Adsorption of heavy metals from acid mine drainage by natural zeolite

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A B S T R A C T

The adsorption behaviour of natural zeolite (clinoptilolite) has been studied in order to determine its applicability in treating acid mine drainage (AMD) containing 400, 20, 20 and 120 mg l⁻¹ of Fe³⁺, Cu²⁺, Mn²⁺ and Zn²⁺ respectively. Tests to determine both the rate of adsorption and the uptake at equilibrium were performed under batch conditions from single and multi-component solutions. The optimum conditions for the treatment process were investigated by observing the influence of pH levels, the presence of competing ions, varying the mass of zeolite and thermal modification of the natural zeolite (calcination and microwaves). The adsorption studies showed rapid uptake in general for the first 40 mins, corresponding to ~80% total removal. After this initial rapid period, the rate of adsorption decreases. According to the equilibrium studies, the selectivity sequence can be given as Fe³⁺ > Zn²⁺ > Cu²⁺ > Mn²⁺, with good fits being obtained using Langmuir and Freundlich adsorption isotherms. Preliminary tests using AMD samples from Wheal Jane Mine, UK, showed that natural zeolite has great potential as an alternative low cost material in the treatment of acid mine drainage.

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1. Introduction

Acid Mine Drainage (AMD) poses a serious threat to human health, animals and ecological systems. This is because AMD contains heavy metal contaminants, such as Cu²⁺, Fe³⁺, Mn²⁺, Zn²⁺, Cd²⁺ and Pb²⁺ which are not biodegradable and thus tend to accumulate in living organisms, causing various diseases and disorders (Moreno et al., 2001; Myroslav et al., 2006; Bailey et al., 1999).

The main sources of AMD are mining operations (such as Wheal Jane Mine, Cornwall, UK), metal plating facilities and tanneries (Leinonen and Letho, 2001). Treatment processes for metal contaminated waste streams include chemical precipitation, ion exchange, adsorption and ultra-filtration; the choice of method is based jointly on the concentration of heavy metals in the solution and the cost of treatment (Richardson and Harker, 2002). Adsorption is a popular method for the removal of heavy metals from the waste water (Omer et al., 2003; Heping et al., 2006), particularly when natural materials that are available in large quantities or certain waste products from industrial or agricultural activities may have potential as inexpensive sorbents (Bailey et al., 1999). Examples include dead biomass, blast furnace slag, fly ash, clay, tree bark, tea leaves and natural zeolite (Krishna and Susmita Sen, 2006; Ahmet et al., 2007; Bailey et al., 1999).

Zeolites are naturally occurring alumino-silicates with a 3 dimensional framework structure bearing AlO₄ and SiO₄ tetrahedra. These are linked to each other by sharing all of the oxygen to form interconnected cages and channels (Englert and Rubio, 2005) where exchangeable cations are present which counterbalance the negative charge on the zeolite surface generated from isomorphous substitution (Barrer, 1978; Dyer, 1988).

The use of natural zeolite as an adsorbent has gained interest among researchers; mainly because its sorption properties provide a combination of ion exchange and molecular sieve properties which can also be easily modified (Cincotti et al., 2006).

Despite the great interest in ion exchange with natural zeolite, there is very little literature published on the influence of competing cations on the removal of certain heavy metals from mixed solutions by natural zeolite. Other areas that need further investigation are the effect of grain size, pH, use of “as received” (untreated) and thermally treated natural zeolite on the adsorption process. Limited data are also available for cation exchange with untreated clinoptilolite in terms of equilibrium isotherms and reaction kinetics (Wingenfelder et al., 2005; Myroslav et al., 2006).

The work presented in this paper is a study of the uptake efficiency of Fe³⁺, Cu²⁺, Mn²⁺ and Zn²⁺ from single and multi-component synthetic solutions of AMD similar to those from the Wheal Jane Mine, using untreated and thermally modified natural zeolite under batch conditions. Results of preliminary test works on the removal of these heavy metals from samples of Wheal Jane Mine AMD are also presented.

2. Materials and Methods

2.1. Materials

In this study natural zeolite (clinoptilolite) samples from Turkey were used, provided by IMERYS Minerals Ltd, UK. The samples were...
used in their natural state ("as received") with no chemical modifications, unless stated. The particle size distribution of the samples was determined using screens and a sieve shaker. The particle size range of the natural zeolite used in this study was 1 to 3 mm, unless stated otherwise. Mineralogical analysis of the natural zeolite samples was carried out using X-Ray Diffraction (XRD). The results showed that the natural zeolite contained clinoptilolite in the majority, and small quantities of quartz, feldspar and mica (Courtesy of IMERYS Minerals Ltd, UK). Chemical analysis to determine the chemical composition of the samples was obtained by X-Ray Fluorescence (XRF) [a]. The predominant exchangeable cations for the natural zeolite were found to be Na+, K+, and Ca2+. Synthetic solutions of Fe3+, Cu2+, Mn2+ and Zn2+ were prepared from analytical grade Fe2(SO4)3.5H2O, CuSO4.5H2O, MnSO4.4H2O and ZnSO4.7H2O respectively (Fisher Scientific, UK). The required metal concentrations were 400, 120, 20 and 20 mg l−1 of Fe3+, Zn2+, Cu2+ and Mn2+ respectively (McGinness, 1999). The pH was adjusted using sulphuric acid.

Samples of acid mine drainage from Wheal Jane Mine were also collected. The concentration of heavy metals in the samples was 200, 85, 12, 15, 19 mg l−1 and 1 of Fe3+, Zn2+, Cu2+, Mn2+, Al3+, As3+ and Cd2+ respectively.

2.2. Batch sorption studies

Batch sorption tests were conducted by mixing different quantities (3.7 g, 7.5 g and 15 g) of natural zeolites with 100 ml of synthetic solutions containing the desired concentration of heavy metal ions, at 22 ± 2 °C. The mixture was agitated in 200 ml plastic bottles using a stirring device for the desired time interval (15–360 min) and then filtered, using 150 mm diameter filter papers (Fisherbrand QL100/ qualitative). The final concentration of the heavy metal ions in the aqueous phase was then determined using Atomic Absorption spectrophotometer (AAS). The error in analysing the cations was approximately ±6.64%, 6.49%, 5.68% and 6.61% for Fe3+, Cu2+, Mn2+ and Zn2+ respectively.

The percentage adsorption (%) was calculated using

\[
\% \text{Adsorption} = (C_i - C_f) \cdot 100 / C_i, \tag{1}
\]

where, \(C_i\) and \(C_f\) are the concentrations of the metal ions in the initial and final solutions respectively.

The distribution coefficient/ratio, \(K_d\) can also be calculated as follows.

\[
K_d = q_e / C_e, \tag{2}
\]

where \(q_e\) is that amount of solute adsorbed per unit mass of adsorbent at equilibrium and \(C_e\) is the residual solute concentration at equilibrium. The distribution coefficient is important because it implicitly indicates the selectivity, capacity, and affinity of an ion for ion exchange.

The percent adsorption and \(K_d\) (mg g−1) are related as follows (Khan et al., 1995):

\[
\% \text{Adsorption} = 100K_d / (K_d + V / m). \tag{3}
\]

The equilibrium amount of metal adsorbed from aqueous solution was determined by the following equation

\[
q_i = m_i / m = (C_0 - C_e) / V / m, \tag{4}
\]

where \(q_i\) is the amount of heavy metal ions adsorbed at time \(t\) (mg g−1 adsorbent); \(m_i\) is the mass of metal adsorbed (mg); \(m\) is the adsorbent mass (g); \(C_0\) is the initial concentration of heavy metal ions (mg l−1) and \(V\) is the volume of solution from which adsorption occurs, I.

2.2.1. Adsorption Isotherms

Several equilibrium models have been developed to describe adsorption isotherm relationships, the two main isotherm models used in this work are the Langmuir and Freundlich models (Seader and Henry, 2006).

2.2.2. Kinetic studies

The mass of zeolite used was 3.7, 7.5, 15 and 30 g in a constant volume (100 ml) of synthetic solution containing the different metal ions, at different concentrations (20 to 400 mg l−1). The agitation time was varied from 15–360 min, in the following intervals: 15, 30, 45, 60, 120, 180, 240, 300 and 360 min. The sorption experiments were carried out in duplicate in order to observe the reproducibility of the results, and the mean value was used. In each case the percentage error between the duplicated experiments was about ±10%.

2.2.3. Effect of solution pH

The solution pH was varied to 2.5, 3.5 and 4.5 for the single component solutions. 100 ml of solution was contacted with 3.7 g of natural zeolite for 6 hs. The change in solution pH was measured.

2.2.4. Effect of competing ions on the adsorption process

Acid mine drainage normally contains more than one cation (Fe3+, Cu2+, Mn2+, Zn2+, Pb2+, Cr3+ etc). Tests were performed to investigate the influence of the presence of other cations on the adsorption capacity of natural zeolite for each of the cations under investigation in this study. Multi-component solutions containing equal concentrations (40 mg l−1 and 120 mg l−1) of each cation were made and contacted with natural zeolite for 6 hs.

2.2.5. Effect of heat treatment on natural zeolite

Heat treatment was carried out using two processes: by heating in an air atmosphere muffle furnace for 30 min at 200, 400 and 800 °C and by exposing the natural zeolite to microwave energy of 2.45 GHz at 950 W for 15 and 30 min. The thermally modified zeolite samples were then contacted with synthetic solutions for 6 hs.

2.2.6. Treatment of acid mine drainage (AMD)

The objective of this study was to treat AMD from Wheal Jane Mine. Thus synthetic solutions containing a mixture of Fe3+, Cu2+, Mn2+ and Zn2+ at 400, 20, 20 and 120 mg l−1 respectively were prepared (these concentrations are similar to the ones in AMD produced by Wheal Jane Mine (McGinness, 1999)). 100 ml of the solution was contacted with 3.7 g of natural zeolite for 6 hs. After the desired contact period the mixture was filtered and the filtrate was analysed using the AAS. Preliminary tests were then conducted to treat real AMD from Wheal Jane Mine. 30 g of thermally modified natural zeolite (heated in a furnace at 200 °C for 30 mins) was used to treat 100 ml solution of real AMD.

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Table 1

<table>
<thead>
<tr>
<th>Chemical composition (%) from XRF</th>
<th>Turkish zeolite</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>72.43</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>11.92</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>1.18</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.08</td>
</tr>
<tr>
<td>K₂O</td>
<td>3.38</td>
</tr>
<tr>
<td>CaO</td>
<td>2.12</td>
</tr>
<tr>
<td>MgO</td>
<td>1.38</td>
</tr>
<tr>
<td>Na₂O</td>
<td>1.10</td>
</tr>
<tr>
<td>Si/Al</td>
<td>5.36</td>
</tr>
<tr>
<td>Cation exchange capacity (meq g⁻¹)</td>
<td>2.36</td>
</tr>
<tr>
<td>Specific surface area (m² g⁻¹)</td>
<td>15.88</td>
</tr>
</tbody>
</table>

[a] Courtesy of IMERYS Minerals Ltd, UK.
3. Results and Discussion

3.1. Kinetic Studies

The results of the kinetics experiments to measure the ion-exchange adsorption of cations from aqueous solutions onto the untreated natural zeolite as a function of zeolite mass and time are shown in Fig. 1. The results show that the adsorption is a heterogeneous process with an initial rapid adsorption rate followed by a slower rate. This is particularly noticeable for the Fe$^{3+}$ and Zn$^{2+}$ cations which are adsorbed more slowly (Fig. 1b, d). In the first 40 min, the adsorption sites are available and the cations interact easily with the sites and hence a higher rate of adsorption is observed. This initial stage of fast adsorption corresponds to ion exchange in micro-pores on the surface of the zeolites grains (Inglezakis et al., 2002). Furthermore, the driving force for adsorption, which is the concentration difference between the bulk solution and the solid–liquid interface, is initially very high and this also results in a higher adsorption rate. However, after the initial period, slower adsorption may be due to slower diffusion of cations into the interior channels of natural zeolite, the cations subsequently occupy the exchangeable positions within the crystal structure (Amarasinghe and Williams, 2007; Myroslav et al., 2006). In this case it is suggested that ion exchange is between the exchangeable cations (Ca$^{2+}$, Na$^+$ and K$^+$) within the zeolite crystal structure and heavy metal ions (Fe$^{3+}$, Cu$^{2+}$, Mn$^{2+}$ and Zn$^{2+}$).

The effect of the adsorbent dose on the uptake of heavy metal ions is also shown in Fig. 1. It was observed that an increase in dosage resulted in an increase in the rate of heavy metal uptake; this is because with an increase in mass/dosage there is an introduction of more adsorption sites which adsorb more cations from the solution.

The legal concentrations of Fe$^{3+}$, Mn$^{2+}$, Zn$^{2+}$ and Cu$^{2+}$ in drinking water are 0.2, 0.05, 5 and 2 mg l$^{-1}$ respectively, according to the Water Supply Regulations, 2000. From Table 2, it is seen that 30 g of natural zeolite was able to treat Cu$^{2+}$ and Zn$^{2+}$ solutions to below the legal requirement, but not solutions of Fe$^{3+}$ and Mn$^{2+}$. Thus for water quality levels that are within the legal requirements it is suggested that solutions containing metal ion concentrations similar to those used in this study, be passed through more than a single adsorption stage.

3.2. Effect of solution pH

The amount of heavy metal ions adsorbed from solution increases with an increase in initial solution pH as shown in Table 3. Natural zeolite preferentially adsorbs H$^+$ ions from solution to heavy metal ions (Inglezakis et al., 2003; Myroslav et al., 2006), and thus in more acidic conditions more H$^+$ ions are adsorbed from solution. At higher pH values the H$^+$ ions concentration is lower, giving way to more heavy metal ions being adsorbed from solution as indicated by the increase in $q_e$. An increase in initial pH from 2.5 to 3.5 resulted in an increase in $q_e$ of about 49%, 38% and 20% for Mn$^{2+}$, Zn$^{2+}$ and Cu$^{2+}$ respectively. Mn$^{2+}$ adsorption is the most affected by pH changes. The efficiency of metal adsorption depends on solution pH levels; this is in agreement with results obtained by Moreno et al. (2001) and Alvarez-Ayuso et al. (2003).

Natural zeolites are generally weakly acidic in nature and sodium-form exchangers are selective for hydrogen ($\text{R-Na + H}_2\text{O} \leftrightarrow \text{RH} + \text{Na}^+ + \text{OH}^-$), which leads to high pH values when the exchanger is equilibrated with relatively dilute electrolyte solutions (Erdem et al., 2004) making metal hydroxide precipitation feasible. Thus as reaction proceeds the solution pH increases. A slight precipitate was observed in all the

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**Table 2**

<table>
<thead>
<tr>
<th>Final concentration (mg l$^{-1}$) of the different mixtures</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.7 g</td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
</tr>
<tr>
<td>Mn$^{2+}$</td>
</tr>
<tr>
<td>Zn$^{2+}$</td>
</tr>
</tbody>
</table>

---

Fig. 1. Kinetics of heavy metal ion adsorption from single-component solutions (grain size: 1–3 mm, 100 ml of solution, pH 3.5).
adsorption reactions for all the metals, indicating that removal of heavy metal ions from solution was not only due to ion exchange but also precipitation.

3.3. Adsorption Isotherms (Equilibrium Studies)

The adsorption of heavy metals from solution by natural zeolite was fitted to both the Langmuir and Freundlich adsorption isotherm models as shown in Fig. 2 and Table 4.

The Langmuir gives a better fit compared to the Freundlich adsorption isotherm. According to the Langmuir adsorption model, the values of \( q_0 \) follow the sequence: \( \text{Fe}^{3+} > \text{Zn}^{2+} > \text{Cu}^{2+} > \text{Mn}^{2+} \).

The Freundlich adsorption isotherm is usually used to fit experimental data over a wide range of concentrations. This isotherm gives an expression encompassing the surface heterogeneity and the exponential distribution of active sites and their energies. Values of \( n \) (Freundlich isotherm) between 2 and 10 represent good adsorption (Erdem et al., 2004), thus from Table 4, \( \text{Fe}^{3+}, \text{Cu}^{2+}, \text{Zn}^{2+}, \text{Mn}^{2+} \) have \( n \) values of 6.1, 5.6, 5.6 and 4.6 respectively which is an indication of good adsorption of these cations by natural zeolite. The Freundlich model also shows a similar adsorption capacity sequence as the Langmuir isotherm according to the \( k \) values; \( k \) being a constant related to adsorption capacity.

The difference in adsorption capacity of the natural zeolite for the heavy metal ions may be due to a number of factors which include hydration diameters, hydration enthalpies and solubility of the cations. The hydration radii of the cations are: \( r_{\text{HZn}^{2+}} = 4.30 \text{ Å}, r_{\text{HFe}^{3+}} = 4.57 \text{ Å}, r_{\text{HCu}^{2+}} = 4.19 \text{ Å} \) and \( r_{\text{HMn}^{2+}} = 4.38 \text{ Å} \) (Nightingale, 1959). The smallest particles should ideally be adsorbed faster and in larger quantities compared to the larger particles, since the smaller particles can pass through the micropores and channels of the zeolite structure with ease (Erdem et al., 2004). Furthermore, adsorption should be described using hydration enthalpy, which is the energy that permits the detachment of water molecules from cations and thus reflects the ease with which the cation interacts with the adsorbent. Therefore, the more a cation is hydrated the stronger its hydration enthalpy and the less it can interact with the adsorbent (Amarasinghe and Williams, 2007). The hydration energies of the cations are: \( -2010, -1955, -1760 \) and \( -4265 \text{ kJmol}^{-1} \) for \( \text{Cu}^{2+}, \text{Zn}^{2+}, \text{Mn}^{2+} \) and \( \text{Fe}^{3+} \) respectively (Marcus, 1991; Nightingale, 1959). According to the hydration diameters the order of adsorption should be \( \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Mn}^{2+} > \text{Fe}^{3+} \) and also according to the hydration enthalpies the order should be \( \text{Mn}^{2+} > \text{Zn}^{2+} > \text{Cu}^{2+} > \text{Fe}^{3+} \). \( \text{Fe}^{3+} \) has a greater charge density compared to the other 3 cations which have an ionic charge of 2+, thus its greater hydration diameter and enthalpy. The above series according to the hydration diameters and enthalpy are different from the experimentally obtained series which is \( \text{Fe}^{3+} > \text{Zn}^{2+} > \text{Cu}^{2+} > \text{Mn}^{2+} \). The difference in the series may be an indicator that adsorption is not necessarily the only mechanism responsible for the removal of heavy metal ions from solution; precipitation of the metal hydroxides may have a significant influence in the treatment process by natural zeolite.

3.4. Effect of competing cations on adsorption

In practice, acid mine drainage contains a mixture of different heavy metal ions. Experiments were carried out to investigate the influence of the presence of competing cations on the individual

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**Table 3**

<table>
<thead>
<tr>
<th>pH</th>
<th>Amount adsorbed, ( q_e ) (mg g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(^{3+})</td>
<td>Cu(^{2+})</td>
</tr>
<tr>
<td>2.5</td>
<td>6.41</td>
</tr>
<tr>
<td>3.5</td>
<td>–</td>
</tr>
<tr>
<td>4.5</td>
<td>–</td>
</tr>
</tbody>
</table>

Contact time: 360 min; Experimental error: pH \( \pm 0.1 \), \( q_e \) (mg g\(^{-1}\)) \( \pm 10\% \).

**Table 4**

<table>
<thead>
<tr>
<th>Adsorption isotherm models</th>
<th>Fe(^{3+})</th>
<th>Cu(^{2+})</th>
<th>Zn(^{2+})</th>
<th>Mn(^{2+})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir adsorption isotherm</td>
<td>( q_0 )</td>
<td>6.61</td>
<td>3.37</td>
<td>5.38</td>
</tr>
<tr>
<td>( b )</td>
<td>2.63</td>
<td>0.11</td>
<td>0.02</td>
<td>0.16</td>
</tr>
<tr>
<td>Freundlich Adsorption isotherm</td>
<td>( k )</td>
<td>2.87</td>
<td>1.09</td>
<td>1.09</td>
</tr>
<tr>
<td>( n )</td>
<td>6.12</td>
<td>5.56</td>
<td>5.64</td>
<td>4.63</td>
</tr>
</tbody>
</table>

---

**Fig. 2.** Adsorption isotherms of heavy metal ions (Cu\(^{2+}\), Fe\(^{3+}\), Mn\(^{2+}\) and Zn\(^{2+}\)) described by Langmuir and Freundlich models.
adsorption of Cu$^{2+}$, Fe$^{3+}$, Zn$^{2+}$ and Mn$^{2+}$ by natural zeolite. Fig. 3 compares adsorption of the heavy metals from both single- and multi-component solutions. Only the adsorption of Fe$^{3+}$ was significantly unaffected by the presence of competing ions. This may be because the main mechanism responsible for Fe$^{3+}$ removal from solution is thought to be precipitation, from observation. The adsorption of the other 3 cations was affected significantly: the amount adsorbed from multi-component solutions of concentration 40 mg/l$^{-1}$, decreased by 33%, 41% and 39% for Cu$^{2+}$, Zn$^{2+}$ and Mn$^{2+}$ respectively compared to their respective single component solutions. When the solution concentration was increased from 40 mg/l$^{-1}$ to 120 mg/l$^{-1}$, the relative decrease in the amount adsorbed between the multi-component and single component cases increased further. The total amount of heavy metal ions adsorbed per unit mass of natural zeolite increased in all concentrations of multi-component solutions compared to the amount of solute adsorbed from single component solutions. This indicates that different adsorption mechanisms may be involved in the adsorption of each cation from solution (Amarasinghe and Williams, 2007).

3.5. Effect of heat treatment on natural zeolite

Fig. 4 shows how heat/thermal pre-treatment of the natural zeolite affects its efficiency in heavy metal ion adsorption. For zeolite exposed to microwave radiation, the adsorption rate increased with exposure time, but to a limit. Rate of adsorption by zeolite exposed to microwave
radiation begins to decrease as exposure time approaches 30 mins, as shown for sample MTZ (30) \( \text{MTZ(30)} \). Also, the rate of adsorption by calcined zeolite is faster compared to untreated zeolite, Fig. 4, but the efficiency decreases for zeolite exposed to very high temperatures (800 °C).

The increase in rate of adsorption and adsorption capacity as a result of thermal treatment may be a result of the removal of water from the internal channels of natural zeolite; this leaves the channels vacant and hence increases the adsorption capacity of the zeolite (Turner et al., 2000; Tatsuo and Nagae, 2003). The removal of water results in a change in the surface area of the samples after thermal treatment, Table 5. Surface area measurements were determined by Nitrogen adsorption fitted to the BET equation (Brunauer, 1943). The samples that were exposed to extreme thermal conditions had lower surface areas; this is because of thermal runaway, whereby the zeolite structure collapses (Akdeniz and Ulku, 2007; Tatsuo and Nagae, 2005). When the structure collapses the porosity of natural zeolite decreases and thus the adsorption capacity is reduced.

### 3.6. Treatment of synthetic acid mine drainage (sAMD)

The potential of natural zeolite as an adsorbent for treatment of acid mine drainage from Wheal Jane Mine was determined by contacting synthetic AMD with natural zeolite for 6 hs. Fig. 5 shows the amount of each cation adsorbed from solution with time.

As before, more Fe\(^{3+}\) ions were adsorbed from solution in comparison with the other cations. The amount of Fe\(^{3+}\) ions adsorbed by natural zeolite from synthetic AMD was more or less equal to that adsorbed from its respective single component solutions. The order of adsorption from synthetic AMD was found to be: Fe\(^{3+}\) > Zn\(^{2+}\) > Cu\(^{2+}\) > Mn\(^{2+}\), which is in agreement with the series obtained in Section 3.3.

The above series shows that more Zn\(^{2+}\) ions were removed from synthetic AMD compared to Cu\(^{2+}\) and Mn\(^{2+}\) ions; this is contrary to the results obtained for Zn\(^{2+}\) removal in the presence of competing ions. The higher uptake of Zn\(^{2+}\) ions may be due to the higher concentration of Zn\(^{2+}\) (120 mgl\(^{-1}\)) compared to that of Cu\(^{2+}\) and Mn\(^{2+}\), which is just 20 mgl\(^{-1}\) each. Thus the concentration driving force may be responsible for its greater adsorption capacity.

It was found that natural zeolite efficiently removed Zn\(^{2+}\) ions more than the other cations from synthetic AMD. Percent adsorptions of 67.8%, 59.9%, 56.8% and 18.9% for Zn\(^{2+}\), Fe\(^{3+}\), Cu\(^{2+}\) and Mn\(^{2+}\) respectively were achieved after 6 hs of contact with natural zeolite. Fig. 5 compares the adsorption capacity of each cation from synthetic AMD and that from its single component solution. The final heavy metal concentration in the synthetic AMD was 160.6, 38.6, 16.2 and 8.7 mgl\(^{-1}\) of Fe\(^{3+}\), Zn\(^{2+}\), Mn\(^{2+}\) and Cu\(^{2+}\) respectively, after 6 hs of contact between 3.7 g of natural zeolite and 100 ml solution. These final concentrations fall short of the legal requirements and thus a greater mass of natural zeolite was used and the final concentrations

### Table 5

<table>
<thead>
<tr>
<th>Samples</th>
<th>Surface area (m(^2) g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural zeolite</td>
<td>15.879</td>
</tr>
<tr>
<td>Microwave heated samples</td>
<td></td>
</tr>
<tr>
<td>MTZ (15)(^a)</td>
<td>16.601</td>
</tr>
<tr>
<td>MTZ (30)</td>
<td>15.400</td>
</tr>
<tr>
<td>Furnace heated samples</td>
<td></td>
</tr>
<tr>
<td>200 °C</td>
<td>17.667</td>
</tr>
<tr>
<td>400 °C</td>
<td>14.331</td>
</tr>
<tr>
<td>800 °C</td>
<td>11.463</td>
</tr>
</tbody>
</table>

\(^a\) MTZ (15) — Natural Turkish zeolite exposed to microwaves for 15 min; Error \(\pm 0.01\) m\(^2\) g\(^{-1}\).

Fig. 6. Treatment of 100 ml of real AMD from Wheal Jane Mine, using 30 g of thermally modified natural zeolite.

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Fig. 5. Comparison of adsorption capacities from single component solutions and synthetic acid mine drainage containing 400, 120, 20 and 20 mgl\(^{-1}\) Fe\(^{3+}\), Zn\(^{2+}\), Cu\(^{2+}\) and Mn\(^{2+}\) ions respectively, pH 3.5.
obtained where: 15, 29.1, 9.8 and 4.9 mg l\(^{-1}\) of Fe\(^{3+}\), Zn\(^{2+}\), Mn\(^{2+}\) and Cu\(^{2+}\) respectively for 15 g of natural zeolite. These concentrations still fall short of the legal requirement and thus it is recommended that natural zeolite be used to treat relatively dilute solutions.

Results of the preliminary tests on actual AMD from Wheal Jane Mine are shown in Fig. 6. The final concentrations in the AMD were 0.07, 5.96, 0 and 1.3 mg l\(^{-1}\) of Cu\(^{2+}\), Zn\(^{2+}\), Fe\(^{3+}\) and Mn\(^{2+}\) respectively. These concentrations are within the legal limit for drinking water except for Mn\(^{2+}\).

4. Conclusion

The adsorption of the heavy metal ions from solution onto natural zeolite was determined. The adsorption was rapid for the first 40 min and then gradually decreased. About 80%, 95%, 90% and 99% of Fe\(^{3+}\), Mn\(^{2+}\), Zn\(^{2+}\) and Cu\(^{2+}\) respectively were adsorbed from single component solutions in this first stage. Removal of the heavy metal ions was not only due to ion exchange but also due to precipitation of metal hydroxides from the solution.

The rate of adsorption was directly proportional to the pH value of the solution. Adsorption decreased in more acidic solutions, due to hydrogen ion competition. Adsorption rate and capacity also depends on the adsorbent mass and heat treatment by either microwaves or heating in a furnace.

Efficiency of metal removal from solution by natural zeolite is inversely proportional to the initial solution concentration. Adsorption of heavy metal ions from solution follows the sequence: Fe\(^{3+}\) > Zn\(^{2+}\) > Cu\(^{2+}\) > Mn\(^{2+}\).

The experimental data obtained from batch studies gave a good fit for the Langmuir and Freundlich isotherm models. Preliminary treatment of actual acid mine drainage showed that natural zeolite has the potential to effectively remove heavy metals from relatively dilute acid mine drainage. This naturally occurring mineral can be used as a substitute for the more expensive adsorbents like activated carbon or other treatment methods like electro-dialysis, due to it availability and low cost.

Acknowledgements

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