The zeolite modified by chitosan as an adsorbent for environmental applications

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Abstract
Fly ash (FA) and zeolite Na-A obtained on it were modified by chitosan (CS) and investigated for heavy metal ions removal from aqueous solutions. FA–CS and Na-A–CS were characterized by the X-ray fluorescence method, X-ray diffraction, scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDX), nitrogen adsorption/desorption measurements, Fourier transform infrared spectroscopy (FTIR) and atomic absorption spectroscopy (AAS) methods. Cation exchange capacity and pH\textsubscript{zpc} of used sorbents were also determined. The kinetic and sorption characteristics were made as regard Cu(II), Fe(III), Mn(II) and Zn(II) ions removal from one- and multi-ion solutions. It was found that the phase contact time (1–1440 min), pH (3–5), the amount of fly ash and zeolite (2.5–25 g/dm\textsuperscript{3}), the initial concentration of metal ions (20–240 mg/dm\textsuperscript{3}) and zeolite modification (glutaraldehyde and epichlorohydrin) affect the sorption process. The best adsorptions were obtained at 250 mg/L concentration, pH solution of about 5.0 and 120 min contact time for Cu(II), Fe(III), Mn(II) and Zn(II) ions. The results suggested that the sequence for sorption efficiency decreases in the order in the one- and multi-ion systems: Cu(II) > Fe(III) > Zn(II) > Mn(II).

Keywords
Fly ash, zeolite, chitosan, heavy metal ions, adsorption

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Introduction

Production of electricity and thermal energy in Poland is mainly based on the combustion of fossil fuels in electric power plants. The use of coal in power generation results in the formation of an enormous amount of by-product – fly ash (FA). Thus, the search for effective and inexpensive ways of managing wastes from the coal combustion is necessary. In the last few years, there has been a growing interest in zeolites obtained from FAs (Ojumu et al., 2016; Visa, 2016; Wu et al., 2008). Considerable attention has been paid to synthetic zeolites due to much better sorption properties than those of natural zeolites. The structure makes zeolites be good ion exchangers, adsorbents or catalysts (El-Naggar et al., 2008). Choosing the conditions for the process of converting FA into zeolite makes it possible to provide the material of the desired structure. As reported in Koshy and Singh (2016), few approaches for the synthesis of zeolites are as follows: conventional hydrothermal treatment, alkali fusion-assisted hydrothermal treatment, microwave-assisted hydrothermal treatment, ultrasonication-assisted hydrothermal and molten salt. However, the most important and simple one is hydrothermal reaction. All well-known types of zeolites such as zeolite Na-P1, Na-X, Na-A and ZSM-5 can be obtained from FA using this method (Wang et al., 2008).

Chitosan (CS) is another by-product. It contains amine, hydroxyl and acetamide functional groups, which are responsible for the removal of pollutants from waters and wastewaters (Wan Ngah et al., 2012; Xie et al., 2013). Therefore, taking into account the excellent properties of CS, preparation and modification of FAs or zeolites by this biodegradable polymer is a new challenging approach alternative to traditional sorbents. The aim of the study was the management of a by-product, FA to synthesize zeolite, which will be an attractive sorbent for environmental applications. The innovative element of the research is the use of FA activated in the milling process by means of magnetic core and the utilization of post-reaction solution of sodium hydroxide (NaOH) to modify obtained zeolites with biodegradable CS. This will allow to obtain new kind of products with broad potential application in the removal of pollutants from the environment. Moreover, the direction for usage of both zeolites and zeolite–CS composites can be the removal of heavy metal ions, radionuclides, phenols, dyes and construction of geochemical barriers. As a result of the research, measurable ecological and environmental benefits will be achieved.

Materials and methods

Materials

The samples of FAs used for the synthesis of zeolite came from the heat and power generating plant in Kozienice, Poland. They were denoted as FA1000-1004 and FA2000-2006. In the initial step, FAs were activated by milling in the magnet circuit. The zeolite Na-A (denoted as Na-A) was obtained by hydrothermal synthesis of the FA1004 and 2006 FAs with NaOH at atmospheric pressure described by Derkowski et al. (2006). CS as flakes with the deacetylation degree >75% come from Sigma–Aldrich. Stock solutions of Cu(II), Zn(II), Mn(II) and Fe(III) ions of the concentration 1000 mg/dm³ were prepared by dissolving proper amounts of CuCl₂·2H₂O, ZnCl₂, MnCl₂·4H₂O and FeCl₃·6H₂O in distilled water, respectively. The substances used to prepare solutions were obtained by Avantor Performance Materials Poland S.A.
Preparation of the sorbents: CS modified FAs and zeolite Na-A–CS

The first step in the sorbent preparation was to dissolve CS in 1% glycolic acid and then FA1004, FA2006 and Na-A were added to the CS solution at weight ratio equal to 1:1, 4:1 and 8:1, respectively. The solution was continuously shaken using a magnetic stirrer at 1000 r/min for 6 hours at 293 K. The obtained mixture was precipitated with 1 M NaOH solution, then filtered and washed with distilled water to neutral pH. The resulting product denoted as FA1004-CS, FA2006-CS or Na-A–CS was dried, ground and used for further modifications.

Characterization of FA, Na-A and Na-A–CS

The particle size distribution measurements of FA1004, FA2006, Na-A and Na-A–CS samples were conducted using the particle analyzer Mastersizer 2002 (Malvern). The chemical composition was determined by X-ray fluorescence method (XRF) using the PANalytical Epsilon 3\(^x\) spectrometer with an X-ray tube equipped with the Rh anode. The phase structure was determined by means of the X-ray diffraction analysis (XRD) for 2\(^{\theta}\), ranging from 5° to 65° using Philips X’pert APD diffractometer (PANalytical) with Cu lamp. The surface morphologies were examined by scanning electron microscopy (SEM) using FEI Quanta 250 FEG microscope with the energy dispersion scattering mode (EDS/EDX) system. For the determination of specific surface area, pores size and their volume ASAP 2040 Micromeritics analyser was applied. Zeolites obtained after modification with CS Na-A–CS were also characterized using the Fourier transform infrared spectroscopy (FT-IR) method with the ATR mode (Cary 630 spectrometer, Agilent Technologies). The pH value of the point of zero charge \(\text{pH}_{\text{zpc}}\) of FA1004, FA2006, Na-A and Na-A–CS was measured by the pH drift method. All steps were conducted under the controlled conditions using the analytical and measuring set (Metrohm). The cation exchange capacity (CEC) was determined on the amount of Ba(II) ions desorbed by MgCl\(_2\). Different amounts of the samples were shaken with 100 cm\(^3\) of 0.1 M BaCl\(_2\). In the desorption step, the washed and dried samples were shaken with 1 M MgCl\(_2\). The contents of exchanged Na(I), K(I), Mg(II) and Ca(II) ions were determined by the AAS method.

Sorption experiments

In the studies, one- and multi-ion solutions were used. Multi-ion solutions were obtained with the molar ratio Cu(II):Fe(III):Mn(II):Zn(II) = 1:2:4:2. The kinetic parameters for Cu(II), Fe(III), Mn(II) and Zn(II) ions sorption on the FA1004, FA2006, Na-A and Na-A–CS sorbents were measured using the static method. The studies were carried out by shaking 0.1 g of sorbent with 20 cm\(^3\) of one- or multi-ion solutions of the appropriate concentrations. The dependence of the sorbent dose was carried out for 0.05, 0.1, 0.2, 0.3, 0.4 and 0.5 g samples. After each test, the samples were filtered and the concentrations of Cu(II), Fe(III), Mn(II) and Zn(II) ions were determined by the inductively coupled plasma optical emission method (ICP-OES) using a spectrometer ICP-OES 720 (Varian).

The sorption amount of metal ions at time \(t\) \(q_t\) (mg/g) and the sorption percentage \(\%S\) (%) were calculated according to equations (1) and (2), respectively

\[
q_t = (c_0 - c_t) \times \frac{V}{m}
\]
\[ \%S = \left( \frac{c_0 - c_t}{c_0} \right) \times 100\% \]  

where \( c_0 \) is the initial concentration of metal ion in the solution (mg/dm\(^3\)); \( c_t \) is the concentration of metal ion in the solution at time \( t \) (mg/dm\(^3\)); \( V \) is the volume of the solution (dm\(^3\)); and \( m \) is the mass of the sorbent (g).

**Results and discussion**

**Sorbents characterization**

The FA was initially activated in the magnetic circuit made up of closed loop paths containing a magnetic flux. The macroscopic structure of FA1006 and FA2006 FAs is presented in Figure 1(a). As follows from the particle size analysis used, FAs are characterized by modal particle size distribution. As an example, FA1000-1004 samples are presented in Figure 1(b). In Figure 1(c), the analogous results for FA1004, 1004Na-A as well as FA2006 and 2006Na-A are presented. Both FA and Na-A are characterized by a homogeneous granulation which was confirmed by the SEM analysis. Zeolite Na-A was observed to take the form of a cube (Figure 2). The shape of the hysteresis loop obtained from the Brunauer–Emmett–Teller (BET) nitrogen adsorption/desorption method reflects the pore structure of the raw FA and obtained zeolite Na-A. The hysteresis loops of the samples 2006Na-A are type H3, reflecting the existence of the slit-shaped pores with parallel plates. However, for Na-A zeolite, it tended to generate hysteresis loops combining these two of them, for example H2 and H3 (Table 1). Their specific surfaces are equal to 12 and 11 m\(^2\)/g and CEC 6.28 and 7.34 meq/g for FA1004 and FA2006, respectively. The obtained zeolite Na-A has higher CEC than the commercial Na-X zeolite (Kim and Lee, 2009). The XRD pattern of the phase composition of Na-A zeolite indicates the presence of quartz and mullite. The higher ion exchange potential of Na-A zeolite can be explained by higher alumina content inside the crystalline structure which contributes to a larger surface negative charge for incorporating more cations. The chemical composition of FA1004 was determined by the XRF method (in wt\%) (Table 1). The studies of the composition of FA indicate clearly class F (ASTM C618) (Polish Committee of Standardization).

As follows from the FT-IR analysis, H\(_2\)O stretching vibrations occur at 3362 and 1648 cm\(^{-1}\) (Ugal et al., 2010; Wang et al., 2014). The structural vibrations of Si–O (Si) and Si–O (Al) bridges occur in the range 1200–400 cm\(^{-1}\). Taking into account the different FA:CS ratios, it was found that for FA1004 at FA:CS 1:1, 4:1 and 8:1 ratio, there is observed an intensive band originating from stretching vibrations of the –OH and –NH\(_2\) groups. For FA1004, it appears at the wave number 3544 cm\(^{-1}\), and for FA1004:CS = 1:1, FA1004:CS = 4:1 and FA1004:CS = 8:1 are shifted towards longer wavelength being 3363, 3350 and 3362 cm\(^{-1}\), respectively. For these samples, the bands at 2870, 2867 and 2868 cm\(^{-1}\) are associated with stretching vibrations of –CH group, which indicates the presence of CS. Characteristics of CS bands connected with bending vibrations of –NH\(_2\) group occur at 1649 and 1576 cm\(^{-1}\) (for FA1004:CS = 4:1 and FA1004:CS = 8:1). On the spectra of FA modified with 1:1 and 4:1 ratios, one can observe the band originating from the stretching vibrations of –C–N group at the wavelength 1375 cm\(^{-1}\). For raw FA and FA1004:CS = 8:1, this band is not observed. For FA1004:CS = 1:1 at the wavelengths 1418 and 1314 cm\(^{-1}\), the doublet originating from the stretching vibrations of –C–O group can be found. The bands
indicating the presence of FAs, that is the asymmetric stretching vibrations of the Si–O–T, where T = Al or Si) are situated in the wavelength 1085–1009 cm\(^{-1}\). For the raw FA, this band appears at the wavelength 1022 cm\(^{-1}\) but modification of these bands are shifted towards 1024, 1035 and 1038 cm\(^{-1}\). The bands appearing on all spectra in the wavelengths 797–776 cm\(^{-1}\) come from the stretching symmetric group Si–O–Si.

\(\text{pH}_{zpc}\) values for FA1004, FA2006 and Na-A were obtained by the pH-drift method. It is evident that the pH zero point of charge \(\text{pH}_{zpc}\) is varied in the range 6.9–7.8. For Na-A, this
value can be as 7.8. This value is higher than that for alumina and silica. The pH\textsubscript{zpc} is reported to be 8.2 and 2.3 for alumina and silica, respectively (Kosmulski, 2014).

**Sorption experiments**

For optimization of dose, different doses of FA, Na-A and Na-A–CS ranging from 2.5 to 5 g/dm\(^3\) were added to the flasks containing 20 mL of 100 mg/dm\(^3\) Cu(II) ion solution (data not presented). It was observed that %S increases and sorption capacity \(q_e\) decreases. The 2.5 g/dm\(^3\) FA dosage was found to be optimum for the Cu(II) removal. Analogous results were obtained for Na-A zeolite and its modification with CS. As follows from the studies of

| Composition | FA1004 | FA2006 |
|-------------|--------|--------|
| Na\(_2\)O   | 2.122  | 1.96   |
| MgO         | 1.639  | 1.096  |
| Al\(_2\)O\(_3\) | 23.551 | 24.455 |
| SiO\(_2\)   | 52.539 | 50.418 |
| P\(_2\)O\(_5\) | 0.912  | 1.351  |
| SO\(_3\)    | 0.741  | 0.854  |
| K\(_2\)O    | 3.483  | 3.061  |
| CaO         | 2.562  | 1.64   |
| TiO\(_2\)   | 1.277  | 1.578  |
| Cr\(_2\)O\(_3\) | 0.027 | 0.043  |
| MnO         | 0.075  | 0.036  |
| Fe\(_2\)O\(_3\) | 6.193 | 6.203  |
| NiO         | 0.017  | 0.03   |
| CuO         | 0.016  | 0.022  |
| ZnO         | 0.021  | 0.021  |
| BaO         | 0.067  | 0.071  |
| \(S\textsubscript{BET}\) (m\(^2\)/g) | 12     | 11     |
| CEC (meq/g) | 6.28   | 7.34   |

**Figure 2.** SEM micrographs of (a) fly ash FA1004, (b) fly ash FA2006 and (c) zeolite Na-A.
the effect of the sorbent dosage on Cu(II), Fe(III), Mn(II) and Zn(II) ions sorption, capture of Cu(II), Fe(III), Mn(II) and Zn(II) ions increased with the increasing amount of the sorbent. This is due to a larger adsorption surface area and a larger number of active sorption sites present in the structure of the sorbent. The highest adsorption percentage, %S, obtained at the largest dosage of sorbent was observed for copper(II) (100%) and then was as follows: Fe(III) (99.3%), Zn(II) (96.7%) and Mn(II) (77.6%).

The sorption capacity of Cu(II), Fe(III), Mn(II) and Zn(II) ions with the effect of the initial concentration was studied (Figure 3). With the increasing metal ion concentration, there is an increase in the amount of metal ion sorbed due to the increasing driving force of the metal ions towards the active sites on the used sorbents. The sorption data on FA, Na-A and Na-A–CS were analysed using the most popular Langmuir and Freundlich isotherm models. Moreover, based on the Langmuir isotherm, the dimensionless constant \( R_L \) was also calculated (Table 2). It can be seen that the equilibrium data described the Langmuir model better than the Freundlich one in the case of Cu(II), Fe(III), Mn(II) and Zn(II) ions. The \( R_L \) values of FA, Na-A and Na-A–CS are greater than zero and less than unity, which suggests that the sorption processes are favourable. As follows from the thermodynamic parameters obtained by the sorption in the range 293–333 K with the increasing temperature the equilibrium capacity decreases (Table 3). The negative values of \( \Delta H^o \) indicate the exothermic nature of the sorption process. Moreover, the negative values of \( \Delta G^o \) confirm its feasibility and the decreasing the value of \( \Delta G^o \) with the increasing temperature can be associated with more favourable sorption at lower temperatures. The positive values of \( \Delta S^o \) indicate the increasing randomness.

Figure 3. Effect of initial concentration and time on the adsorption of (a) Cu(II), (b) Fe(III), (c) Mn(II) and (d) Zn(II) ions on Na-A–CS (m = 0.1 g, pH = 5, T = 293 K, A = 7, revolutions = 180 r/min).
As for kinetic studies, the pseudo-first-order (PFO) and the pseudo-second-order (PSO) kinetic models were applied to test the experimental data. Table 4 reports the obtained data calculated from the slope and intercept of the plots. On the basis of the obtained data, it can be concluded that the PSO model is appropriate to describe the kinetic one. It was found that the determined coefficient $R^2$ values obtained from the PSO model are much higher than those from the PFO model (equal to 0.99 or 1.00). Furthermore, the values $q_2$ are the same as the values of sorption capacities determined experimentally, in contrast to that obtained using the PFO model. Moreover, analysing the results obtained at the same initial concentration, for example 20 mg/dm$^3$, the following trend sorption affinity was found: Cu(II) $>$ Fe(III) $>$ Zn(II) $>$ Mn(II). In all studied multi-ion solutions, these were in the same order.

### Table 2. Comparison of estimated parameters obtained from the Langmuir and Freundlich isotherms for Cu(II), Fe(III), Mn(II) and Zn(II) ions on Na-A and Na-A–CS.

| Isotherm | Parameters | Cu(II) | Fe(III) | Mn(II) | Zn(II) |
|----------|------------|--------|---------|--------|--------|
| Na-A     |            |        |         |        |        |
| Langmuir | $K_L$ (dm$^3$/mg) | 7.174  | 0.979   | 0.071  | 0.346  |
|          | $R_L$      | 0.003  | 0.124   | 0.393  | 0.214  |
|          | $q_0$ (mg/g) | 3.93   | 5.98    | 3.12   | 2.69   |
|          | $R^2$      | 0.9958 | 0.9787  | 0.9987 | 0.9989 |
| Freundlich | $K_F$ (mg/g) | 3.96   | 5.57    | 2.93   | 2.38   |
|          | $R^2$      | 0.9331 | 0.9707  | 0.9634 | 0.8751 |
| Na-A–CS  |            |        |         |        |        |
| Langmuir | $K_L$ (dm$^3$/mg) | 9.234  | 1.224   | 0.099  | 1.111  |
|          | $R_L$      | 0.007  | 0.178   | 0.428  | 0.365  |
|          | $q_0$ (mg/g) | 4.99   | 7.42    | 5.55   | 4.26   |
|          | $R^2$      | 0.9932 | 0.9982  | 0.9999 | 0.9991 |
| Freundlich | $K_F$ (mg/g) | 4.12   | 6.62    | 4.15   | 3.45   |
|          | $R^2$      | 0.9456 | 0.9666  | 0.9789 | 0.9123 |

### Table 3. Thermodynamic parameters for the sorption of Cu(II), Fe(III), Mn(II) and Zn(II) ions on Na-A and Na-A–CS.

| M(II)/(III) | $H^o$ (kJ/mol) | $S^o$ (J/K mol) | $G^o$ (kJ/mol) |
|------------|----------------|----------------|----------------|
|            | 293 K          | 313 K          | 333 K          |
| Na-A       |                |                |                |
| Cu(II)     | $-47.42$       | $150.21$       | $-20.81$       | $-18.78$       | $-13.73$       |
| Fe(III)    | $-23.49$       | $90.27$        | $-14.12$       | $-13.70$       | $-11.65$       |
| Mn(II)     | $-42.68$       | $175.62$       | $-8.61$        | $-8.19$        | $-6.50$        |
| Zn(II)     | $-34.60$       | $140.35$       | $-10.60$       | $-10.22$       | $-10.09$       |
| Na-A–CS    |                |                |                |
| Cu(II)     | $-38.23$       | $129.76$       | $-19.66$       | $-16.60$       | $-14.64$       |
| Fe(III)    | $-21.55$       | $112.33$       | $-12.99$       | $-14.62$       | $-13.51$       |
| Mn(II)     | $-36.24$       | $155.22$       | $-11.23$       | $-12.27$       | $-12.44$       |
| Zn(II)     | $-24.51$       | $143.81$       | $-9.55$        | $-10.38$       | $-11.12$       |

As for kinetic studies, the pseudo-first-order (PFO) and the pseudo-second-order (PSO) kinetic models were applied to test the experimental data. Table 4 reports the obtained data calculated from the slope and intercept of the plots. On the basis of the obtained data, it can be concluded that the PSO model is appropriate to describe the kinetic one. It was found that the determined coefficient $R^2$ values obtained from the PSO model are much higher than those from the PFO model (equal to 0.99 or 1.00). Furthermore, the values $q_2$ are the same as the values of sorption capacities determined experimentally, in contrast to that obtained using the PFO model. Moreover, analysing the results obtained at the same initial concentration, for example 20 mg/dm$^3$, the following trend sorption affinity was found: Cu(II) $>$ Fe(III) $>$ Zn(II) $>$ Mn(II). In all studied multi-ion solutions, these were in the same order.
The introduction of foreign ions to the solution resulted in reduced sorption (Figure 4). The only increase of %S was found for Fe(III) ions in the presence of SO$_4^{2-}$/Co$_2^+$ ions (from 68.9% to 100%). The decreased %S of the other studied ions was at least caused by the presence of SO$_4^{2-}$/Co$_2^+$ ions. In the case of Cu(II) and Fe(III) ions sorption, the presence of NO$_3^-$/Co$_2^+$ ions resulted in the greatest decrease in %S. In contrast, sorption of Mn(II) and Zn(II) ions was the most adversely affected by the presence of chloride ions. It has been found that the greatest effect on %S due to the presence of foreign ions was observed for Mn(II) ions. In further studies, application of the test sorbents as fertilizers for plants will also be determined as effects of Ca(II) and Mg(II) ions.

Zeolite Na-A modification by CS was confirmed by elemental analysis. The presence of 10.2% of nitrogen in Na-A–CS and 4.2% and 2.1% for Na-A:CS = 4:1 and Na-A:CS = 1:1 ratio. The higher amino content (%N) during the investigations indicates a higher percentage of conversion. For sorption on Na-A modified by CS, it was found that in acidic solutions protonation of amine groups of CS (–$\text{NH}_3^+$) occurs reducing the number of binding sites for the Cu(II), Fe(III), Mn(II) and Zn(II) sorption. At higher pH, adsorption increases; however, at the pH values higher than 7, the studied ions start to precipitate. The analogous results were described by Ngah et al. (2005). As for CS cross-linking, zeolite Na-A was suspended in glutaraldehyde (GLA) or epichlorohydrin (ECH) solutions (Ngah et al., 2005). However, it was found that the cross-linking does not affect the sorption efficiency. In contrast, the competition of Cu(II), Fe(III), Mn(II) and Zn(II) ions with Na(I) (K(I) or

### Table 4. Kinetic parameters for the adsorption of Cu(II), Fe(III), Mn(II) and Zn(II) ions on Na-A–CS.

| C$_0$ (mg/dm$^3$) | q$_0$,exp (mg/g) | q$_1$ (mg/g) | $k_1$ (1/min) | $R^2$ | q$_2$ (mg/g) | $k_2$ (g/mg min) | $R^2$ |
|-------------------|-----------------|-------------|--------------|-------|-------------|-----------------|-------|
| **Na-A–CS–Cu(II)** |
| 5                 | 1.05            | 12.30       | 0.88         | 0.8067| 1.05        | 77.13           | 1.0000|
| 10                | 1.94            | 49.09       | 0.02         | 0.5466| 1.95        | 15.83           | 1.0000|
| 15                | 3.14            | 3.45        | 0.03         | 0.9059| 3.15        | 0.88            | 1.0000|
| 20                | 3.85            | 1.09        | 0.02         | 0.9891| 3.87        | 0.18            | 1.0000|
| **Na-A–CS–Fe(III)** |
| 10                | 1.77            | 2.01        | 0.07         | 0.91  | 1.79        | 0.48            | 0.9999|
| 20                | 3.27            | 1.03        | 0.01         | 0.88  | 3.29        | 0.32            | 0.9999|
| 30                | 4.65            | 1.66        | 0.01         | 0.30  | 4.66        | 0.94            | 1.0000|
| 40                | 5.51            | 1.17        | 0.01         | 0.92  | 5.47        | 0.25            | 0.9999|
| **Na-A–CS–Mn(II)** |
| 20                | 2.61            | 1.16        | 0.01         | 0.89  | 2.57        | 0.28            | 0.9999|
| 40                | 3.46            | 1.65        | 0.004        | 0.57  | 3.49        | 0.40            | 1.0000|
| 60                | 3.89            | 1.76        | 0.01         | 0.88  | 3.80        | 0.14            | 0.9999|
| 80                | 3.90            | 1.38        | 0.002        | 0.37  | 3.90        | 0.90            | 1.0000|
| **Na-A–CS–Zn(II)** |
| 10                | 1.90            | 1.43        | 0.02         | 0.95  | 1.89        | 0.28            | 0.9999|
| 20                | 2.75            | 1.09        | 0.01         | 0.69  | 2.76        | 0.31            | 0.9999|
| 30                | 3.35            | 1.58        | 0.01         | 0.87  | 3.30        | 0.18            | 0.9999|
| 40                | 4.23            | 1.22        | 0.01         | 0.98  | 4.21        | 0.15            | 0.9999|
Ca(II) ions from the zeolite can be associated by their competition with the surface hydroxyl groups of zeolites.

Preliminary regeneration studies have been carried out using different desorbing agents. And 0.1 M solutions of HCl, NaCl, H₂O as well as MeOH and EtOH were used. It was found that using 1.0 M HCl more than 90% of the sequestered Cu(II) ions were recovered.

Conclusions

The obtained sorbents showed good structural properties and high removal efficiency for heavy metal ions: Cu(II), Fe(III), Mn(II) and Zn(II). It was observed that the sorption capacity increased with increasing pH value to 5.0 and decreased with the increase in the sorbent to sorbate ratio. The process followed the Langmuir isotherm model. The sorption capacity was found to increase with the increasing initial concentration of Cu(II), Fe(III), Mn(II) and Zn(II) ions as well as decrease with increasing temperature. The values of $\Delta H$ indicate that the sorption process is exothermic. The rate of sorption was found to follow the PSO kinetic model. Experiments were also conducted to regenerate the sorbent by HCl solution. Its good reuse creates a wide potential for its practical application in the removal of heavy metal ions from polluted waters and wastewaters. It is also important as the method for FA utilization on a wide scale.

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