

Regenerability of fly-ash derived zeolite NaP1: Evaluation via copper recovery

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Abstract

Effective regeneration of adsorbents is considered as one of the essential qualities for commercial use. However, most of the studies have only reported the adsorption properties and overlooked the reuse of adsorbents. In this study, we determined the regenerability and reusability of fly-ash derived zeolite (FADZ) NaP1. These adsorbents have become popular to remove pollutants from water, including toxic metals, since they are less expensive, compared to their counterparts, and can be synthesized from a waste product. We evaluated the efficiency of copper (Cu^{2+}) ions recovery from water using multiple regeneration solutions due to medium adsorption selectivity towards Cu^{2+} . We determined the time required for the regeneration using acid, base, and salt solutions. The suitable pH and solution while maintaining the structure of the zeolite were studied. Up to 90% recovery was achieved via three successive regenerations, each taking 3 h using 3 M KCl and 3 M NaCl solutions. X-ray diffraction (XRD) and fluorescence showed changes in structure after regeneration at $\text{pH} < 5$ and contact time < 6 h. The desorption kinetics using KCl solutions can be described by pseudo-second order model. Freundlich model represents the desorption of Cu^{2+} ions better than the Langmuir model due to regression coefficient (R^2) values in the range of 0.998–1.0. Results suggest a strong ion exchange mechanism as the main driving force for desorption. The type of anions (such as Cl^- and OH^-) in solution influences regeneration in addition to the exchanging cation.

KEYWORDS

adsorption, desorption, fly-ash derived zeolites, NaP1, regeneration

JEL CLASSIFICATION

Chemical engineering

1 | INTRODUCTION

Many studies showed suitable adsorbents for toxic metal removal with little focus on the management of used adsorbents.^{1,2} Careless disposal of spent adsorbents in environment is considered as a secondary source of pollution, which

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consequently negate the aim of metal removal.^{3,4} Thus, effective toxic metal recovery and adsorbent reuse are considered as essential qualities of a suitable adsorbent. Ali et al.⁵ described these qualities as controlling factors for the cost of water treatment technology. Lata et al.³ identified various inorganic adsorbents such as activated carbon, activated alumina, silica gel, hematite, and hydrous zirconium oxide, for toxic metal removal. These adsorbents were, however, deemed unsuitable for developing countries due to high cost, low removal efficiency, and loss during regeneration.

Previous studies listed requirements of a suitable adsorbent.⁶ These include cost effective, reusable, efficient and rapid uptake/recovery, selective and cheap regeneration.⁷ Although, there is a strong relationship between economical adsorbents and reusability, an adsorbent can still be termed economical when a suitable solution is used for regeneration.^{6,8} In addition, Das⁹ mentioned that a successful regeneration process requires the proper selection of regeneration solution, which depends strongly on the adsorbent and mechanism of sorption. Therefore, the economic viability of an adsorbent, of which regeneration plays a significant role, is not solely dependent on the adsorbent properties but also the recovery solution. Thus, there is a need to determine an efficient, cost effective, and eco-friendly solution, which maintains adsorbent structure through the regeneration.⁹ Although studies have used various adsorbents to remove toxic metals from water,^{10–13} regenerability has only been considered by the limited number of publications.^{12–17}

Fly-ash derived zeolites have been attracted great attention due to relatively less expensive synthesis and recycling waste from coal power plants, reinforcing sustainability.^{18,19} To date, zeolite X,^{20,21} zeolite A,^{22,23} K-chabazite,²⁴ sodalite²⁵ and NaP1^{25,26} have been synthesized from fly-ash. Amongst them, zeolite NaP1 is a less expensive alternative due to its high yield, low cost, and shorter synthesis. In our recent study, we studied the toxic metal removal mechanism and determined the ion selectivity of NaP1.²⁷ Our recent results showed that the uptake capacities for Zn (34 mg/g) and Pb (192 mg/g) were higher than other FADZ NaP1 and adsorbents such as clinoptilolite and activated carbon. The selectivity followed this order: $Pb^{2+} > Cu^{2+} > Zn^{2+}$.

Although many studies have investigated performance of NaP1 for toxic metal removal such as copper, zinc, lead and nickel,^{28–32} reports concerning the regeneration of zeolite NaP1 in literature are scarce. Bień et al.³² used chitosan modified NaP1 for the simultaneous removal of acid dye and Cu^{2+} . They reported that 1 M HCl was the suitable regeneration solution for the desorption rather than ethanol, methanol, acetic acid, NaOH and NaCl. Deng and Ge³³ demonstrated 99% Cu^{2+} regeneration from NaP1 using 0.1 M NaOH solution. Prasad et al.³⁴ used 0.1 M NaCl solution to recover 75% and 88% of $CaCO_3$ and calcium, respectively, from NaP1 in 1 h. These studies utilized base and salt solutions to determine recovery efficiency from NaP1 with different properties. Therefore, a systematic study to determine a regeneration solution and conditions suitable for NaP1 while maintaining its structure is essential.

In this study, the regenerability and reusability of zeolite NaP1 was explored for toxic metal removal from water. The Cu^{2+} ions were used due to the medium adsorption selectivity, which was previously reported for NaP1.²⁷ The regeneration solution, pH and solution concentration were studied to determine the Cu^{2+} removal efficiency and to demonstrate an understanding of the regeneration process through the characterization of samples. The regeneration agents were selected due to the ease in accessibility on industrial scale and their history of being efficient agents from previous research. pH of the regeneration solutions was changed to determine the relation between recovery efficiency vs zeolite stability. Desorption kinetics and isotherms were also studied. Techniques such as XRD, X-ray fluorescence spectroscopy (XRF) and Fourier Transform Infrared spectroscopy (FTIR) were used to characterize the samples before and after adsorption and regeneration tests to determine the structural changes in zeolite and thus suitability of the regeneration conditions.

2 | EXPERIMENTAL

2.1 | Materials

Zeolite NaP1 was provided by Lublin University of Technology, Poland, synthesized from class F fly-ash, obtained from a Polish power plant. In a typical synthesis, 10 g of fly was mixed with 200 ml of 1 M NaOH and 100 ml of 3 M NaCl for 24 h at 105°C. After reactions, the products were washed three times with distilled water and dried.³⁵ The properties of the zeolite were shown previously.²⁷

Copper nitrate ($\text{Cu}[\text{NO}_3]_2 \cdot 3\text{H}_2\text{O}$, 98%), sodium hydroxide pellets (NaOH , 99.9%), nitric acid (HNO_3 , 68%), sodium chloride (NaCl , 99%), potassium chloride (KCl , 99%) hydrochloric acid (HCl , 37%) and ammonium acetate (NH_4COOH , 98%) were purchased from Fisher Scientific.

2.2 | Characterization

Bruker D8 Advance XRD was used to characterize the powder samples before and after adsorption and desorption of Cu^{2+} ions. Samples were oven dried at 50°C for 6 h after regeneration before analysis. Samples were measured with a 0.6 slit for 2 h at $25 \pm 2^\circ\text{C}$. Samples were scanned between 5 and $65^\circ 2\theta$ with increments of 0.05° in 2 s. $\text{Cu K}\alpha$ radiation was used at 40 kV and 35 mA.

Panalytical Epsilon 3XL XRF was used to determine Si/Al ratios of the zeolite samples. Powder samples (~ 5 g) were ground, placed in a plastic cup (approx. 4.9 cm in depth) and covered with a plastic film at the bottom (source of radiation).

FTIR spectroscopy measurements of NaP1 samples before and after adsorption were conducted using a Bruker IFS 66/S between $4000\text{--}4050\text{ cm}^{-1}$ via diffuse reflectance mode.

2.3 | Adsorption and regeneration experiments

Adsorption and regeneration experiments were conducted at two stages. During the adsorption, copper concentrations were set to 30 mg/L (0.5 g/L NaP1) and 50 mg/L (5 g/L) to ensure Cu^{2+} to fully adsorbed, informed from our previous results.²⁷

For the initial screen experiments at the first stage, 0.5 g/L NaP1 was loaded with 30 mg/L Cu^{2+} ions by mixing the water samples on a magnetic stirrer up to 3 h at $22 \pm 2^\circ\text{C}$. The pH (Jenway 570 with temperature correction function) of the solutions was maintained at a range of 3–4 using 68% HNO_3 and 2% wt/v NaOH solutions to prevent precipitation of Cu^{2+} . The regeneration experiments were performed at $20 \pm 2^\circ\text{C}$ up to 48 h by using 100 ml HCl , NaOH and NaCl solutions with 0.5 g/L NaP1 (concentrations = 1 M, 3 M and 5 M). The pH of the regeneration solutions was set at 1, 3 and 5 by using 5 M HCl and 5 M NaOH , which were diluted, where needed. Experiments were repeated three times and percentage error was reported.

During the second stage after pH determination, 5 g/L NaP1 was loaded with 50 mg/L Cu^{2+} ions by mixing the water samples on a magnetic stirrer for 3 h at $22 \pm 2^\circ\text{C}$. The pH of the solutions was maintained at 5 by using 68% HNO_3 and 1 M NaOH solutions. Regeneration experiments were performed using 100 ml of KCl , NaCl and HCl solutions (3 and 10^{-5} M) at pH 5, $20 \pm 2^\circ\text{C}$ for 24 h with 5 g/L NaP1. The pH of the regeneration solutions was set at 1, 3 and 5 by using 5 M HCl and 5 M NaOH , which were diluted, where needed. Experiments were repeated three times and percentage error was reported. Cycle tests ($\times 3$ adsorption and regeneration) were also conducted using 3 M KCl solution at pH 5 to ensure structural stability of the zeolite after multiple use. During the adsorption step, 5 g/L NaP1 was loaded with 50 mg/L Cu^{2+} ions by mixing the water samples on a magnetic stirrer for 3 h at $22 \pm 2^\circ\text{C}$, pH 5. This was followed by a desorption step for 3 h.

For the determination of the desorption isotherm, NaP1 was loaded with 50, 80, 120 and 150 mg/L Cu^{2+} using 5 g/L at pH = 5 and $25 \pm 2^\circ\text{C}$ for 24 h. The desorption experiments were then conducted using 3 M KCl for 3 h with the adsorption pH and temperature. Desorption experiments were repeated three times to observe errors associated.

The desorption kinetics of Cu^{2+} ions was determined by employing the pseudo-first (Equation 1) and -second order (Equation 2) kinetic models:

$$\ln(Q_e - Q_t) = \ln(Q_e) - k_1 \times t \quad (1)$$

$$\frac{t}{Q_t} = \frac{1}{k_2 \times Q_e^2} + \frac{t}{Q_e} \quad (2)$$

Q_t (mg/g) and Q_e (mg/g) are the desorbed amount of metal ions at time t (min) and at equilibrium, respectively. k_1 (1/min) and k_2 ($\text{g mg}^{-1}/\text{min}$) are the pseudo first and second order rate constants, respectively. t (min) represents the desorption time.

Freundlich (Equation 3) and Langmuir (Equation 4) models were employed to determine the desorption mechanism and the maximum desorption capacity at equilibrium:

$$Q_e = K_F \cdot C_e^{\frac{1}{n}} \quad (3)$$

Q_e is the amount of solute retained per unit mass of adsorbent (mg/g), K_F is the Freundlich isotherm constant, indicating the desorption capacity of the adsorbent. C_e represents the Cu^{2+} concentration desorbed to the solution (mg/L) at equilibrium and $1/n$ indicates the desorption intensity between the NaP1 and Cu^{2+} ions.

$$\frac{C_e}{Q_e} = \left(\frac{1}{bQ_m} \right) + \frac{C_e}{Q_m} \quad (4)$$

b (L/mg) is Langmuir constant. C_e represents the Cu^{2+} concentration desorbed to the solution (mg/L) while Q_m shows the maximum desorption capacity (mg/g) of the NaP1 at equilibrium, estimated by the linear Langmuir model.

Experiments were also performed to determine the suitable pH for adsorption and regeneration processes. Hence, 0.5 g NaP1 was mixed in 100 ml distilled water at pH values of 3.5, 5 and 10 at $20 \pm 2^\circ\text{C}$ for 24 h. The pH of the solutions was set at 1, 3, and 5 by using 5 M HCl and 5 M NaOH, which were diluted, where needed. Experiments were repeated three times and percentage error was reported.

A 12 ml of samples was taken from the solutions at predetermined times for analyses using an iCAP QC Inductively Coupled Plasma (ICP)–Mass Spectrometry (MS), incorporating high performance liquid chromatography (HPLC, Dionex ICS3000) and an auto-sampler. The adsorbent was separated from solutions via centrifugation (Hettich, Rotofix 32 A) at 4000 rpm for 8 min. The supernatant was decanted and passed through a Minisart® (0.2 μm , hydrophilic) syringe filter. A 10 ml aliquot of the filtered solution was then pipetted in a 15 ml polypropylene conical tube and the sample was acidified with 5 ml of 30% (v/v) nitric acid and refrigerated to prevent metal precipitation and microbial degradation. Calibration standards were prepared by using Cu^{2+} solutions. For quality control, ultrapure water sample (18.2 M Ω cm resistivity) was included in every batch of analysis.

3 | RESULTS AND DISCUSSIONS

Before desorption experiments, concentrations of Cu^{2+} ions in the solutions were measured using ICP-MS to determine adsorbed amount in the zeolite. The preloading amounts were calculated as 28.5 ± 0.5 and 46.6 ± 0.2 mg/L, which are close to the initial Cu^{2+} concentrations 30 and 50 mg/L, respectively. The XRD (Figure S1) and FTIR (Figure S2) analyses were also conducted before and after adsorption to verify the presence of Cu^{2+} ions in NaP1, which are presented in Supplementary Information (SI). The XRD patterns showed that the characteristic peaks of NaP1 were still visible, confirming that the original structure was maintained after Cu^{2+} adsorption. One of the characteristic peaks of Cu was observed at $\sim 43.5^\circ$, which verified the Cu^{2+} adsorption. The FT-IR analysis was performed on NaP1 zeolite before and after the adsorption of Cu^{2+} ions. The band located at 1638 cm^{-1} corresponds to the bending vibration of water molecules that is considered as the presence of zeolitic water. A broad band at $\sim 3400\text{ cm}^{-1}$ is associated with stretching vibrations of O—H bonds present in water molecules, which are adsorbed on the surface of the material. The bands at about 1100 cm^{-1} corresponds to asymmetric stretching vibrations occurring in the Si—O—Si(Al) bridges of the zeolitic structure. Bands present between 400 and 800 cm^{-1} (pseudolattice range) reflect vibrations of structural building units of zeolites. The peak attributed to zeolitic water is located at 1630 cm^{-1} . After Cu^{2+} adsorption, only slight changes were observed in FTIR spectra. Characteristic bands' wavelengths were similar. However, the peak intensities slightly changed after Cu^{2+} adsorption. The changes in the FTIR spectra due to Cu^{2+} adsorption is expected in the range of the pseudolattice vibrations. The three small peaks (marked with arrows) between 770 and 470 cm^{-1} can be attributed to the Cu^{2+} adsorption.³⁶

Figure 1 shows the Cu^{2+} recovery from NaP1 (preloaded with 28.5 mg/L Cu^{2+}) using HCl, NaOH and NaCl solutions. Only 1.1 mg/L Cu^{2+} was recovered using 1 M HCl at pH 3 and 5. After 1 h, there was no significant change in the desorption of Cu^{2+} from the zeolite. In contrast to HCl, when 3 M NaCl was used as regeneration solution at pH 3.5 and 5, ~ 3 mg/L Cu^{2+} was recovered from the zeolite in 25 h, which was significantly slower. These results showed that only 4% of the adsorbed Cu^{2+} from the zeolite was desorbed by using 1 M HCl and 3 M NaCl as desorption solutions.

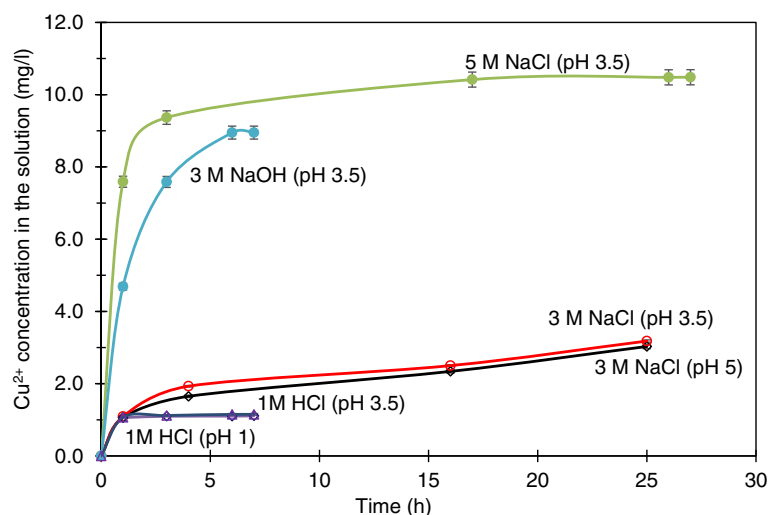


FIGURE 1 Concentration of copper in 1 M HCl (pH = 1, 3.5), 3 and 5 M NaCl (pH = 3.5, 5) and 3 M NaOH (pH = 3.5) regeneration solutions as a function of time, using 0.5 g/L NaP1 (preloaded with $\sim 28.5 \pm 0.5$ mg/L Cu^{2+} at $20 \pm 2^\circ\text{C}$). Percentage error is between 1.0 and 2.0 from triplicate experiments.

TABLE 1 Initial Na^+ quantity present in regeneration solutions

Regeneration solution	Na^+ quantity (g/L) solution
3 M NaCl	69 ± 2
5 M NaCl	115 ± 2
3 M NaOH	69 ± 2

A 36% recovery (~ 10.5 mg/L) was observed from the spent zeolite when the NaCl solution concentration was increased to 5 M at the same pH value. pH had no significant effect on the regeneration process whilst increasing the concentration of NaCl from 3 to 5 M, increased the desorbed Cu^{2+} amount threefold. This may be due to an increased concentration gradient created in the solution by the increase of initial Na^+ and compelling the exchange of copper from the zeolite structure. This suggests that a strong ion exchange mechanism was observed as the main driving force for desorption from these experiments.

However, there is a little/no difference between the NaOH and NaCl solutions in terms of quantity of Na^+ ions present in the solutions (Table 1) whilst they slightly differ in recovery efficiency (9 mg/L and ~ 11 mg/L for recovery for NaOH and NaCl, respectively). This may indicate that the type of anions (such as Cl^- and OH^-) in solution influences regeneration in addition to the exchanging cation.

Erwe et al.³⁷ treated zinc-loaded (57 mg/L) synthetic zeolite P with 20 wt% NaCl at pH 5 and obtained 95% desorption. However, Bieñ et al.³² reported that the most effective solution for the desorption process was 1 M HCl after having studied the recovery of Cu^{2+} and acid red from NaP1 before and after modification via chitosan. This may be due to the presence of mixed pollutants, the structure of the NaP1 and the influence of the modification.

FADZ NaP1 has demonstrated a preference for K^+ to Na^+ ions similar to other zeolites such as clinoptilolite, philipsite, chabazite and mordenite.³⁸ Katsou et al.³⁹ investigated the potential of regeneration agents such as HNO_3 , KCl, NaCl and NH_4Cl , for lead and zinc removal from clinoptilolite. They reported that KCl showed better regeneration efficiency compared to its counterparts. Alternatively, Chunfeng et al.⁴⁰ used 5% NaCl to achieve 93% Cu^{2+} and 86% Zn^{2+} recovery from FADZ A (preloaded with 50 mg/L Cu^{2+} and Zn^{2+}) at pH 3. Although, there is no other study, concerning regeneration of NaP1 using various types of salts, in this study the performance of K^+ over Na^+ and H^+ is in order with ion selectivity, according to electrostatic forces of attraction ($\text{Na}^+ > \text{H}^+$).⁴¹

Following the experiments, XRF and XRD scans of the regenerated zeolite samples were conducted to evaluate the stability of the NaP1. All regeneration conditions showed a reduction in Si/Al ratio (to $\sim 1.0 \pm 0.1$) via XRF, depicting a

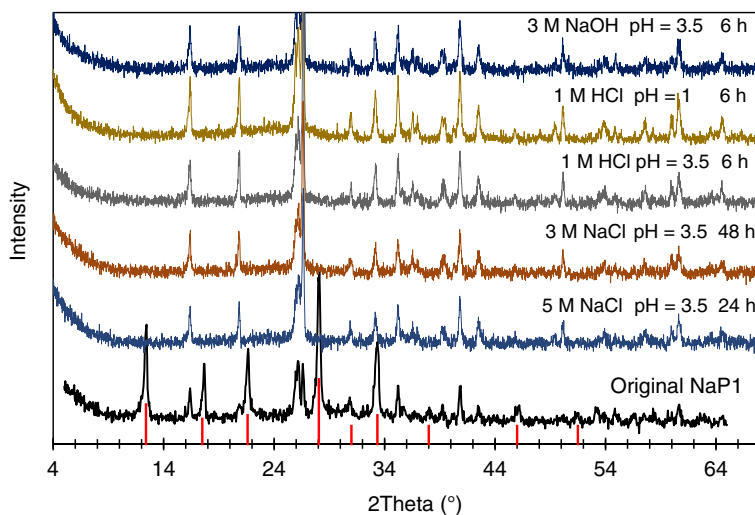


FIGURE 2 X-ray diffraction (XRD) patterns of the NaP1 samples after regeneration process, compared to the original NaP1 (Red lines shows the characteristic peaks of NaP1).

structural change in the spent zeolite, compared to the original Si/Al ratio of 1.5. This may suggest that NaP1 may have transformed to maximum aluminum P (Si/Al ratio ≥ 0.9).^{42,43}

X-ray diffraction (XRD) patterns demonstrated that the low angle characteristic peaks of NaP1 (12.5, 17.5, 21.6, and 28°), assigned for the porous structure, were almost disappeared, or reduced in intensity (Figure 2). The rest of the characteristic peaks (31, 33.3, 38, and 46°) were still observed. These results suggested structural changes after regeneration at pH 3.5 due to pore collapse and thus indicating that NaP1 was not stable at pH 3.5.⁴⁰

Chunfeng et al.⁴⁰ also reported that the possible collapse of the zeolite structure in acidic mediums may prevent the recovery of Cu^{2+} . This may explain the low Cu^{2+} recovery obtained. The results also demonstrated that the low pH range (1–3.5) and extended times (e.g., 6–48 h) are not suitable for the regeneration of NaP1. There was not any other study in literature, reporting the stability of NaP1 after regeneration at various pH values. Although Bień et al.³² studied the efficiency of multiple solutions such as alcohols, they did not investigate the structure after desorption. This may be due to the high regeneration efficiency ($\sim 95\%$) that they observed for Cu^{2+} recovery using HCl, indicating stable structure for the regeneration time.

Figure 3 shows the XRD patterns of NaP1 samples, mixed in distilled water at pH 3.5, 5, and 10.5 for 6 h, compared to the original sample. The characteristic peaks of NaP1 between 12.5–28° were not observed after the experiment at pH 3.5. This suggests pore collapse and structural changes, as previously mentioned. In contrast, the XRD patterns of NaP1 samples from the experiments performed at pH 5 and 10.5, still exhibited all the characteristic peaks of NaP1.

This confirms the structural instability of NaP1 in acidic medium and pH 5 as the most preferred option for adsorption and regeneration processes to avoid collapse of the structure at pH 3.5 and Cu^{2+} precipitation at pH 10.5.¹⁹ However, Bień et al.³² conducted regeneration experiments using 1 M HCl and reported $\sim 95\%$ removal without mentioning any structural changes in the zeolite. The Si/Al molar ratio of their sample was reported as 1.08.⁴⁴ A further test may have not required after regeneration due to the high removal percentage obtained in 2 h, indicating that the structure was maintained during regeneration.³² This suggests that the structure (e.g., Si/Al ratio, other metal oxides and impurities) of the fly-ash-derived zeolite is also one of the critical parameters while determining regeneration conditions.

Copper regeneration was also conducted using 10^{-5} M HCl, 3 M KCl and 3 M NaCl at pH 5 to determine the most suitable regeneration solution and conditions for Cu^{2+} recovery from the spent NaP1 (preloaded $\sim 46.6 \pm 0.2$ mg/L Cu^{2+}). The results indicated a quick desorption process for NaCl compared to HCl and KCl (Figure 4). However, both NaCl and KCl recovered ~ 13.1 mg/L (29%) from the solution within 3 h. On the other hand, using HCl, $\sim 14\%$ of Cu^{2+} was removed from the spent NaP1 over the same 3 h period, which is half of the Cu^{2+} ions desorbed using salt solutions.

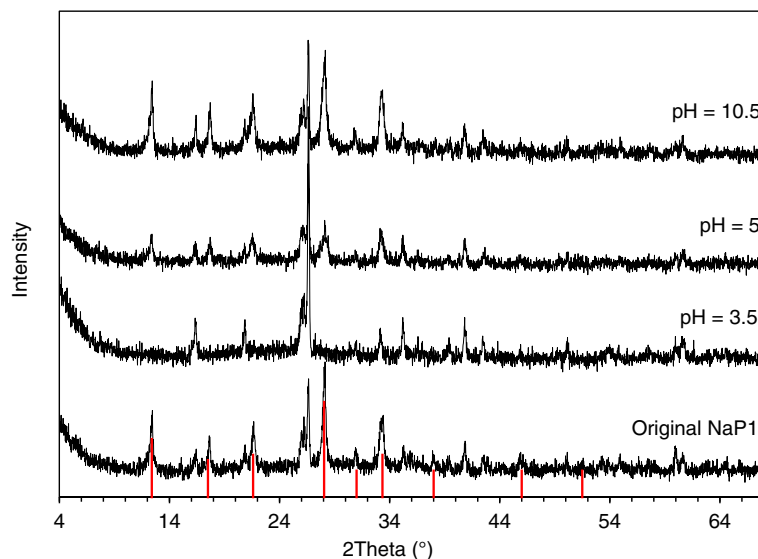


FIGURE 3 X-ray diffraction (XRD) patterns of the NaP1 samples after soaking in distilled water for 6 h at pH values of 3.5, 5, and 10.5, compared to the original sample (Red lines show the characteristic peaks of NaP1).

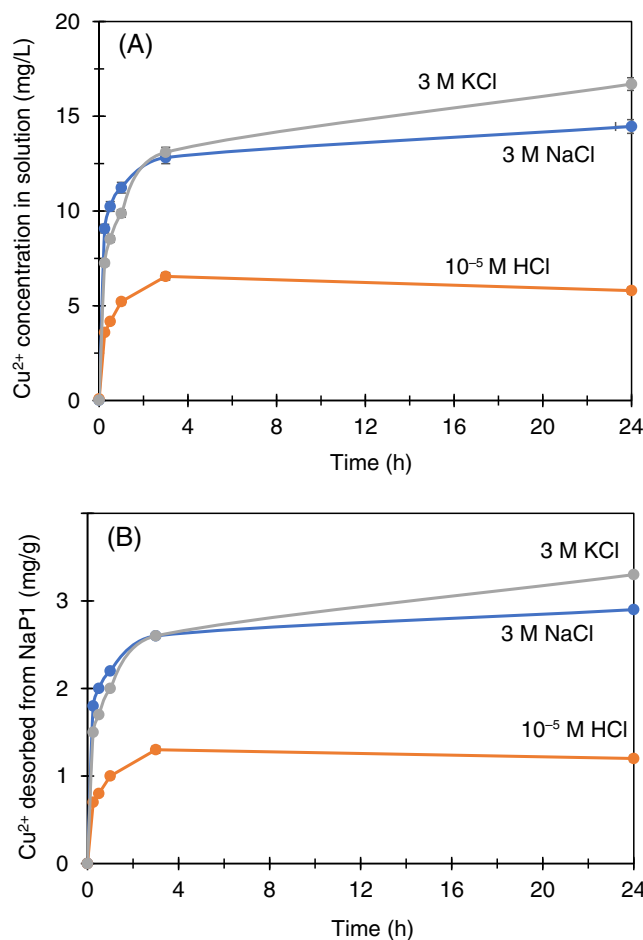


FIGURE 4 (A) Cu²⁺ concentration in regeneration solutions and (B) desorption capacity of NaP1 as a function of time at pH 5 and 20 ± 2°C. (5 g/L NaP1, containing 46.6 ± 0.2 mg/L Cu²⁺). Percentage error is between 2.5 and 3.0 from triplicate experiments.

Using 3 M KCl solution, the highest copper recovery (36%) was recorded in 24 h, compared to 31% with 3 M NaCl. Therefore, 3 h may be accepted as the effective regeneration time, according to the kinetics of the recovery for all regeneration agents (NaCl, KCl and HCl) since the remaining 5%–7% increase in Cu^{2+} recovery was observed in the final 21 h. This may suggest that the diffusion from the pores closer to the surface takes place faster whilst it becomes slower ones Cu^{2+} ions travel through the porous structure. The Cu^{2+} desorption capacity reached to 3.34 mg/g (24 h) when 3 M KCl was used as desorption solution (Figure 4B). Although similar desorption capacity was measured at 4 h by using 3 M NaCl, compared to 3 M KCl, there was not significant increase until 24 h and thus capacity only reached to 2.9 mg/g. The desorption capacity was 1.2 mg/g for 10^{-5} M HCl solution.

Desorption kinetics for NaP1 has not been determined in studies conducted to date. In this work, the kinetics of desorption was considered using the pseudo-first and -second order models for the experiments conducted using 3 M KCl and 3 M NaCl. The results for the two kinetic models and plots are presented in Table 2 and Figure S3, respectively. The regression coefficient (R^2) value of the pseudo second-order model was 0.999 for both desorption solutions. This is higher than the R^2 values obtained for the pseudo-first-order model (0.92 and 0.94 for KCl and NaCl, respectively). Therefore, the desorption kinetics are described by the pseudo-second-order kinetic model for Cu^{2+} ions desorption from NaP1 and the equilibrium capacity of the zeolite was calculated as 3.4 mg/g (3 M KCl) and 2.9 mg/g (3 M NaOH). This model suggests a heterogenous adsorbent surface. Since physisorption via weak Van der Waal's forces is suggested as the mechanism for toxic metal uptake using NaP1, desorption is expected to be fast. Therefore, the rate controlling step is possibly diffusion of Cu^{2+} ions through the porous channels of zeolite NaP1.¹⁹

For the desorption experiments using 3 M KCl, NaP1 was mixed with 50, 80, 120 and 150 mg/L Cu^{2+} for 24 h. The actual concentrations of Cu^{2+} ions adsorbed in NaP1 were measured as 46.6 ± 2 , 72.4 ± 5 , 110 ± 4 , and $135 \pm$ mg/L, respectively. Figure 5 shows that the desorption isotherm did not reach to the plateau for the concentration range that was investigated. The shape of the isotherm may suggest that the desorption suits Freundlich model rather than Langmuir model.

TABLE 2 Pseudo-first and second order kinetic model parameters for Cu^{2+} desorption from NaP1 using 3 M KCl and 3 M NaCl as desorption solutions

Parameters	Pseudo-first order		Pseudo-second order	
	NaCl	KCl	NaCl	KCl
Q_e (mg/g)	1.1	1.9	2.9	3.4
k_1 (h^{-1})	0.21	0.13	—	—
k_2 ($\text{g mg}^{-1} \text{h}^{-1}$)	—	—	1.65	0.62
R^2	0.94	0.92	0.999	0.999

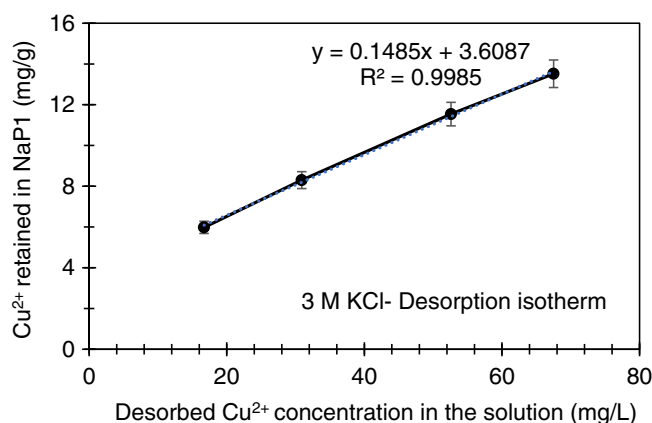


FIGURE 5 Desorption isotherms of Cu^{2+} ions from NaP1 using 3 M KCl. Error: ~ 5% from triplicate experiments.

TABLE 3 Parameters of the Langmuir and Freundlich isotherm models for desorption of Cu²⁺ ions from NaP1 using 3 M KCl as desorption solutions

Langmuir model parameters		Freundlich model parameters	
Q _m (mg/g)	23.5	1/n	0.59
b (L/g)	0.021	K _F (L/g)	1.14
R ²	0.974	R ²	0.998

TABLE 4 compares the regeneration efficiency and solutions for Cu²⁺ ions for selected adsorbents

Adsorbent	Recovery (%)	Regeneration solution	Reference
bamboo charcoal-layered double hydroxides	100	0.1 M HCl	14
Conjugate nanomaterial	98	0.2 M HCl	17
FADZ NaP1	95	1 M HCl	32
FADZ NaP1	99	0.1 M NaOH	33
Zeolite P	95	20% NaCl	37
Clinoptilolite	90	1 M KCl	39
FADZ A	93	5% NaCl	40
Activated carbon	87	6 M HCl	45
FADZ NaP1	>95	3 M KCl	This study

Therefore, data from the desorption isotherms were evaluated using Langmuir and Freundlich isotherm models (Table 3, Figure S4). The R² value for Langmuir model was 0.974. The b value and max desorption capacity were found to be ~0.021 L/g and 23.5 mg/g, respectively. Freundlich model was also investigated to describe the desorption isotherm. Desorption capacity (K_F) was obtained as 1.14 L/g while the desorption intensity (1/n) was 0.59. Freundlich isotherm model was considered as a better fit due to R² value of 0.998.

Table 4 compares the regeneration efficiency and solutions for Cu²⁺ ions for selected adsorbents. The recovery efficiency fluctuated between 87% and 100%, regarding the adsorbent and recovery solution used. HCl was the mostly used solution for Cu²⁺ recovery, whilst salt solutions (KCl, NaCl) and NaOH were also utilized. Regarding the recovery percentage published, FADZ NaP1 is a promising adsorbent for Cu²⁺ recovery.

The pH of the regeneration solutions was set at 5, meaning that the H⁺ concentration was a common condition across all regeneration solutions. This condition can be described as the exact concentration of HCl (10⁻⁵ M). Strong acids dissociate completely in water to produce hydrogen ions of the same concentration as the acid. Therefore, a 10⁻⁵ M HCl solution is equivalent to pH 5. This suggests that all the regeneration solutions may have ~10⁻⁵ M H⁺ ions at pH 5 as a common denominator. Therefore, the actual effect of each regeneration solution without the influence of H⁺ ions can be determined as ~29 and 27.5% Cu²⁺ recovery for KCl and NaCl in 3 h, respectively. However, without pH adjustments, metal recovery is almost impossible thus making H⁺ ions a necessary element and can be classified as a catalyst in the regeneration process. In industrial application of the regeneration process, 3–3.5 successive regeneration stages would be required to obtain >95% metal recovery. This is reasonable as 3 successive regeneration processes could be used to achieve a 100% Cu²⁺ recovery in less than 8 h (1 working day). In addition to this, the process will not require frequent acid dosing to maintain pH 5 and use cheap or readily accessible salts (NaCl and KCl) as regeneration agents, which are environmentally friendly. Furthermore, structure of the FADZ NaP1 was maintained after 3 successive adsorption and regeneration cycles, which is evidenced by the characteristic peaks (12.5, 17.5, 21.6, 28, 31, 33.3, 38, and 46°) of the zeolite on the XRD pattern, ensuring that the salt solutions are suitable for regeneration (Figure S5).

4 | CONCLUSIONS

Regeneration and reusability of adsorbents are important while considering the suitability of adsorbents towards the removal of pollutants, including toxic metals, from water. However, reports concerning regeneration of adsorbents, especially FADZ, are scarce. Therefore, in this study, we explored the reusability of FADZ NaP1 by recovering Cu^{2+} ions from water. Zeolite NaP1 is a less expensive FADZ due to its high yield, low cost, and shorter synthesis. Suitable pH for Cu^{2+} removal and regeneration were determined as 5. More than 90% recovery can be achieved via 3 successive regenerations, each taking 3 h using KCl and NaCl solutions. The Cu^{2+} desorption capacity reached to 3.3 mg/g and 2.9 mg/g for KCl and NaCl solutions, respectively, after one regeneration cycle (for 24 h). XRD and XRF scans showed structural changes at pH < 5 for contact time < 6 h. The type of anions (such as Cl^- and OH^-) in solution influences regeneration in addition to the exchanging cation (such as K^+ and Na^+). The desorption kinetics can be described by pseudo-second order model with 3.4 and 2.9 mg/g equilibrium capacities using 3 M KCl and 3 M NaOH solutions, respectively. The Freundlich model represents the desorption of Cu^{2+} better than the Langmuir model due to R^2 value of 0.998. Results indicate that a 100% Cu^{2+} recovery can be achieved in less than 8 h (1 working day) and thus FADZ NaP1 is a promising candidate for toxic metal recovery in commercial settings. The selection of pH and type of the regeneration solution is critical while maintaining the adsorbent structure and thus for FADZ NaP1, salt solutions may be more suitable. The concentration of the salts can be further explored to determine if these can be reduced to achieve the same recovery reported in this study.

AUTHOR CONTRIBUTIONS

Archibald Frank Ankrah: Data curation (lead); methodology (lead); validation (equal); writing – original draft (equal). **Dr Begum Tokay:** Funding acquisition (lead); methodology (supporting); resources (lead); supervision (lead); writing – original draft (equal); writing – review and editing (lead). **Colin E. Snape:** Funding acquisition (lead); methodology (supporting); resources (lead); supervision (lead); writing – original draft (supporting).

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CONFLICT OF 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.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are presented in Supplementary information.

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SUPPORTING INFORMATION

Additional supporting information can be found online in the Supporting Information section at the end of this article.

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