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STUDIES ON THE REMOVAL OF Sr(II) IONS FROM WATER USING CARBONIZED ORANGE JUICE RESIDUE

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Abstract

The adsorbent for Sr(II) ion removal was prepared from orange juice residue (OJR) after carbonization at 800^{0}C. An energy dispersive X-ray (EDX) spectroscopic analysis showed the existence of trace amounts of P, Na, K, and Fe together with C and Ca in the examined sample of COJR. The adsorption parameters such as effect of pH, contact time, initial Sr(II) concentration and adsorbent dosage were studied. COJR selectively adsorbed Sr(II) from the mixed solution containing Sr(II) and Cs(I). Experimental data obtained for the adsorption of Sr(II) were analyzed by using Langmuir and Freundlich isotherm models, and the data were well fitted with both the models with R^2 higher than 0.98. Adsorption equilibrium was achieved within one hour by using a 24.3 mg/L Sr(II) solution at a solid-liquid ratio of 1g/L. The maximum adsorption capacity (Q_{max}) and adsorption equilibrium constant (b) of COJR for Sr(II) ion were found to be 322.58 mmol/kg and 1.93 L/mmol, respectively. The concentration of Sr(II) was successfully lowered down to the EPA standard (4 mg/L) by using COJR dosage higher than 4 g/L. The adsorbed Sr(II) could be successfully desorbed using a dilute (0.5M) solution of hydrochloric acid. These results indicated that COJR investigated in this study showed a high affinity for Sr(II) ion thus it is expected to be employed as a promising adsorbent for the removal of Sr(II) ions from polluted water.

Keywords: Orange juice residue (OJR), Carbonization, Carbonized orange juice residue (COJR), Sr(II) adsorption, Isotherm modeling

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Introduction

The strontium generally exists in very low concentration on the earth's crust. Because of its high reactivity, it is rarely found in pure form; however, it occurs in the form of minerals like strontianite and celestite (Pangeni et al., 2014). The strontium occurs in its various radioactive as well as non-radioactive isotopes. ^{90}Sr and ^{85}Sr are the most common and very important radioactive forms of strontium which are used as fuel in nuclear reactors (Murthy and Pamar2011; Sachse et al., 2012). Apart from this, ^{87}Sr is another widely used non-radioactive isotope of strontium and its compounds like strontianite and celestite are used in manufacturing X-ray absorbing glass for cathoderay tubes, removal of lead from $ZnSO_4$ solution in the electrolytic zinc processing, electro-ceramic, oxide superconductors, oxygen eliminator in electron tubes, and production of glasses for color television (Maskani and Ghazvini 2009; Ahmapur et al., 2010; Murthy and Pamar, 2011). Toxicity of non-radioactive isotopes of Sr (II) is less for human health as compared to radioactive forms. The wastewater generated in the nuclear reactor contains a considerable amount of radioactive ^{90}Sr (Ma et al., 2010). Because of its chemical similarity to Ca(II), it can be easily accumulated in our bone tissue by replacing Ca(II) ions of hydroxyapatite (Grynpas et al., 1996). Once the radioactive ^{90}Sr(II) incorporated into the bone tissue, it continues to irradiate localized tissues and promote the development of bone sarcomas, leukemia, and cancer (Karasyova et al., 1999; Pangeni et al., 2014). Due to the high toxicity of ^{90}Sr(II) and its compounds, it is desired to bring the concentration in the wastewater to less than or equal to 8 pC_i/L which is equivalent to 5.67×10^{-11} mg/L. However, in the case of the non-radioactive Sr(II), the maximum acceptable level in drinking water is set as 4 mg/L by United State Environmental Protection Agency, EPA, (Murthy and Pamar 2011). Naturally, the water insoluble strontium compounds may be dissolved due to different geochemical reactions on the earth's crust which then easily mixed with the portable water resources thereby invites strontium pollution whereas anthropogenic pollution is caused from the discharge of waste water generated from strontium based industries, nuclear energy manufacturing and testing of nuclear weapons. The water soluble strontium based pollutants are a greater threat to human health than the water insoluble ones (Garcia et al., 2007; Paudyal et al., 2014).Therefore, it is necessary to remove excess concentration of Sr(II) and its soluble compounds from drinking water and wastewater as much as possible. The methods such as adsorption supported liquid membranes with strip dispersion, ion exchange, solvent extraction, and precipitation are widely used for the removal of Sr(II) from water. These methods require either synthesis of resin and ion exchange membrane or use some soluble chemicals as precipitant. The precipitation of Sr(II) produced huge amount of toxic sludge and may also invite the trouble of incomplete removal due to solubility limit. Although the use of plastic based commercially available ion exchange resins for Sr(II) removal is effective, however, it produced huge amount of Sr(II) rich solid waste of non-degradable polymer which further invites the environmental pollution. Other methods such as membrane and reverse osmosis are little bit expensive for water treatment (Paudyal et al., 2014). Owing to this, the adsorption of Sr(II) using waste agricultural biomass after some chemical modification can be one of the promising and economical process because feed material for this is waste biomass itself and has functional varieties for modification in natural biopolymer for selective adsorption of targeted ion.

The orange is one of the very popular citrus fruit cultivated worldwide mainly for juice. There are two varieties of orange fruits i.e., sweet and bitter, former are most commonly consumed. The juice of orange fruits is rich in essential minerals and vitamins which provide a necessary health benefit to our body. The antioxidants and insoluble dietary fiber present in the juice of these fruits are considered to decrease the risk of many chronic diseases, cancers, and heart diseases; hence, orange juice processing is one of the most important food industries in the world. Because of the increasing population and consumption rate of orange juice worldwide, its cultivation and juicing industries are also increasing. After juicing, nearly one half of the orange fruit is converted into orange juice which is commercial product whereas another half remains as waste residue called orange juice residue (OJR). A large amount of OJR is thus produced from orange juice factories every year worldwide. Now, such waste is usually composted to make organic fertilizer or dumped into landfill sites. To improve the economic status of orange farmers and effective management of OJR, it is necessary to prepare some value added material from this wasted OJR. In our previous study (Paudyal et al., 2014), the natural cation exchanger containing exchangeable Ca(II) was prepared after the saponification of OJR using $Ca(OH)_2$ for Sr(II) ion removal. Although saponified OJR successfully removes Sr(II) from water, it is suffered from some troubles for practical use such as decaying which generates bad smell during repeated usage together with destruction of active sites and requires many times of water washing to remove residual calcium and water-soluble organics, resulting in high production cost. To extend the field of effective use of OJR, the dried powder of OJR was first incinerated at high temperature to produce much stable and robust carbonized orange juice residue (COJR) in the present work to remove Sr(II) ion from water. In addition to this, effectiveness of COJR for Sr(II) was studied by evaluating effect of pH, contact time, COJR dosage and initial Sr(II) concentration together with desorption behavior in batch mode.

Materials and Method

Materials and chemicals used

The feed material, orange juice residue (OJR), employed for the preparation of adsorbent was kindly supplied from JASaga beverage Co. Ltd., Japan free of cost. The anhydrous strontium chloride ($SnCl_2$), hydrochloric acid (HCl), and sodium hydroxide (NaOH) were purchased from Wako Chemicals Co. Ltd., Japan. The stock solution of strontium (1000 mg/L) was prepared by dissolving 1.78 g of anhydrous $SrCl_2$ in one liter of de-ionized water. The working solutions were prepared by diluting the stock solution at the time of experiment. The pH of the solution was adjusted by adding some drops of either 0.1MHCl or 0.1M NaOH solution. The standard solution of strontium (1000 mg/L) purchased from Sigma Aldrich, Japan was used for the calibration of ICP-AESfor Sr(II) measurement.

Instrumentation and analysis

The muffle furnace (KJ-M1200-X) with $Cr_2Al_7Mo_2$ resistance at heating element having insulating double layer of alumina ceramic fiber was used for the carbonization of OJR. The pH of the solution was controlled by using pH meter (TOA DKK model, HM-30R).The concentration of Sr(II) was determined by an inductively coupled plasma atomic emission spectrophotometer (ICP-AES-8100).The elemental analysis of the COJR and Sr(II) loaded COJR were carried out by using an energy dispersive X-ray (EDX) spectrometer (Shimadzu model, EDX-800HS) whereas SEM images were recorded using scanning electron microscope (JEOL model JSM-5900) at acceleration voltage of 15 kV.

Carbonization of orange juice residue

From our previous experience, it was found that if we use raw orange juice residue (OJR) directly as an adsorbent, some organics such as citric acid, pectic acid, sugar, and limonene compounds were partly dissolved in water which may impede the adsorption reaction. Thus raw OJR is not effective to use as an adsorbent for Sr(II) ion removal. Here, the chemical stability and aqueous insolubility of OJR was improved by carbonization reaction at high temperature. Before carbonization, the OJR was first washed several times with distilled water to remove external dirt and water soluble organics then it was dried in a convection oven at 70°C for 4 days. After complete drying, the dried product was grounded into fine particles and was employed for carbonization reaction as follows.

For the carbonization, a very simple method of carbonization without using any activation process was employed. Fifty gram of the dried OJR was placed in an alumina crucible with an alumina cover then this crucible was placed in another larger alumina crucible and covered with graphite powder and capped with an alumina cover to prevent oxidation in a Muffle furnace. The crucible set was put into a furnace with a heating rate of 5°C/min up to 800°C temperatures. The carbonized product was kept inside the furnace and left for cooling until the temperature inside the furnace became equal to temperature of the laboratory to prevent the oxidation of carbonized material in air at high temperature. After cooling, the carbonized product was collected, washed with distilled water to remove soluble impurities and minerals then finally subjected to drying using a convection oven at 70°C. The product obtained in this way is inferred to carbonized orange juice residue and abbreviated as COJR henceforth, which was employed as an adsorbent for the removal of

Sr(II) ion from water. The details of the COJR preparation and removal pathways of Sr(II) ion onto investigated COJR adsorbent is demonstrated in the flow sheet shown in **Fig. 1.**

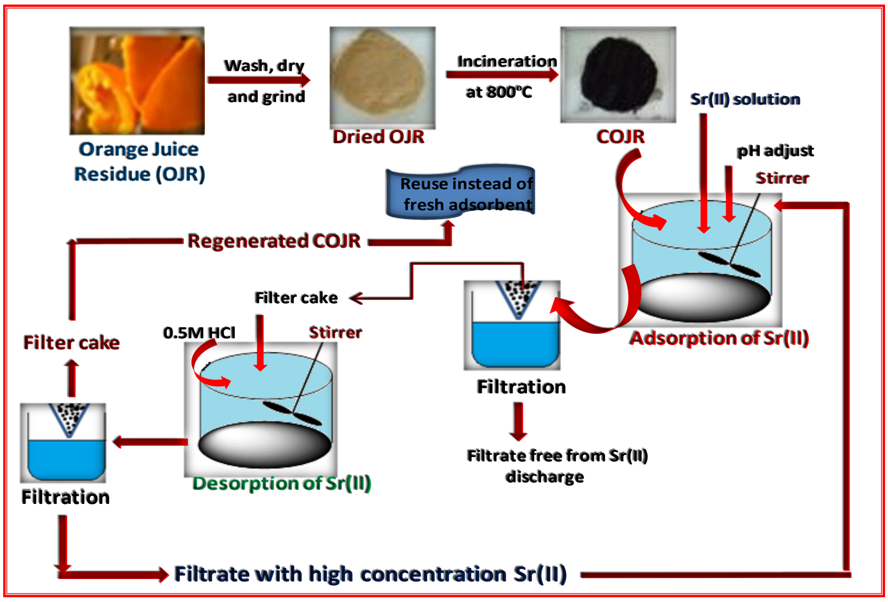

Fig. 1. Flowsheet showing the details of the preparation of COJR for the removal of Sr(II) from water.

Batch wise studies for the adsorption of Sr(II) ion

The batch experiment was generally carried out by mixing a predetermined amount of adsorbent and adsorbate followed by shaking and solid liquid separation. In the present study, each batch experiments were performed by contacting COJR with modeled solution of Sr(II) ion. The batch adsorption test of Sr(II) onto COJR from aqueous medium was investigated at 30°C. The effect of pH for the adsorption behavior of Sr(II) by COJR was carried out by shaking a series of sample bottles containing 10 mL of metal solution (0.05 mmol/L Sr(II) and 7.5×10^{-3} mmol/L Cs(I)) and 10 mg of COJR at varying pH ranging from 2 to 9. The kinetics and isotherm studies were conducted with COJR at optimal pH of 5.6. The bottles were horizontally agitated on a shaker at 150 rpm for 24 hrs at 30°C using thermo-stated shaker. The optimum time to attain adsorption equilibrium was investigated by shaking COJR and Sr(II) solution (0.25 mmol/L) at solid liquid ratio of 1 g/L by varying the contact times up to 4 hours. The adsorption isotherm studies were carried out by mixing 10 mg of COJR with 10 mL of Sr(II) solution at different concentrations. After shaking with a predetermined interval of time, the samples were filtered then the filtrate were analyzed for Sr(II) ion concentration by using ICP-AES. The pH of the solution was adjusted to required value by adding 0.1M HCl or 0.1M NaOH solution in all the experiments. The percentage adsorption (A%) of Sr(II) ions and Sr(II) uptake capacity (Q, mmol/kg) were evaluated by using following mass balance relationship as:

$$Q = \frac{C_i - C_e}{W} \times V \qquad (1)$$

$$(2)\quad \%A = \frac{C_i - C_e}{C_i} \times 100$$

Where, C_i and C_e are initial and equilibrium Sr(II) concentrations (mg/L), respectively, W is the dry weight of COJR used(g) and V is the volume of feed solution in liter.

Desorption of Sr(II) ion

Prior to Sr(II) desorption, the Sr(II) loaded COJR was first prepared by shaking 5 g of COJR with 500 mL of Sr(II) solution (4 mmol/L) for 24 hrs. After that it was filtered, residue was collected, and dried which is termed as Sr(II) loaded COJR and abbreviated as Sr(II)-COJR here after. To identify the effective solution for desorption of Sr(II) ion, the preliminary desorption tests were carried out by using acid (1M HCl), base (1M NaOH) and neutral (1M NaCl) solution at 5 g/L solid liquid ratio. From this, the acid solution was found to be effective for the desorption of Sr(II) from Sr(II)-COJR. Thus optimization of desorbing hydrochloric acid was done by varying its concentration ranging from 0 to 1M. It was confirmed from three independent replicates that the batch experiments were reproducible within at most 2% error. The percentage desorption (%D) was determined according to Aryal et al., 2022 using following equation

$$\%\,D = \frac{A_r}{A_a} \times 100 \qquad (3)$$

Where, A_r and A_a are the amounts of Sr(II) released and adsorbed (mmol/kg), respectively.

Determination of total organic carbon

The dissolution of total organic carbon (TOC) from adsorbent not only interfere adsorption process but also destroys the active sites or adsorbent structure thus it is necessary to lower the dissolution of TOC from adsorbent for its effective usage during adsorption process. The adsorbent with low or negligible leakage of TOC are more stable and considered as effective material for adsorption of pollutants. To investigate the stability of COJR, the leakage of TOC from feed material (OJR) and COJR were compared. For this, 50 mg of OJR and 10 mL water were mixed and stirred for 24hrs at different pH. After filtration, the TOC concentrations were measured by using TOC analyzer. Exactly a similar procedure was adopted in case of COJR adsorbent.

Results and discussion

Characterization of adsorbents by EDX and SEM

The energy dispersive X-ray (EDX) spectroscopic technique is very important for the qualitative determination of the various elements in the tested samples. Thus direct evidence of Sr(II) adsorption onto investigated COJR adsorbent was obtained from the comparisons of EDX spectra of adsorbents before and after Sr(II) treatment. To examine the existence of various elements on the surface of COJR adsorbent before and after Sr(II) adsorption, the qualitative analysis of the samples of COJR and Sr(II)-loaded COJR (Sr(II)-COJR) were carried out using an energy dispersive X-ray (EDX) spectroscopy and the results are shown in **Fig. 2(a)**.It is obvious from the results of this figure that there appears the peaks corresponding to elemental Carbon (C, 0.27 keV), Sodium (Na, 1.05keV), Phosphorus (P, 1.96 keV), Potassium (K, 2.74 keV), Calcium (Ca, 3.69 keV and 4.02 keV),and Iron (Fe, 6.41 keV) in COJR before the treatment of Sr(II) ions.The appearance of intense peaks of Ca and C in COJR strongly suggested that carbon and calcium are the major elements in the COJR adsorbent. However, after Sr(II) adsorption, entirely new peaks corresponding to elemental state of strontium were observed at binding energy of 14.17keV and 15.72 keVwhich provided the direct evidence of Sr(II) adsorption by COJR. Therefore, the COJR investigated in this study effectively adsorbed Sr(II) from water which can be a potential material for the treatment of Sr(II) polluted water.

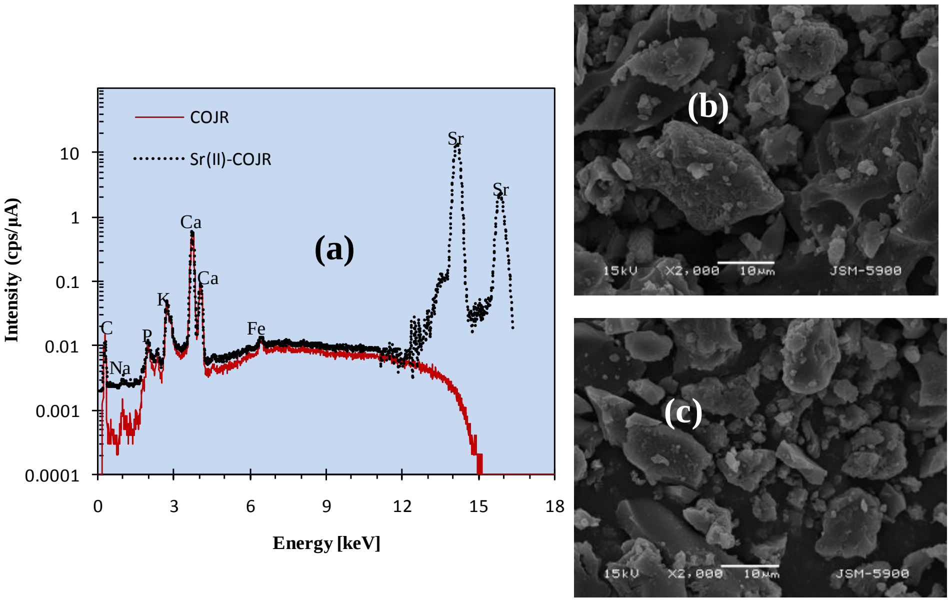

Fig. 2. Characterization of COJR before and after Sr(II) adsorption (a) an energy dispersive X-ray(EDX) spectra, (b) SEM image of COJR, and (c) SEM image of COJR after Sr(II) adsorption.

It is inferred that the surface morphology of the adsorbent changes after adsorbing some adsorbate ions. Thus surface analysis of investigated COJR adsorbent was done before and after Sr(II) adsorption to investigate the variation of surface morphology by Sr(II) adsorption and the results are demonstrated in **Fig. 2(b), and 2(c)**. It is clear from the results of these figures that the surface of COJR (**Fig. 2b**) is a little bit rough, small cracks, and irregular whereas the surface became much smooth and regular after Sr(II) adsorption (**Fig. 2c**), which is resulted due to the coating of adsorbed Sr(II) on the surface of COJR during adsorption process. This also confirms and provides the evidence that COJR effectively adsorbed Sr(II) from water.

Dissolution of TOC from OJR and COJR

Fig. 3 shows the dissolution behaviors of total organic carbon (TOC) from the samples of OJR and COJR at four different pH. It is clear from the result of this figure that the leakage of TOC from both, namely OJR and COJR, increases with the lowering of solution pH. The leakage of TOC from OJR was 262 mg/L at pH 1 which was only 24 mg/L in case of COJR at this pH. TOC leakage from COJR was found to be 6 mg/Lat pH 4 whereas its value is 194 mg/L in case of OJR under same experimental conditions. It provides the strong evidence that the aqueous stability of OJR was drastically improved after carbonization. Some of the low molecular organics and polysaccharides that potentially dissolve in water were possibly converted into carbon material during carbonization reaction thereby decreasing the TOC dissolution in COJR.

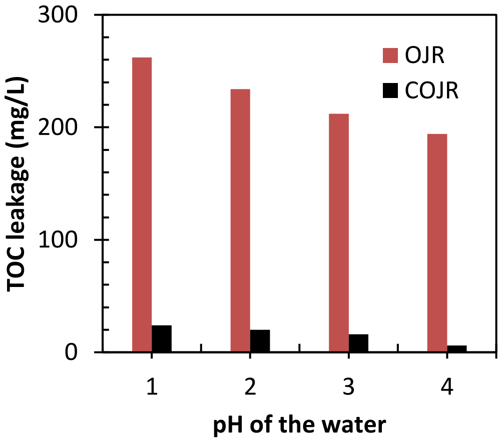

Fig. 3. Influence of pH of the water for the leakage of TOC from OJR and COJR adsorbent (conditions: volume of water = 10 mL, amount of OJR or COJR =50 mg, shaking time = 24 hrs, agitation speed = 150 rpm and temperature = 30°C).

Effect of pH and Sr(II) adsorption mechanism

The pH of the solution is one of the controlling parameter for the uptake of pollutants in aqueous medium because surface charge of adsorbent and adsorbate speciation changes with pH variation. **Fig. 4** shows the relationship between percentage adsorption of Sr(II) and Cs(I) onto COJR as a function of equilibrium pHs. As can be seen from the results that the adsorption of Sr(II) continued to increase when equilibrium pH rose from 2.7 to 5.3 and became constant at higher pH. The reason of increase in adsorption efficiency of Sr(II) at elevated pH is due to cation exchange behavior described as follows. At lower pH, the surface of COJR becomes more and more positive where adsorption of positively charged Sr(II) is unfavorable due to electrostatic repulsion thereby decreasing the percentage adsorption. However, at higher pH the surface of the adsorbent becomes more and more negative due to the increase in concentration of hydroxide ion where adsorption of positively charged Sr(II) is more feasible *via* columbic force of attraction that potentially increases Sr(II) adsorption. Moreover, the result of this figure also provides the evidence that the uptake of Cs(I) by COJR is negligible in entire range of tested pH from the mixed solution containing

Sr(II) and Cs(I), indicating high selectivity of COJR adsorbent for Sr(II) ions. EDX spectrum of COJR (Fig. 2a) contains appreciable amount of calcium whose physiochemical behaviors are similar with strontium sothat adsorption can occur simply by replacing calcium *via* cation exchange process, which is considered to be a main cause of high selectivity of COJR for Sr(II) ion.

The percentage adsorption of Cs(I) was not higher than 2.3 even at optimum pH using COJR adsorbent so that the COJR is not effective for the treatment of Cs(I) polluted water. The radioactive isotopes of Cs(I) and Sr(II) commonly exist in the wastewater produced during nuclear energy generation from where only Sr(II) can be selectively adsorbed using investigated COJR adsorbent.

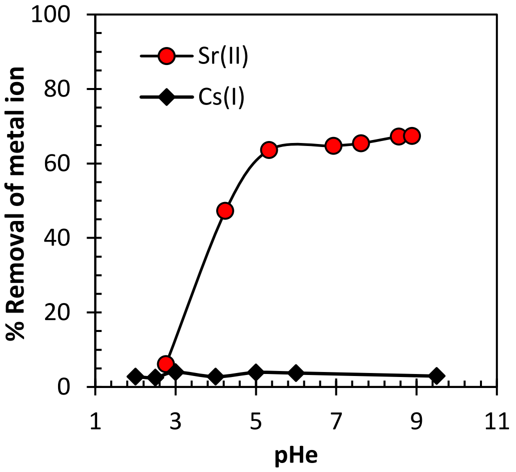

Fig. 4. Effect of pH for the adsorption of Sr(II) and Cs(I) onto COJR (conditions: volume of solution = 10 mL, metal solution = mixture of 0.05 mmol/L Sr(II) and 7.5 × 10^{-3}mmol/L Cs(I),weight = 10 mg, speed = 150 rpm and temperature = 30ºC).

Effect of contact time

Fig. 5 shows the effect of operating contact time on the adsorption of Sr(II) at 30^0C for a COJR dose of 1 g/L. It is clear from the result of this figure that Sr(II) ion adsorption increases rapidly at the beginning or at early contact times. The process achieves almost 136.1 mmol/kg at 0.25 hrs then reached 156.2 mmol/kg after one hour contact and attains equilibrium after 2 hrs. The rapid uptake of Sr(II) onto COJR is due to the presence of large number of available active sites for Sr(II)on the surface of COJR at the start of the experiment. Although the equilibrium was reached within 2 hrs of contact, however, in the subsequent experiments the solid-liquid mixtures were shaken for 24 hrs to ensure complete equilibrium.

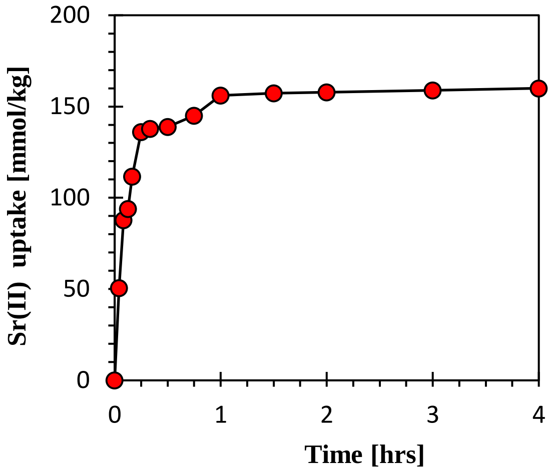

Fig. 5. Adsorption kinetic of Sr(II) from water using COJR (conditions: volume of solution = 200 mL, strontium concentration = 0.25 mmol/L, weight = 200 mg, speed = 150 rpm, pH = 5.6 and temperature = 30ºC).

Adsorption isotherm of Sr(II) ion

The adsorption isotherm is the relationship between the uptake capacity of adsorbent as a function of equilibrium concentration of adsorbate ion. The isotherm studies were carried out to investigate the effect of Sr(II)concentration during adsorption using COJR adsorbent. **Fig. 6** shows the experimental isotherm plots for Sr(II) adsorption by the COJR at pH 5.6. From the results of this figure, the adsorption of Sr(II) increased with increasing equilibrium concentration of Sr(II) at low concentration regions while it tends to approach a constant or plateau values at higher concentrations, exhibiting the formation of monolayer of Sr(II) on the COJR surface during Sr(II) adsorption process. A similar adsorption behavior was observed in case of rare metals adsorption using orange waste gel (Paudyal et al., 2013). Consequently, the adsorption isotherm data were fitted according to the following Langmuir and Freundlich models. The linearized form of Langmuir monolayer adsorption model can be expressed by the equation (Eq. 4) as(Langmuir 1916; Chen et al., 2011; Poudel et al., 2021)

$$\frac{C_e}{Q_e} = \frac{1}{Q_{\max} b} + \frac{C_e}{Q_{\max}} \qquad (4)$$

Where, C_e (mmol/Land Q_e (mmol/kg) are the equilibrium concentration and amount of adsorption, respectively, while Q_{max} is the maximum adsorption capacity and b (L/mmol) is Langmuir constant related to the binding energy of adsorption. The maximum adsorption capacity (q_{max}) and adsorption equilibrium constant (b) were calculated from the slope and intercept of the linear plot of C_e/Q_e *versus* C_e (**Fig. 7a**). These values are listed in **Table 1.** Freundlich isotherm model can be expressed in the form of the equation (Eq. 5) as (Freundlich 1906; Ghaemi et al., 2011)

$$\log Q_e = \log K_F + (1/n) \log C_e \qquad (5)$$

Where, K_F and n are Freundlich constants related to the adsorption capacity and adsorption intensity, which can be calculated from the intercept and slope of the linear Freundlich plot of log Q_e *versus* log C_e (**Fig. 7b).** From the observation of high values of the correlation coefficient (R^2) for both the Langmuir model (R^2 = 0.98) and Freundlich model (R^2 = 0.98), it suggested that the experimental data were fitted to both the isotherm models. From the literature, the Sr(II) uptake capacities of some adsorbents such as hydrous Cr(VI) oxide, dolomite powder, and plant root tissue were reported as 0.61, 13.02, and 143.2 mmoL/kg, respectively (Mishra et al., 1995; Ghaemi et al., 2011). Compared with these results, the maximum uptake capacity of Sr(II) using COJR investigated in this study (322.58 mmoL/kg) is much higher suggesting that COJR can be a good candidate capable of adsorbing Sr(II) from water.

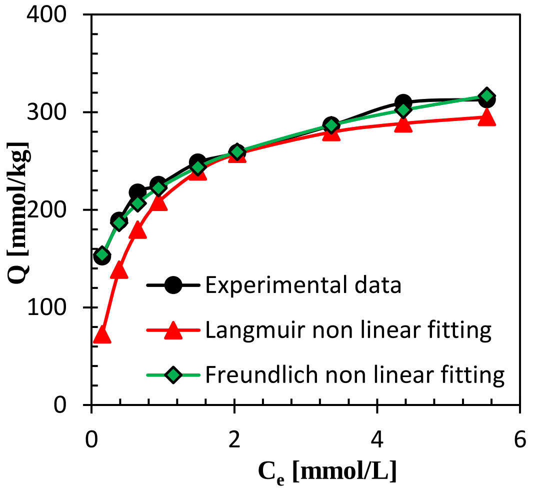

Fig. 6. Adsorption isotherm of Sr(II) by COJR (black line) experimental plot, (green line) Langmuir plot and (red line) Freundlich plot (conditions**:** volume of solution = 10 mL, contact time = 24 hrs,, COJR amount = 10 mg, pH = 5.6 and temperature = 30°C)

To evaluate the feasibility and suitability of the investigated adsorption process, a dimensionless separation factor (R_L) was applied. The R_L value of the system is related to Langmuir constant (b, L/mmol) by following equation (Eq. 6) as (Xia et al., 2011)

$$R_L = \frac{1}{1+bC_i} \qquad (6)$$

Where, b is Langmuir equilibrium constant, C_i is the initial concentration of Sr(II).R_L may be zero, one, or greater than one showing irreversible, linear, and unfavorable nature of reaction, respectively.

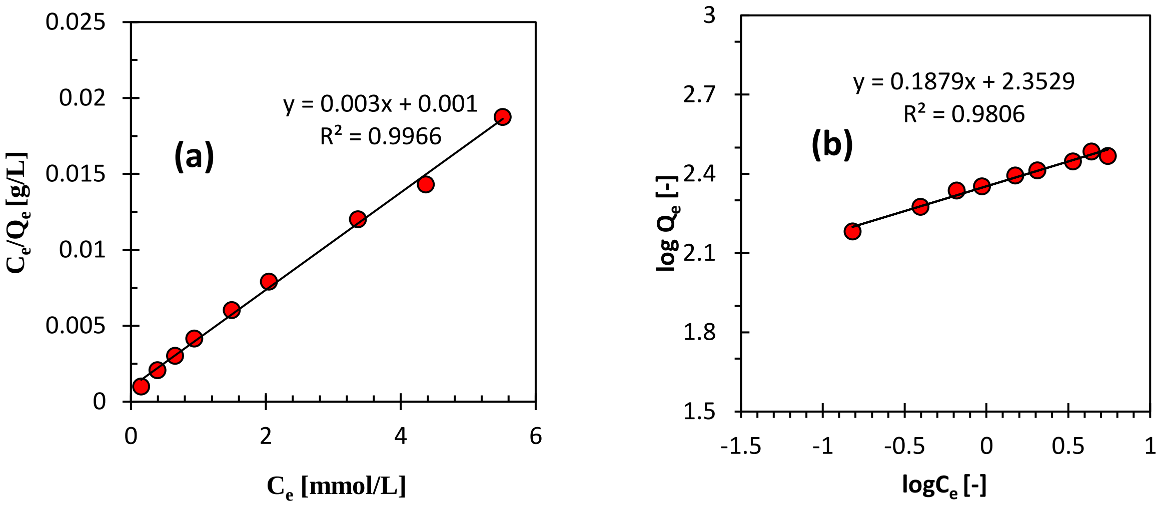

Fig. 7. Modeling of experimental data using (a) Langmuir isotherm model, and (b) Freundlich isotherm model.

The variation of R_L value as a function of initial Sr(II) concentration is shown in **Fig. 8**. It is evident from this result that the values of R_L were found in between 0 to1 for all the concentrations. The value of R_L represent: $0 < R_L < 1$ (favorable), whereas $R_L > 1$ (unfavorable), $R_L = 1$ (linear) and $R_L = 0$ (irreversible). The values of R_L for lowest Sr(II) concentration (0.30 mmol/L) is 0.0187 and highest Sr(II) concentration studied (5.95 mmol/L) is 0.0009 (i.e., $0 < R_L < 1$), which implies that the adsorption process belonging to a favorability. A similar behavior was observed by Poudel et al., 2021 in case of As(V) adsorption using Zr(IV) modified and saponified pomegranate peel (Zr@SPP) adsorbent.

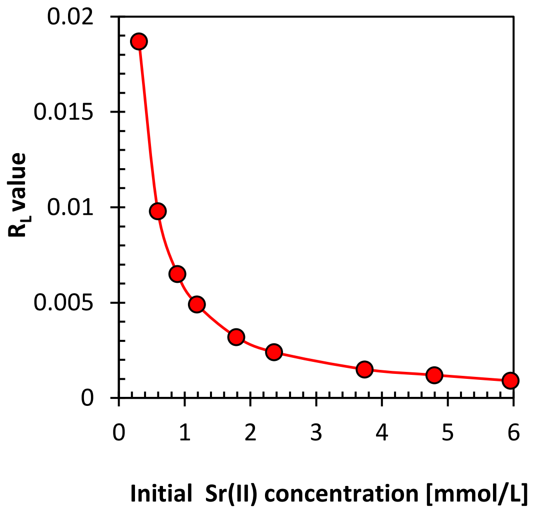

Fig. 8. *Variation of R_L value as a function of initial concentration of Sr(II) ion.*

Table 1. *Langmuir and Freundlich parameters for the adsorption of Sr(II) ion onto COJR*

	Evaluated isotherm parameters for the adsorption of Sr(II)	
Langmuir parameters	Q_{max} (mmol/kg)	322.58
	B (L/mmol)	1.93
	R^2	0.97
Freundlich parameters	K_F (mmol/kg)	324.91
	n	5.32
	R^2	0.98
Experimental uptake capacity of COJR for Sr(II) ion (mmol/kg)		314.98

Effect of solid-liquid ratio

The experiments were carried out with eight different dosages, *viz.* 0.5, 1.0, 1.5, 2.0, 3.0, 4.0, 6.0 and 8.0 g/L of COJR with 54.8 mg/L Sr(II) concentration. This experiment was carried out to optimize the sorbent dosages to lower down the Sr(II)level to the tolerance limit (4 mg/L) set by EPA. **Fig. 9** shows the residual concentration of Sr(II) ions in the aqueous solution after the adsorption onto COJR at different dosages at pH 5.6 . A significant decrease in remaining concentrations of Sr(II) ion with an increase in the dosage of COJR was observed as expected after adsorption. The reason of decreasing Sr(II) level with the increase of COJR dosage is due to the increase of active adsorption sites for Sr(II) at higher mass. The Sr(II) concentration was found to be down to EPA standard by using COJR dosages higher than6g/L. Therefore, the COJR investigated in this study can be expected as an excellent green, low cost and environmentally friendly material to treat the aqueous solution contaminated with Sr(II) ion.

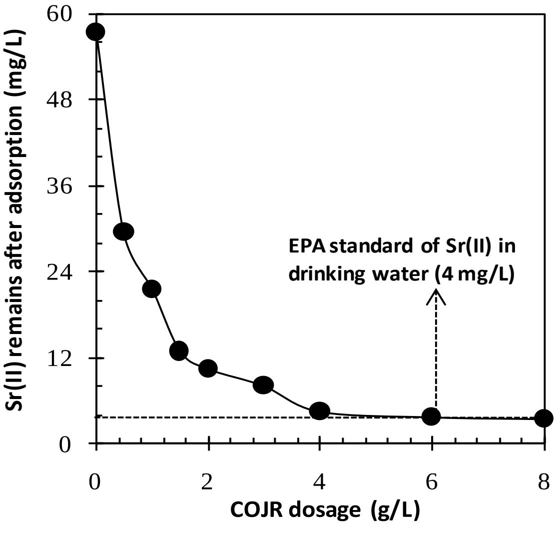

Fig. 9. Effect of COJR dosage for the removal of Sr(II) from aqueous solution (conditions: pH = 5.6, Sr(II) concentration = 57.3 mg/L, volume of test solution = 10 mL, shaking time = 24 hrs and temperature = 30°C).

Desorption of adsorbed Sr(II)

After finding the suitable desorbing solution (HCl solution) from the preliminary test, the optimization of HCl was done by desorbing Sr(II) from Sr(II)-COJR at varying concentration of HCl. **Fig. 10** shows the result of desorbed percentage of Sr(II) using 0.01, 0.05, 0.1, 0.25, 0.5, 0.75 and 1MHCl solution. It is evident from the result of this figure that the percentage desorption of Sr(II) increased sharply from 2.8to 91.5% by increasing HCl concentration from 0.01 to 0.25M whereas more than 97% desorption was achieved at a concentration higher than 0.5M. After that, the desorption percentage of Sr(II) gradually increased with further increase of HCl concentrations. Thus 0.5M HCl was optimized for the effective desorption of Sr(II) from Sr(II)-COJR.

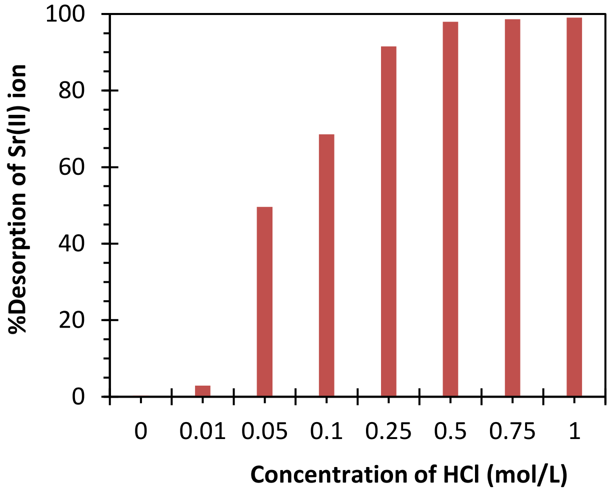

Fig. 10. Desorption of Sr(II) from Sr(II) loaded COJR at different concentration of acidic solution.(conditions: amount of Sr(II) in Sr(II) loaded COJR = 245 mmol/kg, amount of Sr(II)-COJR = 50 mg, amount of acid (HCl) used = 10 mL, and shaking time = 6 hrs)

Conclusions

In this study, the effects of various parameters on the removal of Sr(II) from aqueous solutions were investigated. The experiments showed that adsorption of Sr(II) was highly dependent on pH, and the maximum adsorption was attained at pH around 5.6.The rate of Sr(II) adsorption onto COJR was concluded to be fast and equilibrium was reached within 2 hrs. Aqueous insolubility of OJR could be dramatically lowered after carbonization at 800°C. Langmuir and Freundlich isotherms both demonstrated the satisfactory fitting to experimental data. The maximum adsorption capacity (Q_{max}) of COJR for Sr(II) was found to be 322.58 mmol/kg from Langmuir isotherm modeling. The concentration of Sr(II) could be lowered down to the EPA standard by using COJR higher than 6 g/L. The adsorbed Sr(II) could be quantitatively desorbed by 0.5M HCl. From these results, it is concluded that the COJR investigated in this work can be used as a low-cost, environmentally friendly and effective value-added material for the decontamination of water and wastewater polluted with Sr(II) ion.

Conflicts of interest

The authors declare no conflicts of interest.

Author contribution statements

Project design, Experiment, Resources, Manuscript writing, Revising: **Hari Paudyal**; Data curation, Manuscript review and editing: **Bimala Pangeni and Prabin Basnet**; Conceptualization andsupervision: **Katsutoshi Inoue**.

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