 kJ/mol and the range of chemisorption is −400 to −80 kJ/mol. From Table 5, 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° 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 ligno-cellulose molecules in the cornstalk, reducing the amount of various functional groups exposed to the surface [13,21]. 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 in nature. However, ΔG° 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 bio-adsorption process is exothermic and inversely proportional to temperature [12,15,33]. Kumar et al. [35] 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 cornstalk 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 [12]. On the contrary, there have been reports of several researchers that 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 [30,34]. 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

Table 5
Themodynamic parameters for SOCS and SICS adsorption

Temperature		SOCS			SICS		
		ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (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		

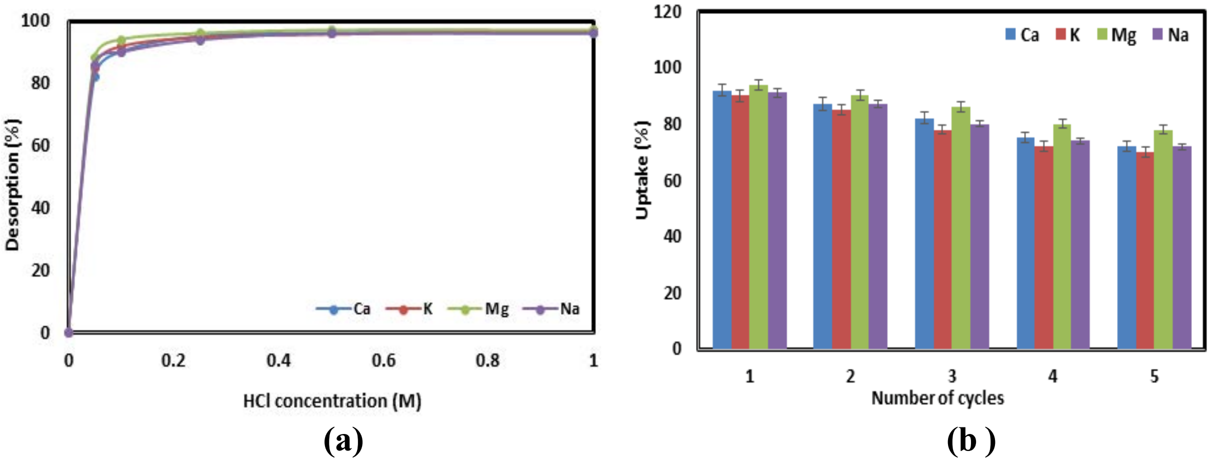


Fig. 6. SOCS regeneration capacity in terms (a) Ca, K, Mg, and Na desorption with HCl at varied concentration and (b) adsorption/desorption of Ca, K, Mg, and Na with 0.1 M HCl ($n = 5$).

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 [12,13,17,34]. Another cause could be the reversible character of the sulfonic groups, these tendencies due to the high temperatures.

3.6. 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 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. 6a). Based on the results, 0.1 M HCl was selected to conduct adsorption/desorption experiments of Ca, K, Mg, and Na ions from SOCS. The regeneration and reuse capacity of SOCS were evaluated by adsorbent and desorption through 5 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. 6b). As a result of adsorption/desorption experiments on SOCS, there is 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, ligno-cellulose derived adsorbents, can be used to recover heavy metal ions in wastewater treatment systems, so they can be seen as having great industrial and economic value.

4. 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 was ligno-cellulose derived adsorbent and has excellent stability as an adsorbent material for cation. 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 pseudo-second-order. Lignocellulose-derived sulfonated cornstalk, capable of adsorbing cation such as Ca, K, Mg, and Na from seawater, were renewable and can be applied in the field. However, regeneration of SOCS in powder form was possible in the 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.

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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 and editing.

Statement 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.

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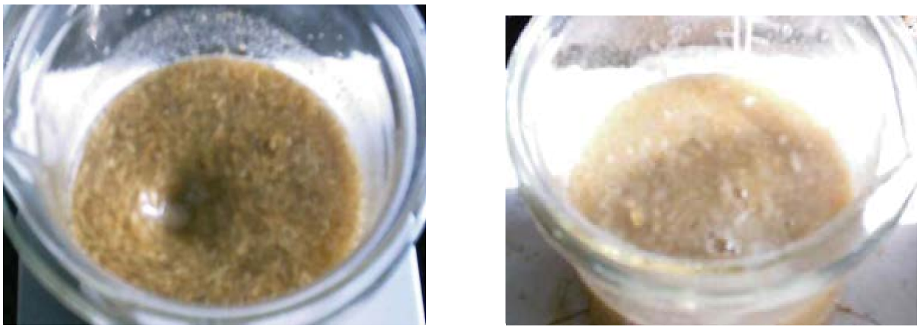
Supplementary information



(a) (b)

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

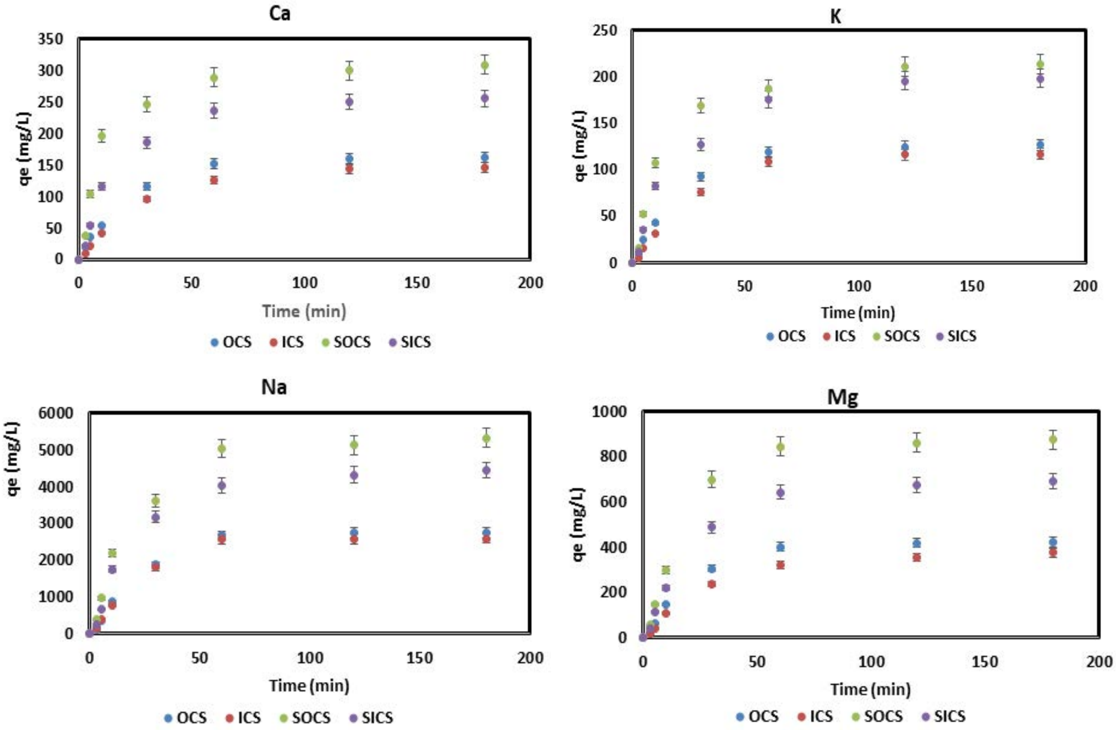
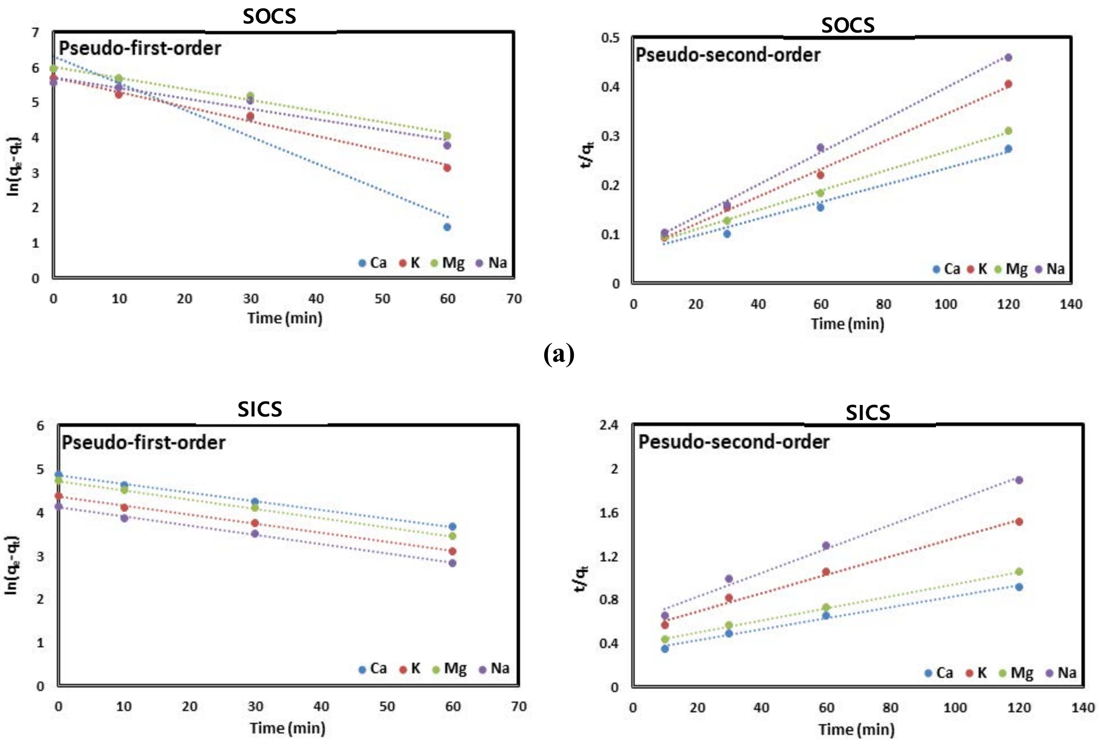


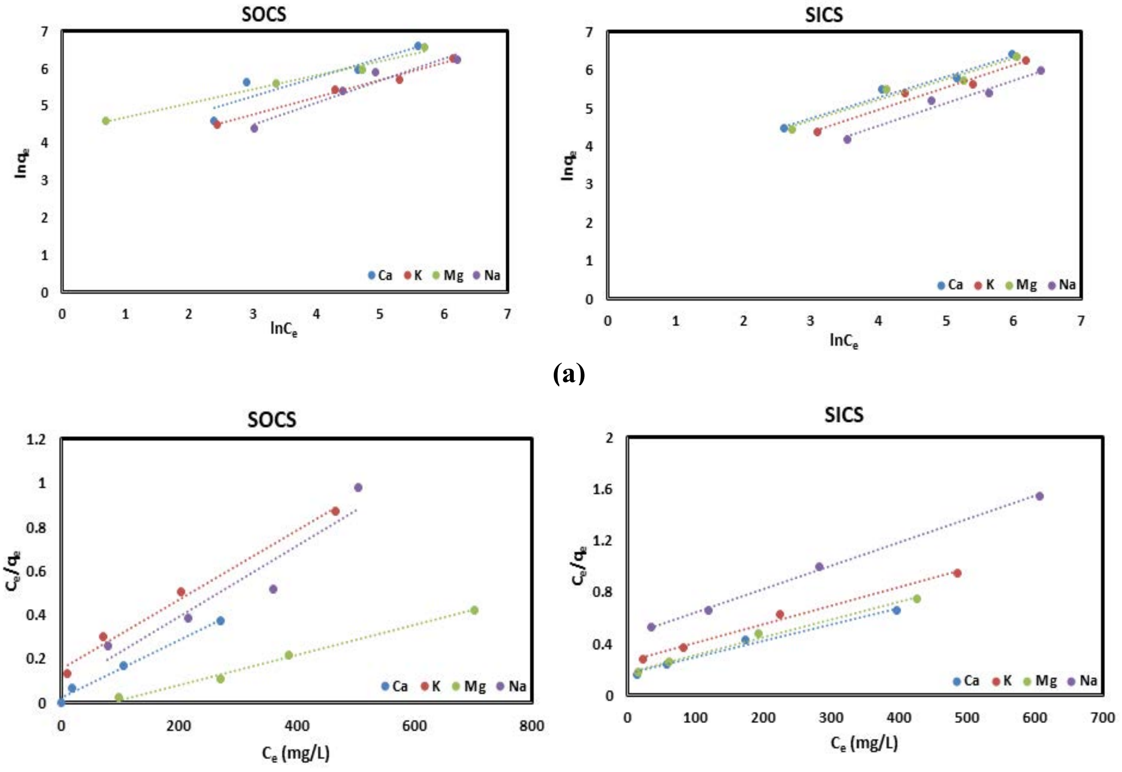
Fig. S2. Change of recovery amount of metal ions onto OCS, ICS, SOCS, and SICS by different temperatures.



(a)

(b)

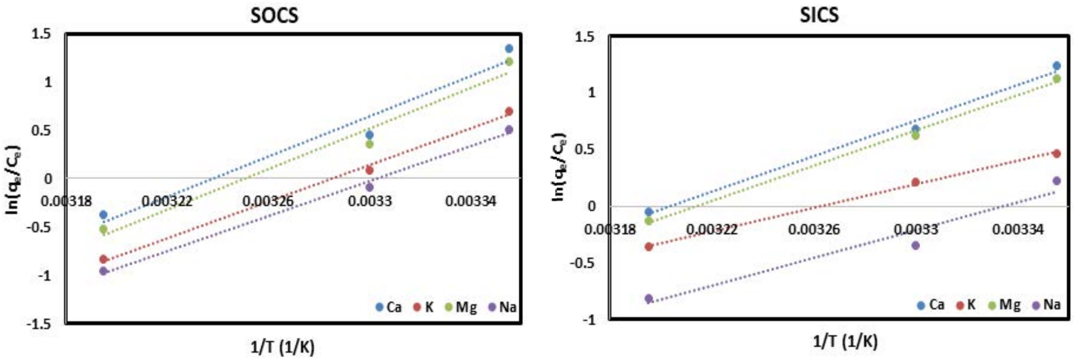
Fig. S3. Plot of pseudo-first-order and pseudo-second-order for SOCS (a) and SICS (b) (*T*: 298 K, amount of SOCS and SICS: 5 g, Time: 180 min).



(a)

(b)

Fig. S4. Adsorption isotherm of Ca, K, Mg, and Na by SOCS and SICS at 298 K (a) Langmuir isotherm and (b) Freundlich isotherm.



(a) **(b)**

Fig. S5. Plot of ln(q_e/C_e) vs 1/T for determining thermodynamic parameters for the adsorption of Ca, K, Mg, and Na onto SOCS and SICS.

Table S1
ICP-MS (7700x) operating conditions for the analysis of Ca, Mg, K, and Na

Parameters	Value
Plasma mode	Normal, robust
Radio frequency power (W)	1,550
Carrier gas flow (L/min)	0.99
Dilution gas flow (L/min)	0.15
Spray chamber temperature (°C)	2
Sample depth (mm)	8
Extract 1 lens (V)	0
Kinetic energy discrimination (V)	4

Table S2
Characteristic of outside and inside cornstalks (unit: %)

	Cell-wall materials						
	Cellulose	Hemi-cellulose	Lignin	Protein	Fat	Ash	Other
Inside of corn-stalk (ICS)	29.6	27.1	5.1	9.3	1.4	9.8	17.7
Outside of corn-stalk (OCS)	36.9	25.1	9.4	6.9	1.0	6.9	13.8