Attenuation of Radioactive Sr(II) from Water Environment Using Sericite Clay

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Abstract. The performance of sericite clay as an adsorbent for attenuation of Sr(II) from aqueous environment was investigated. Batch adsorption experiments were carried with varied solution pH, contact time and initial Sr(II) concentration solutions. The results showed that the kinetics of Sr(II) removal by the sericite clay is prompt in the first 30 min and the adsorption equilibrium was attained after 120 min. The adsorption was best described by pseudo-second-order kinetic model. The sips isotherm model was found to be better applicable to the experimental data as compared to Langmuir and Freundlich as inferred from high value of coefficient of determination. This study provides a low-cost adsorbent for the treatment of Sr(II) contaminated water.

Keywords: attenuation, adsorption, strontium, radioactive, kinetics.

1. Introduction

In recent years, radioactive wastes have been noted and introduced into the environment by nuclear accidents [1]. The accidental release of waste water containing radioactive metal ions may bring the environmental risk to the soil or groundwater system. While there are many radioactive metals ions present in the aqueous environment, this paper has focused on "Strontium". Strontium-90 (^{90}Sr) one of the waste resulting from nuclear reactions which is a typical fission product and is the most abundant radionuclides because of its complexity and long physical half-life approximately 28 years [2]. ^{90}Sr is usually accumulated and absorbed by human's body through the alimentary chain and it may produce damages to human's health by radiation. As a result, removal of Sr(II) from aquatic environment is an important topic in the field of environmental science and technology. Given the strict environmental authorities guidelines regulating the discharge of metal ions to the aqueous environment, it is important to develop attenuating materials capable of adsorbing these pollutants [3].

Clay and clay minerals are widely used as materials for detoxification of metal ions from water environment due to their, chemical and mechanical stability, variety of structural and surface properties, higher values of cation exchange capacities, abundance in nature, good surface area and also they are economic. Sericite is naturally available and low-cost material and is a layered silicate mineral, generally recognized as white fine powders of muscovite in form. The general empirical formula of sericite is $(Al_4(OH)_4(KAl\text{-}Si_3O_{10})_2)$ and it consists of layered structure with interlayer spacing of (0 0 2) plane is 10 Å. Presence of hydroxyl groups on the surface of sericite made it an attractive material for removal of various pollutants from water [4][5]. With the aim to address the important environmental problem illustrated above, in this study the removal of Sr (II) from aqueous solution using naturally abundant sericite clay as an adsorbnet was investigated. The main objective of the present study was to investigate factors influencing Sr(II) removal by sericite such as: pH, contact time and concentration.

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2. Materials and Methods

2.1. Materials

Natural sericite material was obtained from SG mine, Jecheon (South Korea). The material was used as received without any further modifications for adsorption experiments. The stock Sr(II) solution was prepared in distilled water to the concentration of 1000 mg/L. The working solution was prepared by diluting the metal stock solution with distilled water to the required concentration. Fresh dilution was used for each adsorption study.

2.2. Sorption Experiments

In order to determine the sorption capacity of sericite for Sr(II), as well as the influence of contact time, pH and the initial metal ion concentration, sorption experiments were performed by batch equilibration technique. All experiments were performed at constant temperature (25±1 ^{O}C). After equilibrium the solutions were filtered and analyzed for residual metal concentration using Atomic Absorption Spectrophotometry. The adsorption capacity (q) and the removal percentage (R, %) were calculated with the following equations:

$$q = \frac{V.(c_0 - c)}{m}; \quad R\% = \frac{(c_0 - c)}{c_o} x\ 100 \tag{1}$$

Where V is the volume of solution, C_o is the initial metal concentration; C is the equilibrium concentration and m (mg/g) mass of the adsorbent.

2.3. Non-Linear Kinetic Modeling

In order to investigate the mechanism of considered heavy metals biosorption onto honeycomb biomass, Lagergren pseudo-first order and pseudo-second order models were tested to fit the kinetic experimental data and the equations are given respectively as

$$q_t = q_e\ (1 - e^{-k_1 t}) \tag{2}$$

$$q_t = q_e \frac{q_e k_2 t}{1 + q_e k_2 t} \tag{3}$$

Where, q_e (mg g^{-1}) and q_t (mg g^{-1}) are the adsorption amount at equilibrium and time t (min), respectively. k_1 (min^{-1}) and k_2 are the pseudo-first and pseudo-second (g mg^{-1} min^{-1}) order model rate constants. Also the initial adsorption rate (mg g^{-1} min^{-1}) for pseudo-second order kinetics was calculated.

3. Results and Discussion

From previous studies on sericite clay it was found that sericite contains a high amount of hydroxyl groups of silinol and aluminol functional groups [4][5]. From the previous finding we hypothesize that this hydroxyl groups will be useful for the removal Sr(II) from aqueous solution. In present study we have studied the surface morphology of sericite.

3.1. Effect of pH

pH of the solution is an important parameter affecting the removal of metal ions by adsorption. As calculated by visual Medusa equilibrium diagram speciation program, strontium species occurs in solution as divalent cation Sr(II) at pH between 2.0 and 11.0. The influence of pH on the adsorption of strontium ions from aqueous solution was investigated by adjusting the solution pH from 2.0 to 10.0 using 0.1 M HNO$_3$ or NaOH. Removal of strontium ions onto the sericite was slightly affected when pH increased from 2.0 to 8.0, while the removal percentage increased when the pH > 8.0 shown in Fig. 1. This is because precipitation phenomenon occurred to some degree in the aqueous solution at pH 9.0. It can be seen that maximum biosorption of both Sr(II) occurred at pH of 5.0–6.0.
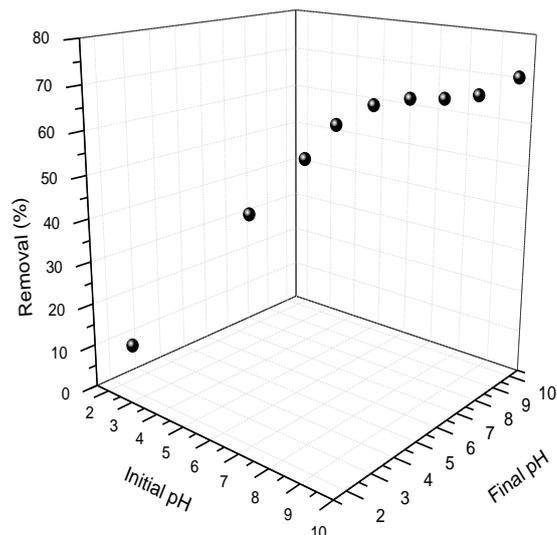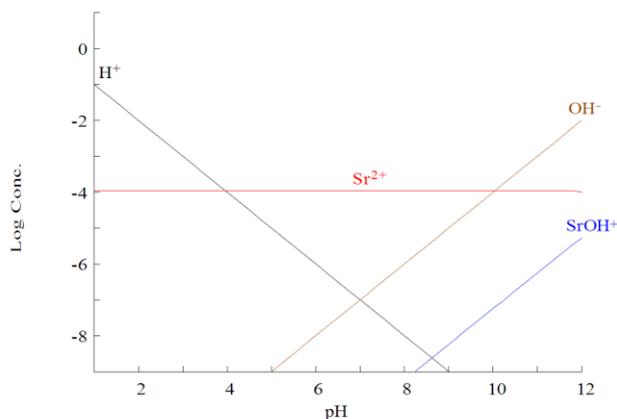
Fig. 1: Distribution of Sr(II) species as a function of pH and removal of Sr(II) at different pH's with sericite.

3.2. Adsorption Kinetics

In order to investigate the mechanism of Sr(II) adsorption onto sericite, the pseudo-first order and pseudo-second order kinetics models were tested to fit the kinetics experimental data shown in Fig 2. The parameters of the pseudo-first order and the pseudo-second order kinetics models, calculated from the non-linear plots of t vs q_e respectively, together with the corresponding correlation coefficients (R^2) are summarized in Table 1. The correlation coefficients ($R^2 > 0.99$) for the pseudo- second order kinetic model are higher in comparison with the pseudo-first order kinetic model, and the calculated values of $q_{e,calc}$ from the pseudo-second order kinetic model are very close to the experimental values ($q_{e,exp}$). These indicate clear that the pseudo-second order kinetic model was better in describing the adsorption kinetics of Sr(II) onto sericite. The pseudo-second order kinetic model is based on the assumption that the rate-controlling step in the adsorption process, are the chemical interactions between superficial functional groups of adsorbent and Sr(II).
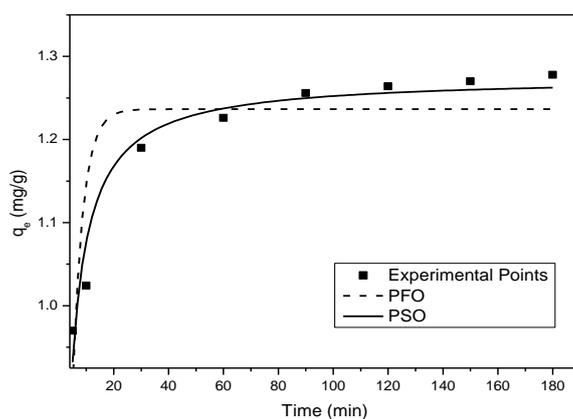

Fig. 2: Pseudo-first, Pseudo-second-order kinetic modelling for Sr(II) onto sericite.

Table 1: Kinetic parameter constants for Sr(II) removal by sericite

Metal ion	Pseudo-first-order kinetic model (PFO)			Pseudo-second-order kinetic model (PSO)		
	q_e (mg g^{-1})	k_1 (min^{-1})	R^2	q_e (mg g^{-1})	k_2 (g mg^{-1}min^{-1})	R^2
Sr(II)	1.2365	0.2624	0.7029	1.2753	0.4261	0.9427

3.3. Adsorption isotherms

For designing purposes, the equilibrium data are represented by theoretical or empirical equations. The change in the adsorbed amount of Sr(II) with equilibrium concentration is given in Fig. 3 also three isotherm models were fitted to the experimental data were shown. Three isotherm models along with their parameter constants were shown in Table 2. Langmuir constant, q_m, represents the monolayer saturation at equilibrium it was found that 2.816 mg/g. The values of K_F and n determined from the Freundlich model were shown and $1 < n < 10$, indicating that Sr(II) ions are favourably adsorbed by sericite. From Table 2, it was found that the Sips isotherm exhibited higher R^2 value and a lower $\chi2$ value, which is a considerably better fit compared with Langmuir and Freundlich isotherms.

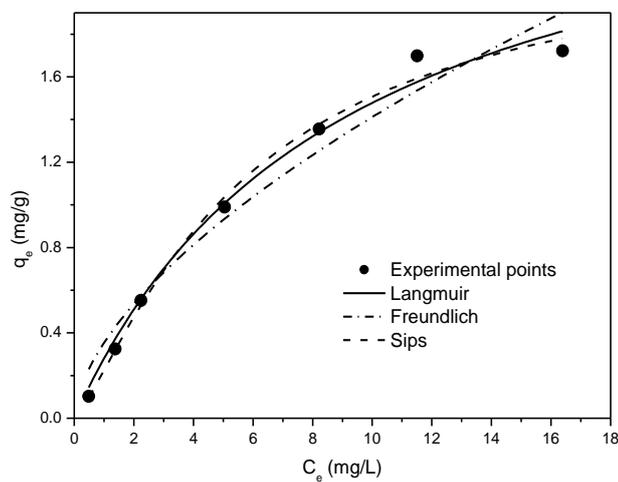| Model	Parameters and goodness of fit	
Langmuir	q_m (mg g^{-1})	2.816
	b (L mg^{-1})	0.110
$q_e = \dfrac{q_m K_L c_e}{1 + K_L c_e}$	R^2	0.9869
	$\chi2$	0.0056
	K_F (mg g^{-1} (dm^3 g^{-1})$^{1/n}$)	0.352
Freundlich	n	0.602
$q_e = K_F C_e^{1/n}$	R^2	0.954
	$\chi2$	0.0198
Langmuir–Freundlich (Sips)	q_{max} (mg g^{-1})	2.251
	n_{LF}	1.260
$q = q_{max} \dfrac{b_{LF} \cdot C_e^{nLF}}{1 + b_{LF} \cdot C_e^{nLF}}$	b_{LF} (dm^3 mg^{-1})	0.111
	R^2	0.9896
	$\chi2$	0.004

Fig. 3: Adsorption isotherm modelling for the equilibrium data

3.4. Adsorption mechanism

The complex adsorption mechanism involved in the removal of Sr(II) was due to the presence of silinol and aluminol hydroxyl groups on the sericite surface and also due to ion-exchange mechanism. Sericite has two different surface-active groups, one is $\equiv$S–OH of the silanol group and the second one $\equiv$S–OH represents aluminol group. The deprotonated surface $\equiv$SO- behaves as Lewis base which bind with the metal ion. This chemical sorption mechanism was also confirmed from pseudo-second order kinetic model which is based on chemisorption phenomena. Along with this SEM images for before and after adsorption were shown in Fig. 4 also SEM image of sericite at 1μm was also shown in Fig. 4 A.
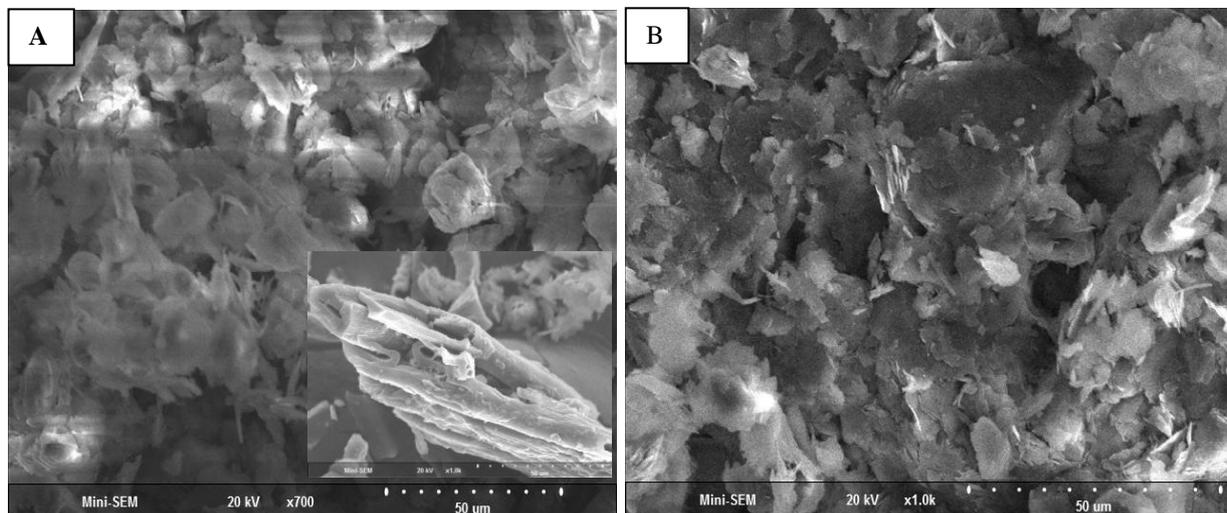

Fig. 4: SEM micrographs of (A) sericite before adsorption (B) after strontium adsorption

4. Conclusions

Sericite is able to adsorb strontium ion from aqueous solutions. The adsorption time of equilibrium is shorter. The experimental results were analyzed by using the Langmuir, Freundlich and Sips equations, thus correlation coefficients and Chi-square for fitting the Sips equation was significantly better. The adsorption quantity of strontium ions was 2.816 mg g^{-1} at 298 K from the Langmuir equation.

5. Acknowledgments

6. References

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