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Effects of γ -irradiation on the Cu^{2+} sorption behaviour of NaOH-modified Philippine natural zeolites

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Abstract

Adsorption kinetic and thermodynamic tests were conducted using non-irradiated and γ -irradiated (400 kGy) NaOH-modified Philippine natural zeolites for the removal of Cu^{2+} ions in aqueous solution. The effects of γ -radiation on zeolites were investigated. Samples were equilibrated with binary systems of $\text{Cu}^{2+} \leftrightarrow 2\text{Na}^+$ at room temperature. There were no significant changes in the elemental composition of the irradiated zeolite. Irradiation primarily results in the shrinking of the zeolite framework and improvements in the crystallinity. The γ -irradiation increases the sorption uptake according to the kinetic study in which the adsorption kinetics followed a pseudo-second-order model. Thermodynamic tests show that the adsorption isotherms of the two samples are best described by the Langmuir model. The maximum adsorption capacities of the non-irradiated and γ -irradiated NaOH-modified zeolites are 33.00 and 43.22 mg $\text{Cu}^{2+} \text{ g}^{-1}$, respectively, suggesting that γ -irradiation might enhance the maximum adsorption capacity by up to 30.8%.

Keywords: γ -radiation, adsorption, heavy metals, natural zeolites

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Natural zeolites have been extensively studied for their heavy metal and radionuclide sorption (Faghihian *et al.*, 1999; Gili *et al.*, 2019a; Olegario *et al.*, 2019). They may be efficient adsorbents for heavy metals depending on the abundance of zeolite components and amount of impurities. To enhance adsorption, zeolites are modified using various methods. Chemical modifications using acidic or basic solutions are typically employed to minimize impurities or change the Si/Al ratio (Ates & Akgul, 2015; Dignos *et al.*, 2019). Ion exchange removes cations initially present on the zeolite, providing additional sites for cation adsorption (Inglezakis *et al.*, 2001; Taffarel & Rubio, 2009; Gili *et al.*, 2019b). Other methods employ plasma modification to increase adsorption (Cagomoc & Vasquez, 2017; Taaca *et al.*, 2019).

A less common method to enhance the sorption capacity of zeolites is through exposure to ionizing radiation. Generally, zeolites are thermally stable and resistant to radiation. However, controlled exposure of the mineral to ionizing radiation causes significant physicochemical changes that might be used to enhance the sorption properties (Daniels & Puri, 1986).

The effects of irradiation on zeolites are often contradictory, as shown by various studies. In a recent report, the exposure of Armenian natural zeolites (mainly clinoptilolite) to 8 MeV electrons at an irradiation dose of 10^{12} – $10^{13} \text{ e cm}^{-2}$ maximizes the sorption of nuclear radioisotopes, which helped reduce the activity of liquid nuclear waste containing ^{137}Cs , ^{134}Cs and ^{60}Co (Yeritsyan *et al.*,

2013). This contradicts an earlier report that e-irradiation with a dose of 10^{12} – $10^{15} \text{ e cm}^{-2}$ at 293K decreases the ion-exchange capacity for Sr^{2+} and Cs^+ not only of the untreated natural clinoptilolite, but also of the cation-modified natural zeolites as well (Akhlabdashvili *et al.*, 2010). Similarly, a decrease in ion-exchange capacity was observed for γ -irradiated clinoptilolite at 293K with 200 and 700 kGy doses (Akhlabdashvili *et al.*, 2010). On the other hand, Moraetis *et al.* (2004) reported a slight increase in the Cs^+ uptake and a decrease in Sr^{2+} uptake of γ -irradiated (700 kGy) Armenian clinoptilolite in single-metal solutions. A net decrease in the Cs^+ uptake was also observed in a γ -irradiated (up to 1008 kGy) zeolite-4A at 303K because of locking of mobile Na^+ cations in the sodalite cages due to the contraction of the zeolite framework, rendering the Na^+ cation inaccessible for cation exchange (Daniels & Puri, 1986). In another study, γ -irradiation at 1.5 and 10.0 Mrad (15 and 100 kGy) was more effective when zeolites were firstly thermally activated (Selim *et al.*, 1992). Accordingly, the exposure to γ -radiation of dehydrated Nd-exchanged NaX and NaY zeolites, previously heated at 550°C, resulted in greater catalytic activity (cracking of cumene) due to the conversion of Brønsted acid sites into Lewis acid sites. The γ -irradiated hydrated (not thermally treated) zeolites showed slightly lower catalytic activity.

A non-linear dependence of adsorption uptake of zeolite NaA was observed after exposure to γ and neutron radiation with doses ranging from 0 to 1200 kGy (Ermatov *et al.*, 1980). At low doses (5–50 kGy), there was an ordering of the lattice structure, while disordering occurs at higher doses. In another study, γ -irradiation of US-HY zeolite affected the sorption by changing protonic conduction through increasing proton mobility, while a high dose led to the resistance of protonic conduction due to water dehydration (Sayed, 1996, 2000).

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The cation-exchange capacity (CEC) for univalent cations of clinoptilolite irradiated with β -radiation (10^{12} , 10^{15} , 3×10^{16} e cm $^{-2}$) and γ -radiation (70 Mrad/700 kGy) barely changed (Moraetis *et al.*, 2007). However, irradiation influenced the selectivity and affinity for various cations. The selectivity for K $^{+}$ was not affected after β -radiation up to 10^{15} e cm $^{-2}$, but increased significantly after 700 kGy of γ -radiation. Selectivity for Cs $^{+}$ increased for all clinoptilolite samples irradiated with β -radiation and γ -radiation. The same authors also performed thermodynamic calculations of ion exchange for bivalent cations for the same set of samples (Moraetis *et al.*, 2008) in the binary systems Ca $^{2+}$ \leftrightarrow 2Na $^{+}$, Mg $^{2+}$ \leftrightarrow 2Na $^{+}$ and Sr $^{2+}$ \leftrightarrow 2Na $^{+}$. After γ -irradiation (700 kGy), the affinity of clinoptilolite for Sr $^{2+}$ increased and that for Mg $^{2+}$ decreased, while the affinity for Ca $^{2+}$ remained unchanged. Irradiation with β -radiation influenced selectivity order, which decreased for Sr $^{2+}$, while it increased for Ca $^{2+}$. At the highest dose of β -radiation, the selectivity was almost identical for Ca $^{2+}$ and Sr $^{2+}$.

In our previous study, it was reported that γ -irradiation does not improve the Cu $^{2+}$ sorption capacity of raw and HCl-treated Philippine natural zeolite (PNZ) (Gili *et al.*, 2019b). It even lowers the sorption uptake, especially at 400 kGy and higher absorption doses. However, γ -irradiation of NaOH-modified zeolite showed promising results, because it increased Cu $^{2+}$ absorption by 16.3% at a dose of 200 kGy. The optimum adsorption, corresponding to an increase by 25.2%, was attained at a dose of 400 kGy. Further increase of the dose to 700 kGy reduced the sorption to 21.36% (Gili *et al.*, 2019b). Natural zeolites preconditioned in various ways react differently to γ -radiation. The adsorption property changes depending on the irradiation dose. The present study aims to verify the previous results by determining the changes in the sorption behaviour and maximum adsorption capacity of the γ -irradiated (400 kGy) NaOH-modified PNZ for Cu $^{2+}$ ions. Changes in the structure and elemental composition were examined and correlated with the sorption uptake. The adsorption kinetics and thermodynamics of the NaOH-modified zeolites were investigated and the possible reasons for the acquired changes were discussed.

Materials and methods

Philippine natural zeolite

The PNZ used in this study was supplied by LITHOS Manufacturing. It was mined from Mangatarem, Pangasinan, Philippines. The chemical composition of the PNZ, according to the supplier's chemical analysis report from an independent laboratory (Chemistry Laboratory of the Mines and Geosciences Bureau, Department of Environment and Natural Resources, Philippines), is given in Table 1.

Pre-treatment and γ -irradiation of PNZs

The raw PNZs (RawZeo0) were preconditioned with 1.5M NaOH (Merck, 99%) solution. For every 250 mL of the base solution, 25 g of PNZ was added and soaked for 6 h. Then it was rinsed with 0.5 L of deionized (DI) water three times, soaked for 24 h in 250 mL of 4.0M NaCl solution and then washed with 0.5 L of DI water three times. On the final wash, drops of 1M HCl solution were added to neutralize the adsorbent. The powder was collected and oven-dried at 150°C for 5 h. Finally, the sample was re-pulverized for 20 min using an agate mortar and pestle (NaOHZeo0).

Table 1. Chemical composition of the PNZs.

Component	Concentration (wt. %)
SiO $_2$	55.29
Al $_2$ O $_3$	12.63
Fe $_2$ O $_3$	3.43
MgO	1.49
CaO	4.69
Na $_2$ O	0.62
K $_2$ O	0.58
H $_2$ O (105°C)	7.04
LOI	14.71

*Computed from Fe $_y$.
LOI = loss on ignition.

The NaOH-modified zeolites were placed in sealed polyethylene (PET) tubes (2.7 cm diameter, 8.5 cm height) and exposed to γ -radiation at the Cobalt-60 Multipurpose Irradiation Facility of the Philippine Nuclear Research Institute until the samples accumulated a dose of \sim 400 kGy (NaOHZeo400). The raw PNZs were also irradiated at the same dose (RawZeo400).

Characterization

Scanning electron microscopy (SEM SU1510, Hitachi High Technologies, Japan) and energy-dispersive X-ray spectroscopy (UltraDry EDX Detector, ThermoScientific, MA, USA) were used to determine the elemental compositions of the samples as well as their Si/Al ratios. The samples were analysed using an X-ray diffraction (XRD; SHIMADZU, XRD-7000 Maxima) with Cu-K α (1.5406 Å) radiation to determine their crystal order and structure. A continuous scan was conducted with a scanning speed of 2.00° min $^{-1}$.

Batch adsorption tests and analytical technique

A stock solution with a concentration of 1000 mg Cu $^{2+}$ L $^{-1}$ was prepared by dissolving copper sulfate pentahydrate (CuSO $_4$ ·5H $_2$ O, Unilab, 95.8%) in 1.0 L of DI water. In every experiment, a feed solution with a 100 mg Cu $^{2+}$ L $^{-1}$ concentration was obtained from the stock solution. To determine the adsorption mechanism, the adsorption kinetic study was performed at room temperature (\sim 25°C). A total of 0.25 g of adsorbent was added to 100 mL of the prepared 100 mg Cu $^{2+}$ L $^{-1}$ solution. The solution was magnetically stirred (WiseStir, MSH-30D) at 500 rpm under ambient conditions. Approximately 10 mL of the mixture was subsequently removed after 0, 10, 30, 60, 90, 120, 150, 180 and 240 min contact time. The adsorbent was separated from the supernatant using a centrifuge (Hsiangtai, China; 5 min, 4000 rpm) and a Nylon syringe filter (0.45 μ m pore size, 25 mm diameter). The concentration of Cu $^{2+}$ in the supernatant solution was measured using a Shimadzu AA-7000 atomic absorption spectrometer (AAS). The AAS was first calibrated before measuring standard solutions to produce a suitable calibration curve ($R^2 \geq 0.996$).

The adsorbed ions per gram of the sorbent were determined using Eq. (1).

$$q = \frac{(C_0 - C_i)V}{m} \quad (1)$$

where C_0 is the initial concentration of ions (mg Cu $^{2+}$ L $^{-1}$), C_i is the concentration (mg Cu $^{2+}$ L $^{-1}$) of the supernatant after time i , V is the batch volume (L) and m is the mass (g) of the adsorbent. It

is assumed that the difference between the initial and the final concentration is attributed to the adsorbed Cu^{2+} ions regardless of the type of adsorption.

Adsorption thermodynamic tests were performed by determining the adsorption uptake at varying concentrations of the feed solution – 25, 50, 100, 200 and 400 $\text{mg Cu}^{2+} \text{L}^{-1}$ – using the same adsorbent-to-feed solution ratio (0.25 g per 100 mL). The mixture was agitated with a batch shaker at 125 rpm for 5 h under ambient conditions. The adsorbent was separated from the supernatant before measuring the concentration using the AAS. All experiments were run in triplicate and the average concentration values were reported.

Adsorption kinetics

To describe the adsorption behaviour, three models were considered: (1) the pseudo-first-order kinetic model (Lagergren, 1989); (2) the pseudo-second-order kinetic model (Ho & McKay, 1998); and (3) the intra-particle diffusion model (Weber & Morris, 1962; Taffarel & Rubio, 2009). The Lagergren pseudo-first-order model assumes that the rate of uptake is directly proportional to the difference in the saturation concentration and amount of adsorbed solute at a given time t . The general equation is as follows:

$$\frac{dq_t}{dt} = K_1(q_{eq} - q_t) \quad (2)$$

where K_1 (min^{-1}) is the Lagergren pseudo-first-order adsorption rate constant and q_{eq} and q_t are the amounts of metal ions adsorbed (mg g^{-1}) at equilibrium and at instantaneous time t , respectively. The linearized form of Eq. (2) is as follows:

$$\log(q_{eq} - q_t) = \log(q_{eq}) - \frac{K_1}{2.303} t \quad (3)$$

The pseudo-second-order kinetic model considers the amount of adsorbate on the adsorbent and is represented as follows:

$$\frac{dq_t}{dt} = K_2(q_{eq} - q_t)^2 \quad (4)$$

where K_2 is the second-order adsorption rate constant ($\text{g mg}^{-1} \text{min}^{-1}$). Its linearized form is given as follows:

$$\frac{t}{q_t} = \frac{1}{K_2 q_{eq}^2} + \left(\frac{1}{q_{eq}}\right)t \quad (5)$$

Metal ions may be transported from the aqueous solution to the adsorbent surface, which subsequently diffuses into the interior of the material. In such cases, adsorption is best described by intra-particle diffusion according to Eq. (6):

$$q_t = K_i t^{0.5} + C \quad (6)$$

where K_i represents the intra-particle diffusion rate ($\text{mg g}^{-1} \text{min}^{-0.5}$) and C is an arbitrary constant (mg g^{-1}).

Adsorption thermodynamics

The adsorption uptake at various initial feed solution concentrations was determined. Langmuir and Freundlich models were used to describe the thermodynamic behaviour. The Langmuir model (Langmuir, 1916) assumes uptake on a homogeneous

surface by monolayer sorption in the absence of interaction between molecules. It is described as follows:

$$q_e = \frac{q_{max} K C_e}{1 + K C_e} \quad (7)$$

where q_e (mg g^{-1}) is the adsorption uptake at equilibrium concentration, C_e (mg L^{-1}), K (L mg^{-1}) is the Langmuir equilibrium constant and q_{max} is the maximum adsorption capacity at equilibrium concentration required to form a monolayer (Perry, 1999). The linear form is given as follows:

$$\frac{C_e}{q_e} = \frac{1}{K q_e} + \frac{1}{q_{max}} C_e \quad (8)$$

The characteristics of the Langmuir isotherm parameters that may be used to predict the affinity between the sorbate and the sorbent are described by a dimensionless equilibrium parameter, R_L , which is also called a 'separation factor' and is represented as follows:

$$R_L = \frac{1}{1 + K C_h} \quad (9)$$

where C_h is the highest initial concentration of the feed solution. The equilibrium parameter specifies the nature of adsorption to be either unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

The Freundlich model is described by Eq. (10):

$$q_e = K_F C_e^{1/n} \quad (10)$$

which takes the following linear form:

$$\log(q_e) = \log(K_F) + (1/n)\log(C_e) \quad (11)$$

where K_F ($\text{mg g}^{-1}(\text{L mg}^{-1})^{1/n}$) and $1/n$ represent the Freundlich capacity factor and the Freundlich intensity parameter, respectively (Weber, 1972).

Results and discussion

Elemental composition

The elemental EDX analyses of the zeolite samples are listed in Table 2. Generally, the samples are mostly made up of Si, Al and O. Commonly found elements include Mg, Ca and Fe. The amount of Na in the base-modified zeolites (NaOHZeo0 and NaOHZeo400) is significantly greater than in raw zeolites (RawZeo0 and RawZeo400) because of ion exchange. The metallic components seem to be unaffected, as they remain in the material even after NaOH modification. The exposure to γ -radiation does not affect significantly the atomic composition of the samples (Table 1).

Structure and crystal order

Figure 1a,b shows the XRD traces of the raw and γ -irradiated PNZs with a 400 kGy absorbed dose. Clinoptilolite-type (Smyth *et al.*, 1990) and mordenite-type (Simoncic & Armbruster, 2004) zeolites and Ca-montmorillonite (Viani *et al.*, 2002) are the main components of the PNZs. Minor quartz (Levien *et al.*, 1980) is also present. These results are consistent with the

Table 2. Elemental composition of the zeolite samples according to EDX spectroscopy.

Sample	Si/Al ratio	Si (%)	Al (%)	O (%)	Na (%)	Mg (%)	Ca (%)	Fe (%)
RawZeo0	3.86	22.54	5.84	60.11	bdl	1.64	1.87	4.25
RawZeo400	4.27	16.95	3.97	53.37	bdl	1.16	1.40	2.58
NaOHZeo0	3.94	23.84	6.05	53.89	3.55	2.36	1.35	4.54
NaOHZeo400	4.34	27.33	6.30	53.48	4.24	2.06	1.84	4.77

bdl = below detection limit.

reported composition of the PNZ based on previous works (Cagomoc & Vasquez, 2017; Gili *et al.*, 2019a, 2019b).

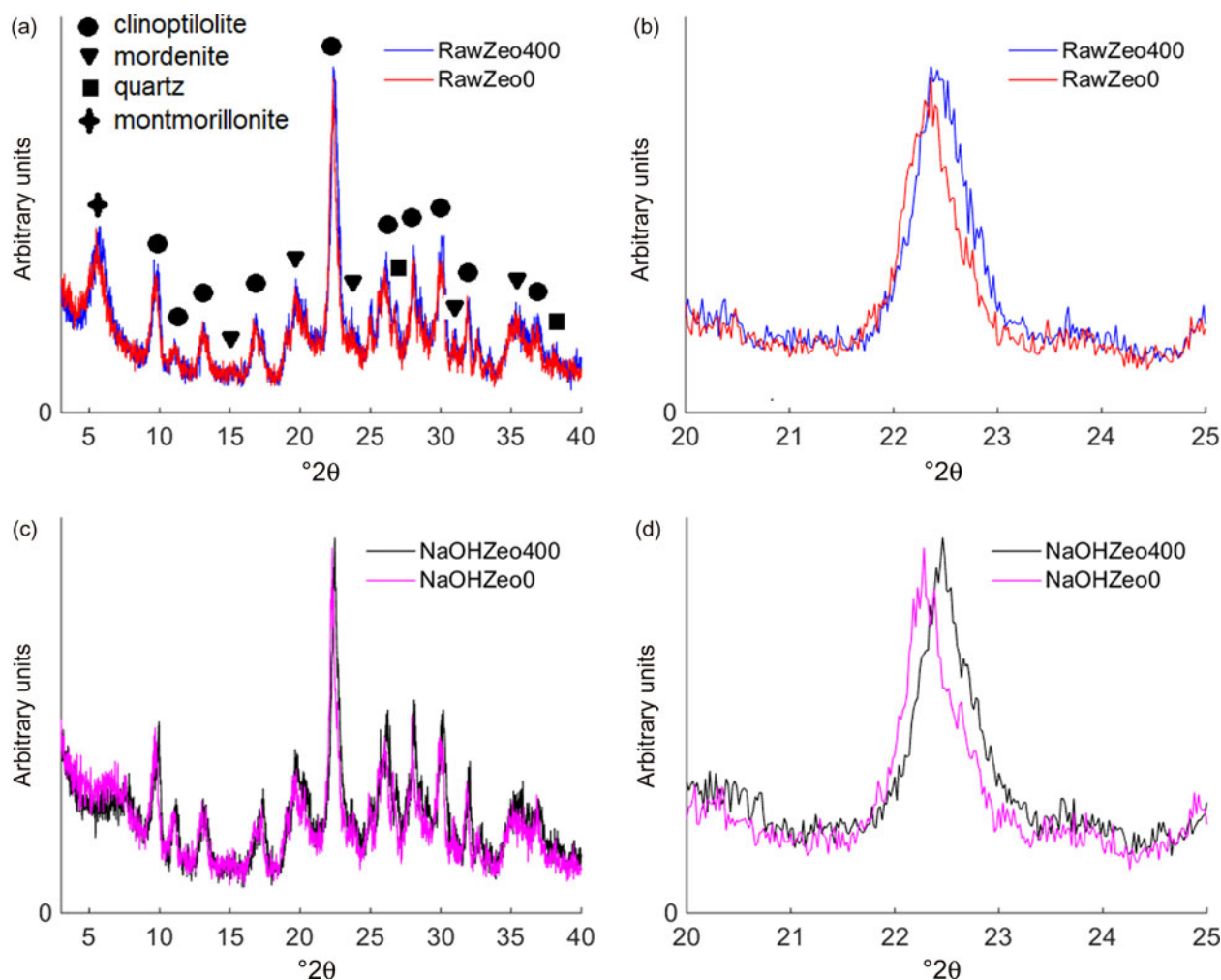
The effects of γ -radiation on the XRD traces of the raw zeolite can be deduced from Fig. 1b. A notable shift in all peaks to lower angles was observed for the irradiated sample and is most apparent in the most intense peak at $2\theta = \sim 22.42^\circ$. A difference of 0.10° in Bragg angle was recorded, suggesting a shrinking of the framework of component zeolites. A similar decrease in the d -spacings observed in zeolite 4A, especially for low 2θ values, suggests the tendency of the framework to contract upon γ -irradiation and was attributed to the fractional loss of water (Daniels & Puri, 1986). Furthermore, there was a slight increase in the intensities of the peaks of the irradiated sample, indicating that irradiation

might have improved the crystal order of the natural zeolite to some extent (Daniels & Puri, 1986).

The changes in the XRD traces of NaOH-modified zeolites after γ -irradiation are shown in Fig. 1c,d. Irradiation by 400 kGy shifted the peaks to lower angles and the peaks became narrower (Fig. 1d). This means that in addition to the contraction of the zeolite framework due to the removal of water, the material became more ordered compared to the non-irradiated NaOH-modified PNZ. This is in accord with a previous study (Ermatov *et al.*, 1980) wherein ordering of the crystal lattice structure of NaA zeolite was detected at small doses (0.5–5.0 Mrad) of γ - and N-radiation. The ordering of the crystal structure was caused by annihilation of initial defects, which are called ‘biographic defects’.

Adsorption kinetics

Figure 2 shows the kinetics of Cu^{2+} adsorption by the non-irradiated and γ -irradiated NaOH-modified zeolites. The adsorption rate was maximal during the first 10 min (2.15 and 2.37 mg $\text{Cu}^{2+} \text{g}^{-1} \text{min}^{-1}$ for the NaOH-modified samples with 0 and 400 kGy absorbed doses, respectively). The adsorption rate gradually decreased with time until the sorbent was saturated at ~ 150 min, attaining an equilibrium adsorption uptake of

**Fig. 1.** XRD traces of the (a) non-irradiated and (b) γ -irradiated raw zeolite (400 kGy) and (c) non-irradiated and (d) γ -irradiated NaOH-modified zeolite (400 kGy).

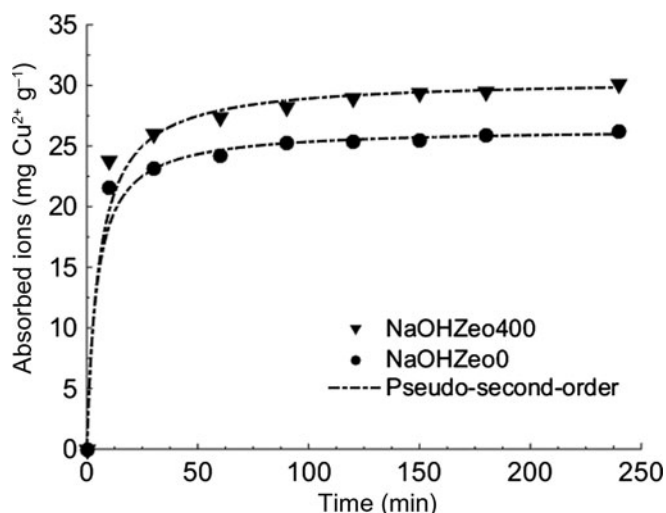


Fig. 2. Adsorption kinetics of Cu^{2+} for the non-irradiated and γ -irradiated NaOH-modified zeolites with 400 kGy absorbed dose through time.

~ 26.15 and $30 \text{ mg Cu}^{2+} \text{ g}^{-1}$ for the non-irradiated and γ -irradiated NaOH-modified zeolites, respectively.

By replottting the adsorption uptake through time using the linearized forms of the kinetic models, the values of the various kinetic model parameters were computed using the best-fit line of each kinetic model (Fig. 3). Table 3 lists the experimental and the computed adsorption uptakes of the non-irradiated and

γ -irradiated NaOH-modified zeolites for each kinetic model considered. The calculated parameters and the coefficient of determination, R^2 , are also included in Table 3. The pseudo-second-order model gives values of the computed equilibrium sorption uptake nearest to the experimental data, which are 26.46 and $30.53 \text{ mg Cu}^{2+} \text{ g}^{-1}$ for the non-irradiated and γ -irradiated (400 kGy) NaOH-modified zeolites, respectively. In addition, the R^2 for this model is closest to 1 among the three models. Thus, the NaOH-modified zeolite sorption behaviour is governed by pseudo-second-order chemisorption kinetics. The resulting kinetic curve is shown in Fig. 2. Several studies report similar behaviour of natural zeolites that follows the pseudo-second-order kinetic model as the best sorption mechanism (Wang *et al.*, 2007; Taffarel & Rubio, 2009; Gili *et al.*, 2019a).

Adsorption isotherms

Figure 4 shows the sorption uptakes of the non-irradiated and γ -irradiated (400 kGy) NaOH-modified zeolites at various equilibrium concentrations of the supernatant solution. The experimental maximum adsorption capacities were $32.87 \text{ mg Cu}^{2+} \text{ g}^{-1}$ for the non-irradiated NaOH-modified zeolite and $43.26 \text{ mg Cu}^{2+} \text{ g}^{-1}$ for the sample irradiated at 400 kGy. The γ -irradiation seems beneficial, as it enhances the maximum adsorption capacity of NaOH-modified zeolites by $\sim 31.6\%$. This confirms the reported enhancement of the Cu^{2+} sorption capacity of γ -irradiated NaOH-modified zeolites in our previous study (Gili *et al.*, 2019b).

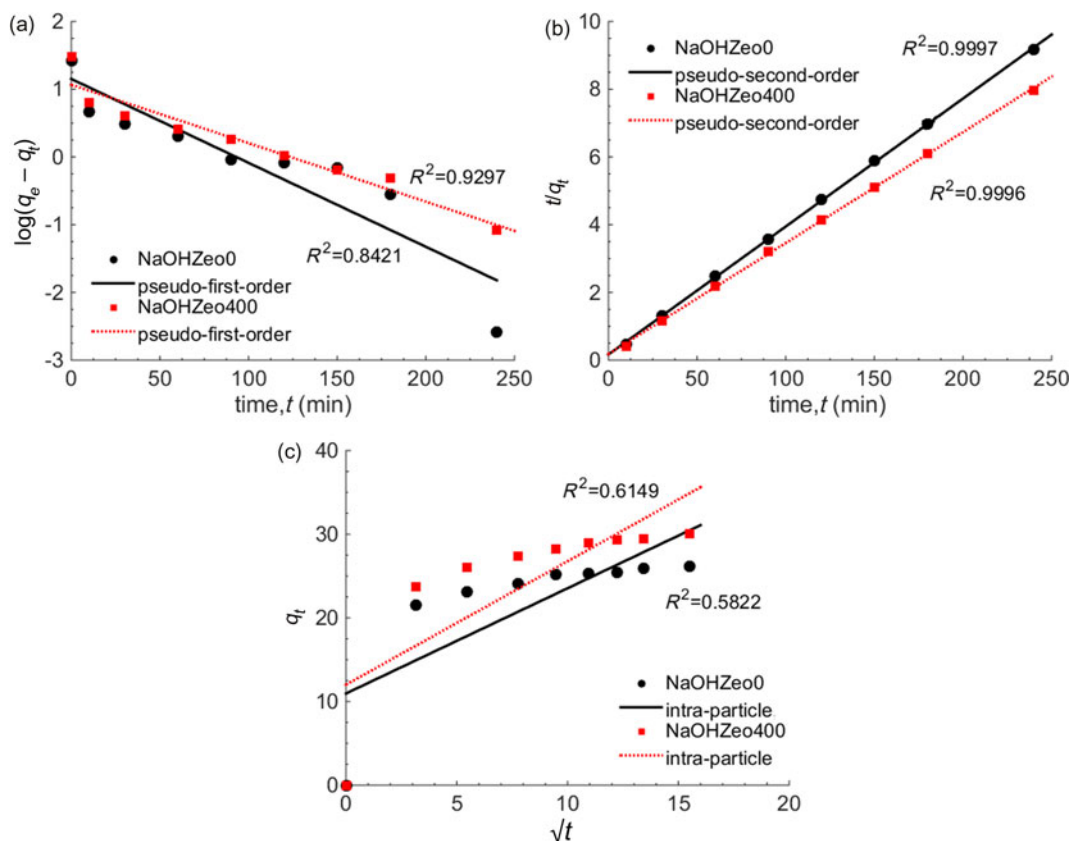
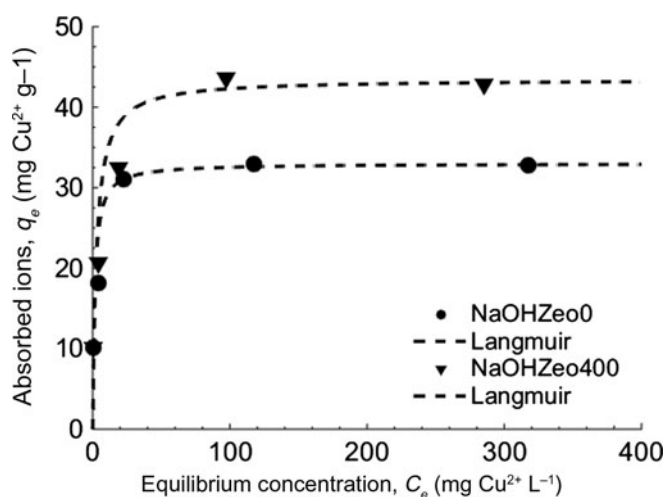


Fig. 3. Best-fit lines of the linearized adsorption kinetic data according to (a) Lagergren's pseudo-first-order kinetic model, (b) the pseudo-second-order kinetic model and (c) the intra-particle kinetic model.

Table 3. Experimental (exp.) and theoretical (theo.) adsorption uptakes of non-irradiated and γ -irradiated NaOH-modified zeolites and corresponding kinetic model coefficients.

Sample	Pseudo-first-order model				Pseudo-second-order model			Intra-particle diffusion model	
	q_e (exp.) (mg Cu ²⁺ g ⁻¹)	K_1 (min ⁻¹)	q_e (theo.) (mg Cu ²⁺ g ⁻¹)	R^2	K_2 (g mg ⁻¹ min ⁻¹)	q_e (theo.) (mg Cu ²⁺ g ⁻¹)	R^2	K_0 (mg Cu ²⁺ g ⁻¹ min ^{0.5})	R^2
NaOHZeo400	30.00	0.0199 ± 0.0009	11.64 ± 1.52	0.9297	0.0059 ± 0.0003	30.53 ± 1.60	0.9996	1.48 ± 0.07	0.6149
NaOHZeo0	26.15	0.0285 ± 0.0014	14.19 ± 2.01	0.8421	0.0086 ± 0.0004	26.46 ± 1.39	0.9997	1.26 ± 0.06	0.5822

**Fig. 4.** Adsorption isotherms of non-irradiated and γ -irradiated NaOH-modified zeolites following the Langmuir model.

Keheyani *et al.* (2005) reported that γ -irradiation at 200 and 700 kGy slightly increased the sorption capacity of raw Armenian clinoptilolite-rich natural zeolites for tritiated water (HTO). However, no direct dependence between the sorption and irradiation dose was observed. Moraetis *et al.* (2004) observed a slight increase in the Cs⁺ uptake in single-metal solution with the highest loadings of Cs for γ -irradiated (700 kGy) clinoptilolite. However, a decrease in the uptake was noted for Sr²⁺, with the equilibrium being attained at significantly longer reaction times compared to Cs⁺. In another study by Moraetis *et al.* (2008), the CEC of γ -irradiated (700 kGy) clinoptilolite showed no significant changes compared to the non-irradiated

clinoptilolite. Although the selectivity/affinity for Sr²⁺ had increased, for Ca²⁺ it was unchanged and for Mg²⁺ it was decreased. The change in selectivity was controlled by the ionic radius of the divalent cations, Sr²⁺ (1.13 Å) > Ca²⁺ (0.99 Å) > Mg²⁺ (0.65 Å), decreasing with the decrease of ionic radius of the incoming cation. The selectivities of the same sample for the monovalent cations K⁺ and Cs⁺ both increased considerably (Moraetis *et al.*, 2007). It is worth mentioning that γ -radiation (200–700 kGy) reduces the ion-exchange capacity of acid (HCl)-treated zeolites for Cu²⁺ (Gili *et al.*, 2019b) and Sr²⁺ and Cs⁺ (Akhilbedashvili *et al.*, 2010).

Comparing the Langmuir and Freundlich models, the former provides coefficients of determination R^2 closer to 1 (Fig. 5). Furthermore, it provides theoretical maximum sorption capacities that are closer to the experimental values (33.00 and 43.22 mg Cu²⁺ g⁻¹ for the non-irradiated and γ -irradiated samples, respectively) than those of the Freundlich model (Table 4). The separation factor R_L is equal to 0.0036 for both samples, which is within the range of 0–1, implying a favourable type of adsorption. In a similar study, the thermodynamic adsorption isotherm of mordenite for Pd²⁺, Cd²⁺, Cu²⁺ and Ni²⁺ was best described by the Langmuir model (Nakamoto *et al.*, 2017). The same model also resulted in a better fit for the adsorption of Ni²⁺ by natural Na-mordenite at 30°C and 40°C (Wang *et al.*, 2007). The Langmuir model also better fit the thermodynamic isotherm for the adsorption of Zn²⁺ ions by raw PNZ (Gili *et al.*, 2019a).

Absorption of γ -photons from the ⁶⁰Co would result primarily in Compton scattering (Daniels & Puri, 1986) and the formation of irradiation products due to water radiolysis (Spinks & Woods, 1990). Energetic scattered electrons as a result of Compton scattering are envisaged to displace mobile cations (Daniels & Puri, 1986) and the framework atoms from their initial positions, to some extent. This means that Na⁺ and other cations originally

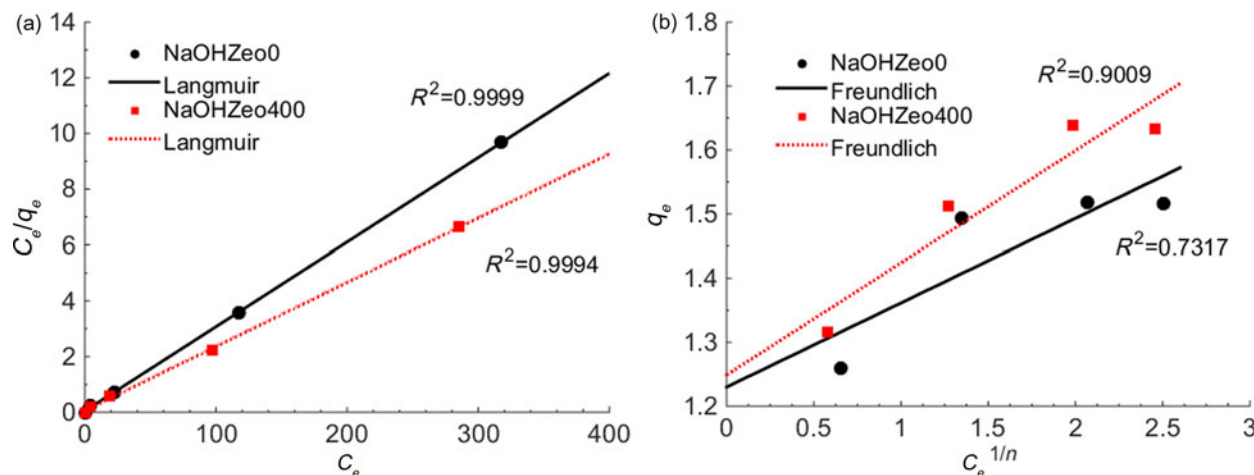
**Fig. 5.** Best-fit lines of the linearized adsorption thermodynamic data according to (a) the Langmuir thermodynamic model and (b) the Freundlich thermodynamic model.

Table 4. Experimental (exp.) and theoretical (theo.) maximum adsorption capacities and corresponding coefficients of the Langmuir and Freundlich thermodynamic models.

Sample	Langmuir model				Freundlich model			
	q_{max} (exp.) (mg Cu ²⁺ g ⁻¹)	K (L mg ⁻¹ Cu ²⁺)	q_{max} (theo.) (mg Cu ²⁺ g ⁻¹)	R_L	R^2	K_F (mg Cu ²⁺ g ⁻¹)	n	R^2
NaOHZeo400	43.26	0.36 ± 0.04	43.46 ± 2.28	0.0068 ± 0.0006	0.9995	17.74 ± 2.74	5.71 ± 0.30	0.9009
NaOHZeo0	32.87	0.70 ± 0.04	33.00 ± 1.73	0.0036 ± 0.0003	0.9999	16.98 ± 2.58	7.60 ± 0.40	0.7317

attached to the active sites of zeolites might be neutralized by the incoming electrons, which might detach them from the zeolite surface, leaving the surface negatively charged. This translates to an increase in the adsorption capacity. Electrons of sufficiently high energy affect the Si and Al atoms in the zeolite framework. Yeritsyan *et al.* (2013) reported that electron (8 MeV) irradiation of natural zeolites resulted in a considerable enhancement of the capacity to sorb radioactive (¹³⁷Cs, ¹³⁴Cs, ⁶⁰Co) cations. This improvement in sorption capacity might be due to the formation of 'A-centres'. The A-centres are charged defects formed upon the change of oxygen state from an interstitial to a lattice site. Irradiation creates vacancies of Si and Al, where mobile interstitial oxygen might move in and form oxygen (hole) vacancy complexes. These A-centres act as acceptors and may capture positively charged radionuclides.

Another influence of γ -radiation is the radiolysis of water, which forms H₂O⁺, H₃O⁺, H₂O₂, electrons (e_{aq}⁻) and hydroxyl (HO[•]) and hydrogen (H[•]) radicals that readily offer electrons due to their excited state from irradiation (Spinks & Woods, 1990; Caër, 2011). The long-lived electrons within the zeolite structure may be trapped in extra-framework cation clusters or in water molecules (Liu & Thomas, 1995; Zhang *et al.*, 1998). Again, these electrons render the zeolite negatively charged, which might attract more cations such as Na⁺ in order to be counterbalanced. This might decrease ion exchange, as there is less Na⁺ available for ion exchange. However, it leaves the active sites available for other cations to fill, such as Cu²⁺, thereby increasing the adsorption capacity of the zeolite. These phenomena are most likely to occur on the irradiated NaOH-modified zeolites because they contain a substantial amount of exchangeable Na⁺, which explains why the improvement in the sorption uptake is very apparent.

The removal of various molecular species originally present in the zeolite cages, such as water, might have provided additional sites for the capture of cations (Yeritsyan *et al.*, 2013). Lower water content in the channels of zeolites increases free space, which facilitates diffusion of incoming cations in the exchangeable sites (Moraetis *et al.*, 2007). This means more room for incoming Cu²⁺ ions (Keheyany *et al.*, 2005), partly related to the slight increase in the HTO sorption capacity of Armenian zeolite due to the dehydration/dehydroxylation of the zeolite surface.

Furthermore, the improved crystal order might also contribute to the improvement of the sorption capacity, as there are fewer amorphous impurities and there is better crystal order of the zeolites, contributing to ion exchange.

Conclusions

γ -irradiation has several effects on the structure and Cu²⁺ sorption of NaOH-modified PNZs. There are no significant changes in the elemental composition of the zeolite, even after receiving

a large dose of γ -radiation. Irradiation causes shrinking of the zeolite framework due to the removal of various molecular species originally present in the zeolite cages, such as water. In addition, γ -radiation enhances the crystal order of the material. γ -irradiation at a dose of 400 kGy improved the adsorption of NaOH-treated zeolites.

Adsorption tests show that both γ -irradiated and non-irradiated NaOH-modified PNZs follow a pseudo-second-order kinetic model. Both samples have adsorption isotherms that are best described by the Langmuir thermodynamic model of the favourable type. The γ -irradiated zeolites have higher maximum adsorption capacities than the non-irradiated samples, which suggests that γ -irradiation at a dose of 400 kGy might enhance the maximum adsorption capacity of the NaOH-modified zeolites. There are three reasons as to why this improvement may have occurred. First, it may be due to the energetic electrons produced from Compton scattering and the formation of long-lived electrons due to water radiolysis. These electrons might neutralize mobile cations such as Na⁺, which results in the presence of active sites capable of attracting Cu²⁺ ions. Second, the removal of water molecules upon irradiation may increase free space, which facilitates the diffusion of incoming cations in the exchangeable sites. Third, it may be due to the improvement of the crystal order of the zeolites, which implies more efficient ion exchange. The results indicate that γ -radiation might be beneficial for capturing heavy metals, specifically at a dose of 400 kGy. However, additional studies would be necessary to determine the effects of γ -irradiation at a higher or lower absorbed dose. More comprehensive experiments on the variation of the surface charge and the production of charged defects with respect to the absorbed dose are necessary. It is also recommended that the study be extended to include γ -emitting cations such as K⁺, Cs⁺ and Sr²⁺ for possible applications in nuclear waste storage.

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