Hierarchically Porous Zeolite X Composites for Manganese Ion-exchange and Solidification: Equilibrium Isotherms, Kinetic and Thermodynamic Studies

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Abstract

This paper deals with the kinetic and isotherm studies of manganese ion removal by zeolite X and its hierarchically porous composites as ion-exchange materials. A hydrothermal treatment was applied to grow a layer of zeolite X over diatomite and carbon surfaces. The hierarchically porous composites used for Mn$^{2+}$ ion removal showed higher ion-exchange capacity when compared to pure zeolite X under same conditions. A thermodynamic study of the rate of ion-exchange revealed that the intra-particle diffusion rate constant of zeolite X/carbon and zeolite X/diatomite was higher than that of pure zeolite X indicating that the intra-particle diffusion was enhanced when zeolite was prepared in form of hierarchically porous composites. The study showed that the thickness of boundary film of zeolite X/carbon and zeolite X/diatomite was less than that of pure zeolite X indicating ion diffusion resistance to the active sites was reduced when the composites were utilised. The experimental data showed good agreement with Freundlich model. The calculated thermodynamic parameters such as ΔG°, ΔH° and ΔS° indicated the ion-exchange process of Mn$^{2+}$ ion by zeolite X and its composites was spontaneous, endothermic and the randomness increased at the liquid/solid interface under the conditions studied. The results of kinetic study showed that the ion-exchange of Mn$^{2+}$ ion by zeolite X and its composites followed a pseudo second order
kinetic model indicating Mn$^{2+}$ ion removal is a chemical reaction related to valence forces. The encapsulation of Mn$^{2+}$ ion was successfully achieved by vitrification and geopolymerization processes demonstrating the efficacy of both processes for environmental management.

**Keywords:** Hierarchical composites, Ion-exchange, Manganese, Solidification, Intra-particle diffusion, Kinetics.

1. Introduction

Zeolites are microporous aluminosilicate crystalline minerals with exchangeable cations having important functions as adsorbents, ion-exchangers or catalysts in many chemical and petrochemical industries and water treatment applications [1,2]. This important role is due to zeolite’s unique properties of high surface area, uniform porosity, shape selectivity, high ion-exchange capacity, strong Brønsted acidity and high (hydro)thermal stability. However, utilization of powdered zeolites for the industrial applications is often limited because of diffusion and access problems arising from the small zeolites pore size ranging of 0.3-1 nm which is similar to the dimensions of molecules [3,4]. The poor diffusion of relatively large reactant molecules or ions to the active sites present in the zeolite micropores may lead to the underutilization of the available zeolite internal surface area and volume, frequent blocking of the diffusion path and rapid zeolites deactivation [3,5]. The catalysis and uptake activity of zeolite is related to both the length of diffusion path and the diffusion coefficient. A shorter diffusion path length increases the diffusion coefficient and thus creates higher intrinsic zeolite activity [6]. To cope with drawbacks resulting from zeolite microporosity, great efforts have been dedicated to reduce the intracrystalline diffusion path length by preparing zeolites with a hierarchically porous structure [4,7]. Hierarchically porous zeolite can reduce
or eliminate the undesired diffusion limitations of the reaction rate by offering shorter diffusion paths for reactant and product molecules inside the pores [8].

Hierarchical structure zeolite advantages come from the presence of micropores and mesopores/macropores [4]. With hierarchical zeolites, the meso- or macropores facilitate the access of bulky reactant molecules to the zeolite active sites in the micropores [3]. Hierarchical zeolites can be obtained by preparing mesoporous zeolites by post-synthesis modification (dealumination, desilication [9]) or removing a template which is introduced during synthesis [4,10,11] or by preparing hierarchical zeolite composites [12]. Making the hierarchical zeolite composite materials is an effective approach because it does not require complicated steps relative to other synthesis routes. The key focus of this approach is finding a cheap and available porous support and achieving a homogeneous and permanent zeolite crystals coating the support surface.

Hierarchical zeolite composites are commonly prepared using a hydrothermal treatment to grow a zeolite layer onto a porous support [9,13–16]; or using a layer by layer approach which involves coating the support with zeolite crystals which have been previously prepared [17–19]. In the case of growing zeolite crystals on a porous support, it is important to generate nucleation sites on the porous support before mixing with zeolite gel and crystallization. Many types of porous support have been used to generate zeolite composites such as alumina [20,21], steel [22,23], carbon [13,19], polymers [24] and diatomite [9,25]. Porous carbons can be obtained from thermal treatment of available natural waste rich in carbon. Diatomite, diatomaceous earth or kieselguhr, is a low-density unicellular algae consisting of amorphous hydrated silica [9]. Diatomite has interesting properties of inherent macroporous structure, abundance and comparatively inexpensiveness [18]. The optimum performance of zeolites for different applications can be achieved by tailoring hierarchical
zeolite structures with inexpensive porous supports targeting the pore architecture required for the process.

Generally zeolites are effective adsorbents or ion-exchangers in wastewater treatment across a range of contaminants [26]. Zeolites with low Si/Al ratio such as NaA and NaX zeolites are used to remove heavy metals from water by ion-exchange process. Their high affinity for ion-exchange is derived from high concentration of exchangeable non-framework cations available in their microporous structure [27].

Removing pollutants from the wastewaters of different industries is important because of the extremely damaging impact of many pollutants on the environment and public health [28]. Heavy metals are highly toxic and non-biodegradable and they can lead to severe diseases of nervous system and cancer [29]. Heavy metals are released with industrial effluents from different industries such as metal finishing, battery manufacture, metal plating, paints and pigments manufacture, mining, fertilizer production and rubber processing [30,31]. Manganese is one of the heavy metals discharged to the environment from the industries making dry battery cells, fertilizers, colorant for bricks, animal feed and electrical coils; also it results from the burning of coal and oil [32,33].

According to the World Health Organisation, the daily nutritional requirement of manganese is 30-50 μg/kg and the allowable concentration in the drinking water is 0.5 mg/l. Excessive concentrations of manganese are harmful to human health. The presence of manganese in water (even at concentrations lower than 0.5 mg/l) causes black staining of food, laundering problems, objectionable stains to sanitaryware and impart a metallic taste. Also, exposure to manganese can cause neurological disorders and liver, kidney and lung damage [30,34]. When the manganese concentration exceeds the legal concentration in the
water, it can cause hallucinations, nerve damage, lung embolism, bronchitis, schizophrenia, permanent disability, paralysis and tumours [35,36].

Different technologies have been used to treat wastewater such as adsorption, electro floatation, evaporation, precipitation, coagulation, reverse osmosis, membrane separation, ion-exchange and liquid extraction [28,37,38]. However, most of these treatments are expensive, generate waste sludge and are not efficient in treating low concentrations of contaminants. Adsorption and ion-exchange approaches are the simplest and most effective methods to remove harmful elements. The effectiveness of these techniques depends on the efficiency of the adsorbent or/and ion-exchanger in uptaking the pollutant. Adsorbents can be activated carbon, biomaterials, clay minerals, zeolites or solid wastes resulting from some industries [26]. The ion-exchange process is a reversible ion-exchange reaction which happens when the ion-exchanger solid is equilibrated with an electrolyte solution having similar charge ions. Commercial ion-exchangers generally contain zeolites or resins.

Ion-exchange efficiently removes ions but it results in a harmful solid which when disposed of can lead to escaping of ions back into the environment. Therefore, solidification/stabilization technology has been widely used to treat contaminated solid waste because it has the merits of high resistance to biodegradation, ease of use, and it is comparatively inexpensive and stable [39]. Encapsulation of the harmful components inside a solid material can be conducted either by vitrification or geopolymerization.

Vitrification involves trapping inorganic wastes at elevated temperatures in a silicate melt provided by glass-forming materials. Vitrification generates solid materials possessing outstanding long-term chemical stability, the possibility of immobilizing relatively large amounts of heavy metal ions and a significant reduction of the waste volume [40,41]. Geopolymerization has been used to immobilize toxic metals due to the containment of the
structure of the ion-exchanger by the geopolymer on solidification\[42\]. The geopolymerization process involves a rapid chemical reaction at ambient or slightly higher temperature under alkaline conditions to activate the Si and Al minerals and results in a three dimensional polymeric chain and ring structure consisting of Si-O-Al-O bonds \[43,44\].

This study investigates the performance of hierarchical zeolite X composites in the removal of manganese ion from aqueous solution by ion-exchange process in comparison with pure zeolites X. Different parameters were investigated to explore the ion-exchange behaviour for the removal of manganese ions involving: contact time, initial ion concentration, pH of solution and temperature of solution. In addition, the equilibrium isotherm models, ion-exchange kinetics and thermodynamic parameters were comprehensively investigated to understand the behaviour and mechanism of the process. Finally, encapsulation of manganese ion was explored by vitrification and geopolymerization.

2. Methodology

2.1 Preparation of ion-exchange materials

Zeolite X was prepared based on the standard published synthesis \[45–47\]. The formula of zeolite X gel used for this work is \[47\]: 3.9Na\(_2\)O: 1Al\(_2\)O\(_3\): 3SiO\(_2\):156 H\(_2\)O, this was prepared by dissolving 0.99 g of NaOH (NaOH pellets 99.9\%wt, Fisher Scientific) in 20 g of deionised water to provide an alkali medium to carry out the reaction. After that, 1.55 g of sodium aluminate (anhydrous sodium aluminate 55-56\%wt Al\(_2\)O\(_3\), Riedel-deHaën) was added to the NaOH solution with vigorous mixing. Once the solution became clear, 5.78 g of sodium silicate solution (10.6\%wt Na\(_2\)O and 26.5\%wt SiO\(_2\), Sigma-Aldrich) was added and mixed gently until a cream coloured gel was formed. Aging of the produced gel was performed overnight at room temperature. The gel was then put in a Teflon-lined autoclave and heated to 100\(^\circ\)C for 6 h. When the crystallization time was over, the product was filtered, washed
with deionized water until the pH of the water was below 9 and then dried overnight at 70-80°C. After that, the sample was collected and characterized by XRD, SEM, EDAX and Nitrogen adsorption/desorption isotherms.

Hierarchically porous zeolite X composite over diatomite and carbon were prepared hydrothermally by adding porous supports to the aluminosilicates gel. Diatomite (filter agent Celatom FW-80) used in this study was provided by Aldrich. The carbonaceous support was obtained by thermal treatment of Iraqi date stones. The collected date stones were washed, dried and the heated to 900°C for 3 h in a tubular furnace under flowing N₂ gas. A suspension solution of zeolite X nanoparticles was prepared using ball milling. Zeolite X which was prepared previously was mixed with water and grinding media in the following proportions: 2 H₂O: 1 zeolite X: 1 grinding media (0.3-0.4 mm diameter glass beads) and put in a plastic bottle with 5 cm diameter. The mixture was then allowed to rotate at a grinding speed 160-190 rpm for 32 h. The resultant suspension was collected and allowed to settle for 2 days to separate large particles from the suspension. The resulting suspension was used later for the synthesis process of composite zeolite.

Before adding the porous support to the zeolite gel, both diatomite and carbon were exposed to ultrasonication for 6 h in the presence of a suspension of zeolite X nanoparticles (support: suspension nanoparticles weight ratio was 15:1 [14]). After ultrasonication, diatomite and carbon were filtered, washed and dried overnight at 50-70°C. A weight of support equal to five times weight of silica present in the silica source was added to the aged gel and mixed for 15 minutes. After that, the resultant mixture were put in Teflon-lined autoclaves and heated in an oven at 100°C. The crystallization time of the composite materials was increased to avoid partially crystallized products. Therefore, zeolite X/diatomite sample was crystallized for 24 h. While, zeolite X/carbon sample was crystallized for 8 h. After that, the produced composites were filtered, washed, dried and
characterized by XRD, SEM, EDAX, Nitrogen adsorption/desorption isotherms and TGA (for zeolite X/carbon composite).

2.2 Ion-exchange experiments

A study of manganese ion removal by zeolite X, composite zeolite X/carbon and zeolite X/diatomite was performed in batch reactors under continuous stirring. Manganese nitrate tetrahydrate (purity of ≥ 97%, Sigma-Aldrich) was utilized to prepare Mn\textsuperscript{2+} ion solutions. To study the effect of contact time and identify the equilibrium time, 0.2 g of ion-exchange material was left in contact with 100 ml of solution (300 ppm initial ion concentration) under mixing for 24 h. To investigate the efficacy of the ion-exchange materials, different doses of media of 0.2, 0.5, 0.8 and 1 g was added to 100 ml of 300 ppm ions solution. For the effect of initial ion concentration and ion-exchange isotherm studies, a series of 125 ml tubes was used, each tube containing a fixed weight of ion-exchange material (0.2 g) was filled with 100 ml of ion solution (50-700 ppm) and shaken for 4 h at room temperature. The manganese solutions were colourless. The thermodynamic studies and temperature effect on the ion-exchange process were performed at different temperatures of 12, 30 and 50ºC (weight of ion-exchangers of 0.2 g, the initial ion concentration of 300 ppm and solution volume of 100 ml). All these studies were conducted at a pH which was given by the initial ion concentration without modification. However to study the effect of the pH of the solution on the performance of ion-exchange materials, the pH of the solutions were changed using HCl (conc. 31.5-33%, BDH laboratory) and NaOH (NaOH pellets 99.9%wt, Fisher Scientific). 0.2 g of carbon support was added to 100 ml of 300 ppm manganese solution to check whether carbon give an ion-exchange capacity for Mn\textsuperscript{2+} ion.

For each run and before adding the ion-exchange materials, 1 ml of the solution present in each tube was taken to measure the initial ion concentration. After which, samples
were taken periodically every 1 h to determine the remaining concentration of manganese in the solution by ICP-OES.

2.3 Solidification of the spent zeolite

The solidification of the ion-exchange materials containing manganese ions was performed by vitrification and geopolymer. Geopolymers used for this study were made of two different raw materials namely kaolin and fly ash. Leaching of manganese ion from the solidified products was evaluated using NaCl solution and H₂SO₄ solution.

2.3.1 Vitrification

Encapsulation of manganese ions (manganese boiling point of 2061°C) was carried out by heating the used ion-exchange materials up to 1200°C (heating rate 5°C) for 2 h at which temperature the zeolite turns to glass a product. The sample weight of the spent materials was measured before and after thermal treatment. The produced solids were then left in contact with 30 ml of deionized water and 30 ml of 0.1 M NaCl solution. The concentration of manganese ion leached to solutions was measured by ICP-OES after 1 month and 6 months. 0.1 M NaCl solution was prepared from sodium chloride (99.5%, BDH laboratory). NaCl was used in this study because it is strong in the striping of ions from ion-exchangers.

2.3.2 Geopolymerization

The geopolymers were prepared according to standard literature procedures [44,48,49] using alkaline solution to activate the geopolymer raw materials. The geopolymer raw materials used here were kaolin (WBB minerals, UK origin) and fly ash (Cemex, 450-S). The elemental analysis of both kaolin and fly-ash given by EDAX analysis is shown in Table 1. Solidification by geopolymers was accomplished by mixing 2.5 ml of NaOH solution (10 M) with 0.5 ml of sodium silicate solution for 15 min to obtain an activator solution. A
homogeneous mixture of 0.25 g of manganese-bearing materials and 2.5 g of kaolin was obtained by hand-mixing for 10 min. 5 g of fly ash was mixed with 0.25 g of manganese-bearing materials when fly ash was used to prepare the geopolymer. 2 g of both raw materials were used in the case geopolymer prepared with this ratio 50% kaolin:50% fly ash. The solid mixture was mixed with 2.5 ml of the activator solution for 15 min at room temperature and then poured into a cast mould.

The curing process of samples was performed at 70°C for 24 h followed by 7 days at room temperature. After that, the resulting samples were left in contact with water, 0.1 M NaCl solution and 0.25 M H₂SO₄ solution. 0.25 M H₂SO₄ solution was prepared from sulfuric acid (96%, ACROS Organics). ICP-OES was used to measure the concentration of manganese leached to the solution after 1 month and 6 months of contact time.

Table 1: The elemental analysis of kaolin and fly ash according to EDAX.

<table>
<thead>
<tr>
<th>Element</th>
<th>C (Wt%)</th>
<th>O (Wt%)</th>
<th>Na (Wt%)</th>
<th>Mg (Wt%)</th>
<th>Al (Wt%)</th>
<th>Si (Wt%)</th>
<th>S (Wt%)</th>
<th>K (Wt%)</th>
<th>Ca (Wt%)</th>
<th>Ti (Wt%)</th>
<th>Fe (Wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaolin</td>
<td>32.57</td>
<td>27.46</td>
<td>0.07</td>
<td>0.28</td>
<td>16.96</td>
<td>20.01</td>
<td>0.17</td>
<td>1.33</td>
<td>0.19</td>
<td>0.15</td>
<td>0.80</td>
</tr>
<tr>
<td>Fly ash</td>
<td>30.78</td>
<td>22.80</td>
<td>0.89</td>
<td>0.75</td>
<td>13.07</td>
<td>17.13</td>
<td>0.35</td>
<td>2.21</td>
<td>3.46</td>
<td>0.73</td>
<td>7.84</td>
</tr>
</tbody>
</table>

2.4 Analytical techniques

The characterization for zeolite and composite samples by XRD was performed on a Miniflex Rigaku X-ray analytical instrument with CuKα radiation source (λ = 1.5418 Å), voltage = 30 kV, current = 30 mA, scan speed = 3° min⁻¹, step size = 0.03, 2θ = 5-45° and total time ~ 20 min. The scanning electron microscopy (SEM) and energy dispersive analysis by X-ray (EDAX) were conducted using model FEI Quanta 200. To conduct the SEM imaging, the samples were coated with gold by a sputter coater. While, EDAX analysis was carried out without coating the samples. The Thermo Gravimetric analyser (TGA, model Q5000IR TA
Instruments Company) was used to determine the percentage of zeolite in zeolite/carbon composite. The sample was heated to 900°C at a rate of 10°C/min under air atmosphere.

Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES, model Vista-MPX by Varian) was used to obtain manganese concentration in the samples resulting from ion-exchange and solidification experiments.

Nitrogen adsorption/desorption isotherms at -196°C were obtained using a Micrometrics ASAP 2020. Surface area was determined using the Brunauer-Emmett-Teller method (BET method). The degassing was carried out at 200°C for 10 h under vacuum prior to the measurement.

3. Results and discussion

3.1 Characterization of zeolite and composites

The XRD patterns of the prepared samples are shown in Figure 1 to demonstrate the structure and purity of the zeolite phase. Fully crystallized zeolite X (X) was prepared by hydrothermal treatment. Hence, the XRD pattern of the prepared sample is identical to the commercial zeolite X. Also, both zeolite X/carbon (XC) and zeolite X/diatomite (XD) gave similar pattern to the pattern of pure form zeolite X. The matching between composites pattern and pure form zeolite indicates that the presence of a solid porous support does not affect crystallization of the required phase or the phase purity.
Figure 1: XRD pattern of commercial zeolite X, synthesized zeolite X, zeolite X/carbon composite and zeolite X/diatomite composite.

Figure 2a shows the SEM images of the porous carbon support produced by a thermal treatment of date stones. Figure 2b shows SEM image of diatomite. The morphology of zeolite X and both zeolite composites are presented in Figure 3. Pure zeolite X was successfully crystallized from the mother gel under the conditions used for preparation (Figure 3a-1). Figure 3b-1 and Figure 3c-1 reveal zeolite coating on the support surfaces. These results confirm that hydrothermal treatment is effective method for preparing zeolite composites with uniform coating of fully crystallized crystals. The EDAX results are presented in Figure 3a-2, b-2 and c-2 and the percentage of each element consists zeolite and composites structure are presented in Table 2 and they indicate that the Si/Al ratio was 1.35 for zeolite X and 1.4 for zeolite X/carbon composite. While, zeolite X/diatomite composite gave higher ratio than those because diatomite skeleton is formed of silica. During TGA analysis, the X/carbon composite was heated to 900°C in air atmosphere. The TGA results
shown in Figure 4 give the percentage of zeolite X present in zeolite X/carbon composite is ~23.91%. The purpose of doing TGA for zeolite X/carbon composite is to obtain the percentage of zeolite X present in the zeolite X/carbon composite which is the responsible of the ion-exchange.

Figure 2: SEM images of porous supports (a) carbon and (b) diatomite.
Figure 3: SEM image and EDAX results of (a) zeolite X, (b) zeolite X/carbon composite and (c) zeolite X/diatomite composite.

Table 2: The elemental analysis of zeolite X, zeolite X/carbon composite and zeolite X/diatomite composite before ion-exchange according to EDAX.

<table>
<thead>
<tr>
<th>Element</th>
<th>X</th>
<th>XC</th>
<th>XD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt. %</td>
<td>Wt. %</td>
<td>Wt. %</td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>43.53</td>
<td>16.31</td>
<td>32.94</td>
</tr>
<tr>
<td>Na</td>
<td>8.26</td>
<td>2.57</td>
<td>3.96</td>
</tr>
<tr>
<td>Al</td>
<td>20.52</td>
<td>4.07</td>
<td>18.18</td>
</tr>
<tr>
<td>Si</td>
<td>27.69</td>
<td>5.70</td>
<td>44.92</td>
</tr>
<tr>
<td>C</td>
<td>-</td>
<td>71.35</td>
<td>-</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>
Figure 4: TGA result of zeolite X/carbon composite.

The structure properties such as BET surface area, pore volume and mesopore volume of zeolite X and zeolite X composites are shown in Table 3. The surface area and pore volume of zeolite X composites were lower (168.288 m²/g and 0.0756 cm³/g for XC, and 100.467 m²/g and 0.0856 cm³/g for XD) than those for zeolite X (656 m²/g and 0.3459 cm³/g) because low amounts of zeolite X coating on the support surface. The mesopore volume (0.0258 cm³/g for XC and 0.0644 cm³/g for XD) appeared in the composites samples due to introducing a mesoporosity within the composite structure. The percentage of zeolite X in the zeolite X/diatomite composite was obtained by estimating the micropores volume relative to the total pore volume and the percentage was 24.79%.

Table 3: The structure properties of ion-exchange materials obtained from N₂ adsorption/desorption isotherms.

<table>
<thead>
<tr>
<th>Ion-exchange materials</th>
<th>$S_{BET}$ (m²/g)</th>
<th>$V_{Total}$ (cm³/g)</th>
<th>$V_{Mesopores}$ (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>656.251±17.241</td>
<td>0.3459</td>
<td>-</td>
</tr>
<tr>
<td>XC</td>
<td>168.288±3.058</td>
<td>0.0756</td>
<td>0.0258</td>
</tr>
<tr>
<td>XD</td>
<td>100.467±0.808</td>
<td>0.0856</td>
<td>0.0644</td>
</tr>
</tbody>
</table>

$S_{BET}$: BET surface area.
$V_{Total}$: Total pore volume.
$V_{Mesopores}$: Volume of mesopores.
3.2 Manganese ion-exchange study

The results will be presented in this section in form of ion-exchange capacity (q) which was calculated according to the following equation:

\[ q = (C_o - C_t) * \frac{V}{W} \]  

Equation 1

Where \( q \) (mg/g) is the amount of ion exchanged per mass of ion-exchange material \( W \) (g), \( V \) (l) is the solution volume, \( C_o \) and \( C_t \) are the concentrations of ion in solution (mg/l) at \( t = 0 \) and \( t = t \) (h) respectively. At equilibrium time, \( C_{eq} \) is the equilibrium ion concentration and \( q_{eq} \) is the ion-exchange capacity at equilibrium.

3.2.1 Effect of contact time

Figure 5 shows the effect of contact time on Mn\(^{2+}\) ion removal from aqueous solutions. The carbon support prepared from date stones show no significant ion-exchange capacity when it was used to remove Mn\(^{2+}\) ion. Generally, Mn\(^{2+}\) ion uptake by the zeolitic materials used increased rapidly with increasing of the contact time, after that it increased gradually until reach to the equilibrium time. This is because, at the beginning, the ion-exchange sites on the zeolites surface, which contain exchangeable cations (Na\(^+\)), are not exchanged. But with time, those cations continue to exchange with the guest ions until reach to the equilibrium and the ion concentration in the solution becomes steady.

The ion-exchange capacity of the ion-exchange materials showed the following order: X > XD > XC. Both XC and XD composites showed lower ion-exchange capacity than X because XC contains 23.91% zeolite X according to TGA results and XD contains 24.79% zeolite X according to BET method results. Therefore, the performance of composites for ion-exchange with manganese ion is due to this percentage of zeolite in the composites. The ion-exchange capacity calculated based on the real weight of zeolite used is in the order: XD
> XC > X. The pH of manganese solutions before ion-exchange was ~ 4.14. But, it was ranging of 6.3-7.5 after ion-exchange due to changing ionic composition of the zeolite.

![Graph](image_url)

**Figure 5:** a) Study of the equilibrium time on the removal of manganese ion, b) a comparison based on the weight of zeolite. Ion initial concentration = 300 ppm, ion-exchange material dose = 2 g, solution volume = 100 ml, pH = 4 and room temperature. TGA refers to the results obtained by TGA and BET refers to the results obtained by N₂-adsorption/desorption isotherms (BET method).

Figure 6 shows the SEM images and EDAX results of ion-exchange materials after ion-exchange with Mn²⁺ ions. The SEM images of the composites materials revealed that mixing during ion-exchange process did not affect the attachment of zeolite crystals on the supports surface. EDAX results showed appearance of peaks relevant to manganese ion (as shown in inset figures) which indicate that the ion-exchange materials successfully take the
Mn$^{2+}$ ion out of solutions. The elemental analysis obtained by EDAX of X, XC and XD after ion-exchange is shown Table 4.

![Figure 6: SEM and EDAX of ion-exchange materials after ion-exchange with Mn$^{2+}$ ion. (a) zeolite X (X), (b) zeolite X/carbon composite (XC) and zeolite X/diatomite composite (XD).](image)

**Table 4:** The elemental analysis of zeolite X, zeolite X/carbon composite and zeolite X/diatomite composite after ion-exchange according to EDAX.

<table>
<thead>
<tr>
<th>Element</th>
<th>X</th>
<th>XC</th>
<th>XD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt.%</td>
<td>Wt.%</td>
<td>Wt.%</td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>45.58</td>
<td>43.55</td>
<td>43.12</td>
</tr>
<tr>
<td>Na</td>
<td>4.47</td>
<td>3.68</td>
<td>3.31</td>
</tr>
<tr>
<td>Al</td>
<td>17.54</td>
<td>10.45</td>
<td>13.94</td>
</tr>
<tr>
<td>Si</td>
<td>23.77</td>
<td>14.87</td>
<td>32.80</td>
</tr>
<tr>
<td>C</td>
<td>-</td>
<td>21.15</td>
<td>-</td>
</tr>
<tr>
<td>Mn</td>
<td>8.44</td>
<td>6.10</td>
<td>6.83</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>
3.2.2 Initial ion concentration

The influence of initial ion concentration on the ion-exchange process of Mn\(^{2+}\) ion is shown in Figure 7. It can be seen that the value of q gradually increased with increasing the initial manganese concentration. For a fixed weight of ion-exchange material, the amount of ions removed per gram of ion-exchange material increased with increasing the initial ion concentration. This is due to increasing the number of ions competing for the same number of ion-exchange sites present in a certain weight of ion-exchange material. Increasing initial manganese concentration leads to increase the concentration gradient which is the driving force for mass transfer and motivate the ion-exchange process.

The pH of manganese solutions was measured before ion-exchange process being conducted as shown in Table 5. It can be seen that the pH of manganese solutions decreases with increasing manganese concentration i.e. manganese solutions become more acidic at high manganese concentration. This fact explains why there is no sharp increasing in the q value with increasing the initial manganese concentration.

<table>
<thead>
<tr>
<th>Concentration of manganese solution, ppm</th>
<th>50</th>
<th>100</th>
<th>200</th>
<th>300</th>
<th>400</th>
<th>500</th>
<th>600</th>
<th>700</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH of the solution</td>
<td>4.8</td>
<td>4.74</td>
<td>4.39</td>
<td>4.14</td>
<td>4.05</td>
<td>3.9</td>
<td>3.83</td>
<td>3.72</td>
</tr>
</tbody>
</table>
3.2.3 Solution pH

Figure 8 shows the ion-exchange capacity of ion-exchange materials against pH of manganese solution. The pH solution is an effective parameter on the ion-exchange process. This is because pH is linked to hydrogen ions which compete with metal ions for actives sites during ion-exchange process. Also, it affects the zeolites structure. The results shown in Figure 8 showed that of the amount of manganese ions exchanged per unit mass of ion-exchange material increased with raising the pH of solution. This is because of reduction of the concentration of $\text{H}^+$ in the alkaline medium which competes with manganese ions for the zeolitic cations. Moreover, reducing of solution pH causing of collapse of zeolite structure and reduces the number of ion-exchange sites present within the zeolite structure. Where, a reduction in the peak height was noticed when XRD was conducted for the zeolitic materials used for experiment conducted at pH = 2. The pH of manganese solution cannot be increased more than $\sim 6.5$ because of manganese ion precipitation.
3.2.4 Temperature of solution

The results describing the effect of temperature on the manganese ions removal from aqueous solution are shown in Figure 9. The amount of manganese ion removed per a certain mass of ion-exchange material increased with increasing temperature to ~ 50°C. This is because the rate of intra-particle diffusion of manganese ions is enhanced by increasing temperature of solution [50]. The diffusing species and the zeolite framework are electrically charged, therefore the rate of diffusion depends on temperature [51]. That means that ion-exchange process of manganese ion is an endothermic process. Temperature is related to the thermodynamic parameters namely free energy of ion-exchange (ΔG°), enthalpy (ΔH°) and entropy (ΔS°). Thus, it is an important to investigate the influence of temperature on the ion-exchange process.
Figure 9: Effect of temperature on the removal of manganese ion. Initial manganese concentration = 300 ppm, ion-exchanger dose = 2 g, solution volume = 100 ml, pH = 4 and t = 4 h.

Evaluating the free energy change ($\Delta G^\circ$) determines the spontaneous behaviour of the ion-exchange process [31,52]. The endothermic nature of the ion-exchange process is determined by calculating the enthalpy of reaction ($\Delta H^\circ$). While, the randomness (degree of disorder resulting from exchanging of ions) at the solid/solution interface is determined by estimating the entropy ($\Delta S^\circ$) [53]. The thermodynamic parameters were calculated using the distribution coefficient ($K_d$ ml/g) expressed by Equation 2 at different temperature.

$$K_d = \frac{(C_0 - C_{eq})*V}{(W*C_{eq})} \quad \text{Equation 2}$$

The Gibbs free energy change of the ion-exchange process was calculated using Equation 3:

$$\Delta G^\circ = -RT \ln K_d \quad \text{Equation 3}$$

The values of $\Delta G^\circ$ (kJ/mol) were calculated at different temperatures using the values of the distribution coefficient [30,53]. The Gibbs free energy change is related to the enthalpy ($\Delta H^\circ$) and the entropy ($\Delta S^\circ$) at any temperature using Equation 4:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad \text{Equation 4}$$
Thus, the values of enthalpy ($\Delta H^\circ$) and the entropy ($\Delta S^\circ$) can be calculated using the van’t Hoff equation (Equation 5):

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$$  \hspace{1cm} \text{Equation 5}

The values of $\Delta H^\circ$ (kJ/mol) and $\Delta S^\circ$ (kJ/mol.K) were calculated by plotting of $\ln K_d$ against $1/T$ [30,54–57]. Table 6 presents the results of $K_d$ and the thermodynamic parameters. The negative values of the Gibbs free energy increased with increasing temperature. This means that the ion-exchange process is spontaneous and the spontaneity of the ion-exchange process increases with increasing temperature which is thermodynamically favourable. The linear plots of $\ln K_d$ against $1/T$ to obtain $\Delta H^\circ$ and $\Delta S^\circ$ values are shown in Figure 10 and the results are shown in Table 6. The positive values of $\Delta H^\circ$ are attributed to the endothermic nature of the ion-exchange process of Mn$^{2+}$ ion. The positive value of $\Delta S^\circ$ implies increasing of the randomness at the ion-exchanger/solution interface film during the ion-exchange of Mn$^{2+}$ ion. Since, more of Mn$^{2+}$ ions replace the zeolites cations leads to more randomness in the system.

<table>
<thead>
<tr>
<th>Ion-exchanger material</th>
<th>T (K)</th>
<th>$K_d$ (ml/g)</th>
<th>$\Delta G^\circ$ (kJ/mol)</th>
<th>$\Delta H^\circ$ (kJ/mol)</th>
<th>$\Delta S^\circ$ (kJ/mol.K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>285</td>
<td>1474.076</td>
<td>-60.657</td>
<td>2.02</td>
<td>0.068</td>
</tr>
<tr>
<td></td>
<td>303</td>
<td>1582.986</td>
<td>-61.250</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>1629.744</td>
<td>-61.492</td>
<td></td>
<td></td>
</tr>
<tr>
<td>XC</td>
<td>285</td>
<td>902.2295</td>
<td>-56.576</td>
<td>4.33</td>
<td>0.072</td>
</tr>
<tr>
<td></td>
<td>303</td>
<td>1038.916</td>
<td>-57.749</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>1118.521</td>
<td>-58.362</td>
<td></td>
<td></td>
</tr>
<tr>
<td>XD</td>
<td>285</td>
<td>1044.736</td>
<td>-57.795</td>
<td>7.7</td>
<td>0.085</td>
</tr>
<tr>
<td></td>
<td>303</td>
<td>1311.739</td>
<td>-59.687</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>1530.919</td>
<td>-60.972</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
3.3 Equilibrium isotherm models

Conducting the equilibrium isotherm study is essential to calculate the maximum ion-exchange capacity and to optimize the ion-exchange process design. Ion-exchange isotherm model generally relates the mass of ion-exchange material with equilibrium concentration of ions in the solution at constant temperature [31,53]. The experimental data were fitted with Langmuir isotherm model, Freundlich isotherm model and Dubinin- Radushkevich (D-R) isotherm model [50]. The correlation factor ($R^2$) was used to indicate the validity of the model to the experimental data. The highest value of $R^2$ indicates a better fit of the model to the experimental data.

The Langmuir isotherm model assumes a monolayer coverage occurs at identical sites with homogeneous energy [28,58,59]. The linear form of Langmuir isotherm equation is expressed as [60]:

$$\frac{q_{eq}}{C_{eq}} = q_mK_L - K_Lq_{eq}$$  \hspace{1cm} \text{Equation 6}
Where \( q_{\text{eq}} \) (mg/g) is the amount of ion removed per a unit mass of ion-exchange material, \( C_{\text{eq}} \) (mg/l) is the equilibrium concentration of ion, \( q_m \) (mg/g) is Langmuir constant and it is the ultimate possible ion-exchange capacity and \( K_L \) (l/mg) is Langmuir constant representing the free energy of ion-exchange corresponds to the affinity between the ion and the surface of the ion-exchanger, respectively [61,62]. The values of \( q_m \) and \( K_L \) were obtained by plotting \( q_{\text{eq}}/C_{\text{eq}} \) against \( q_{\text{eq}} \), see Figure 11.

The Freundlich isotherm model assumes the uptake occurs at a multilayer sites with heterogeneous energy [63,64]. The linear form of Freundlich isotherm model is expressed as:

\[
\ln q_{\text{eq}} = \ln K_f + \left(\frac{1}{n}\right)\ln C_{\text{eq}} \tag{Equation 7}
\]

Where \( K_f \) (mg/g) is the Freundlich constant correlated with the ion-exchange capacity, and \( 1/n \) (unit less) is the Freundlich constant correlated with the intensity of the reaction and energy heterogeneity [61]. The values of \( K_f \) and \( 1/n \) were obtained by plotting \( \ln q_{\text{eq}} \) against \( \ln C_{\text{eq}} \), see Figure 12.

Dubinin-Radushkevitch (D-R) isotherm model can be used to explain both the adsorption on homogenous surfaces and on heterogeneous surfaces [61,63]. The linear form of the D–R isotherm is expressed as [28,61]:

\[
\ln q_{\text{eq}} = \ln X_m - K \varepsilon^2 \tag{Equation 8}
\]

\[
\varepsilon = RT \ln(1 + 1/C_{\text{eq}}) \tag{Equation 9}
\]

Where \( X_m \) (mg/g) is the maximum ion-exchange capacity, \( K \) (mol\(^2\)/kJ\(^2\)) is a constant associated to the ion-exchange energy, \( \varepsilon \) (kJ/mol) is the Polanyi potential, \( R \) (8.314 kJ/kmol.K) is gas law constant and \( T \) (K) is the absolute temperature [61,65]. The values of \( X_m \) and \( K \) were calculated by plotting \( \ln q_{\text{eq}} \) against \( \varepsilon^2 \), see Figure 13.
The calculated values of Langmuir isotherm constants, Freundlich isotherm constants, D-R isotherm constants and $R^2$ are presented in Table 7. Freundlich isotherm model was best fit to the experimental data. Freundlich isotherm model gave the highest correlation coefficients ($R^2$) in comparison with Langmuir and D–R. This result indicates heterogeneous ion-exchange sites on the surface of ion-exchange materials. The numerical value $1/n$ was < 1 which indicates high heterogeneous surface and high ion-exchange intensity at high ion concentrations.

**Figure 11**: Langmuir plots for ion-exchange of Mn$^{2+}$ ion showing bad agreement between the experimental data and Langmuir model.
Figure 12: Freundlich plots for ion-exchange of Mn$^{2+}$ ion showing good agreement between the experimental data and Freundlich model.

Figure 13: D-R plots for ion-exchange of Mn$^{2+}$ ion showing bad agreement between the experimental data and D-R model.
Table 7: The parameters obtained from Langmuir, Freundlich and D-R for Mn$^{2+}$ ion-exchange.

<table>
<thead>
<tr>
<th>Ion-exchanger material</th>
<th>Langmuir</th>
<th>Freundlich</th>
<th>D-R</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$q_m$ (mg/g)</td>
<td>$K_L$ (l/mg)</td>
<td>$R^2$</td>
</tr>
<tr>
<td>X</td>
<td>177</td>
<td>0.0444</td>
<td>0.6867</td>
</tr>
<tr>
<td>XC</td>
<td>134.49</td>
<td>0.0262</td>
<td>0.788</td>
</tr>
<tr>
<td>XD</td>
<td>133</td>
<td>0.0874</td>
<td>0.4948</td>
</tr>
</tbody>
</table>

3.4 Kinetic models of ion-exchange

Investigating of the rate of ion-exchange is an important to obtain kinetic parameters which are necessary for modelling and design the processes. The ion-exchange kinetics were investigated using pseudo first order and pseudo second order rate models [31,50].

The integrated form of pseudo first order rate equation is given as:

$$\log (q_{eq} - q_t) = \log q_{eq} - (K_1/2.303)t$$  \hspace{1cm} \text{Equation 10}

Where $q_t$ (mg/g) ion-exchange capacity at any time $t$ (min) and $K_1$ (min$^{-1}$) is the pseudo first order rate constant of the reaction. The values of $K_1$ and $q_{eq}$ were calculated by plotting of $\log (q_{eq} - q_t)$ against $t$ [27,66].

The pseudo second order model is typically used to correlate the experimental kinetic data when a chemical exchange, which involves valence forces by sharing or electrons exchange between solute and the ion-exchange material, determines the rate of a reaction [60,67]. The linear form of integrated pseudo second order kinetic equation is given as:

$$t/q_t = t/q_{eq} + 1/K_2 (q_{eq})^2$$  \hspace{1cm} \text{Equation 11}

Where, $K_2$ (g/mg.min) is the pseudo second order model rate constant. The values of $K_2$ and $q_{eq}$ were calculated by plotting of $t/q_t$ against $t$. 
Table 8: The parameters obtained from first and second order kinetics models.

<table>
<thead>
<tr>
<th>Ion-exchanger material</th>
<th>X</th>
<th>XC</th>
<th>XD</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>First order kinetics model</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$q_{eq}$(Theoretical) (mg/g)</td>
<td>34.99</td>
<td>55.46</td>
<td>17.865</td>
</tr>
<tr>
<td>$q_{eq}$(Experimental) (mg/g)</td>
<td>112.01</td>
<td>96.514</td>
<td>101.448</td>
</tr>
<tr>
<td>$K_1$ (min$^{-1}$)</td>
<td>$9.4 \times 10^{-3}$</td>
<td>$9 \times 10^{-3}$</td>
<td>$3.9 \times 10^{-3}$</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.9857</td>
<td>0.9958</td>
<td>0.7794</td>
</tr>
<tr>
<td><strong>Second order kinetics model</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$q_{eq}$(Theoretical) (mg/g)</td>
<td>114.94</td>
<td>103.1</td>
<td>103.1</td>
</tr>
<tr>
<td>$q_{eq}$(Experimental) (mg/g)</td>
<td>112.01</td>
<td>96.514</td>
<td>101.448</td>
</tr>
<tr>
<td>$K_2$ (g/mg.min)</td>
<td>$9.7 \times 10^{-4}$</td>
<td>$4.5 \times 10^{-4}$</td>
<td>$9.8 \times 10^{-4}$</td>
</tr>
<tr>
<td>$R^2$</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 8 shows that the highest values of correlation factor ($R^2 = 1$) were obtained for the pseudo second order model. However, the $R^2$ values obtained for the pseudo first order model were 0.7794-0.9958. Also, the theoretical values of $q_{eq}$ calculated according to pseudo second order model were significantly close to the experimental values ($q_{eq}$(Experimental)). While, $q_{eq}$(Theoretical) calculated using pseudo first order model were significantly different from $q_{eq}$(Experimental). These results indicate that the pseudo second order model is more suitable than pseudo first order model to describe the ion-exchange of Mn$^{2+}$ ion by zeolite X and its composites. The good match with the second order kinetics model indicates that a chemical reaction related to valence forces could be the rate determining step of the ion exchange process [27].

3.4 The rate limiting steps

The rate limiting step for the batch ion-exchange system under homogenous mixing could be one of these steps: film diffusion, intra-particle diffusion, ion-exchange reaction or could be mix of these steps. The Weber and Morris intra-particle diffusion model is used when the rate limiting step is a combination of film diffusion and intra-particle mechanisms [68,69]:
\[ q_t = K_i t^{1/2} + C \]  

Equation 12

Where \( K_i \) (mg/g.min\(^{1/2}\)) is the rate constant of intra-particle diffusion and \( C \) is a constant (mg/g) related to the thickness of the boundary layer. The large value of \( C \) means more contribution of boundary layer in the rate controlling step [38,63]. The values of \( K_i \) and \( C \) were calculated by plotting of \( q_t \) against \( t^{1/2} \), see Figure 14.

In addition, it was assumed that the rate of ion exchange is controlled by the chemical exchange if there is a linear relationship between log \((1-q_t/q_\infty)\) and time (Figure 15). \( q_\infty \) (mg/g) is the ion-exchange capacity at equilibrium i.e. \( q_{eq} \) (see Figure 15) [60,70,71].

The calculated values of \( K_i \) and \( C \) are shown in Table 9. The plots of \( q_t \) against \( t^{1/2} \) for ion-exchange of Mn\(^{2+}\) ion show nonlinear relation contains more than one linear zone with large values of \( C \). The obtained results refer to that the rate determining step of the ion-exchange reaction is limited by boundary layer diffusion (which represents the first linear stage of the linear correlation) and the intra-particle diffusion (which represents the second linear stage of the linear correlation). \( C \) value of pure zeolite X was larger than this for the composites, since it was significantly reduced when composites were used for ion-exchange process. The value of the rate constant of intra-particle diffusion (\( K_i \)) considerably increased when composites were applied for Mn\(^{2+}\) ion removal. The reason behind this result is that thickness of the external liquid film or the boundary layer decreased when the ion-exchange materials were prepared in form of composite using meso/macroporous supports and the diffusion of ions to the active sites becomes rapid (high \( K_i \) values of composites) which means that the length of diffusion path was reduced.

Moreover, the plots of log \((1 - q_t/q_\infty)\) against \( t \) show a linear relation and high values of \( R^2 \) (0.9681-0.9996). These results refer to that the significant rate determining step is the ion-exchange reaction over zeolite active sites. Thus, the overall ion-exchange rate is
controlled by a combination of the ion-exchange reaction of Mn\(^{2+}\) ion, the boundary layer diffusion and the intra-particle diffusion, but the utilization of composites in the ion-exchange process makes the effect of the last two steps less effective on the overall rate of ion-exchange process.

**Figure 14:** Intra-particle diffusion plots for ion-exchange of Mn\(^{2+}\) ion show step 1 referring to the boundary layer diffusion and step 2 referring to the intra-particle diffusion.

**Figure 15:** Rate limiting rate plots for ion-exchange of Mn\(^{2+}\) ion.
Table 9: Intra-particle diffusion model parameters obtained for Mn$^{2+}$ ion-exchange.

<table>
<thead>
<tr>
<th>Ion-exchanger material</th>
<th>X</th>
<th>XC</th>
<th>XD</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_i$ (mg/g.min$^{1/2}$)</td>
<td>1.5065</td>
<td>2.5882</td>
<td>2.0124</td>
</tr>
<tr>
<td>C (mg/g)</td>
<td>88.773</td>
<td>56.594</td>
<td>72.126</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.9835</td>
<td>0.9976</td>
<td>0.9713</td>
</tr>
</tbody>
</table>

3.5 Solidification of the spent zeolite

3.5.1 Vitrification

Figure 16 shows samples of zeolite ion-exchange materials used for manganese removal before and after vitrification process. The powder samples converted to hard glass products with a brown pigment because of a reaction happened between aluminate and manganese ions at elevated temperature.

![Zeolite ion-exchange materials before and after vitrification](image)

The characterization was focused on the solution because the major concern of this work is elimination the leaching of metal ions to the environment. The samples resulted from vitrification process were examined for leaching of manganese ion by immersing in water...
and NaCl solution and the results are shown in Table 10. The results showed releasing manganese ions with insignificant concentrations ~ 0.4 ppm. The samples of ion-exchange materials before vitrification released higher concentration of manganese ion and the concentration increased with time. Non-vitrified samples released more manganese ion when immersed in NaOH solution. Therefore, direct disposal of the ion-exchange materials used for harmful elements to the environment without treatment allows continual escaping the harmful ions to the environment. Vitrification process immobilizes the harmful ions and stops ions releasing to the environment. Also, it diminishes the size of waste sludge. Table 11 shows the weight of ion-exchange materials after vitrification process was significantly reduced. Especially, when zeolite/carbon composite was vitrified, its weight becomes significantly smaller than pure zeolite and zeolite/diatomite composite. This is because the carbon involved in the composites turns to CO$_2$. Thus, it can be said that zeolite/carbon composites enhance the mass transfer and the ion-exchange performance, reduce the weight of zeolite required for a given process and consequently diminish the waste size when are vitrified. When zeolite/diatomite composites are vitrified, they produce larger volume products than zeolite/carbon composites produce; because diatomite skeleton is formed of silica and it does not convert to gas when it is heated at elevated temperatures.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Concentration of Mn$^{2+}$ ion leached to the solutions (ppm) after one month</th>
<th>Concentration of Mn$^{2+}$ ion leached to the solutions (ppm) after six months</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H$_2$O</td>
<td>0.1 M NaCl solution</td>
</tr>
<tr>
<td>Spent ion-exchangers before any treatment</td>
<td>0.068-1.76</td>
<td>7.796-116.5</td>
</tr>
<tr>
<td>Vitrified samples</td>
<td>0-0.13</td>
<td>0-0.335</td>
</tr>
</tbody>
</table>

Table 10: Concentration of Mn$^{2+}$ ion leached to water and 0.1 M NaCl solution before and after encapsulation with vitrification.
Table 11: Weight of the vitrified spent zeolitic material per 1 g of the material before vitrification process.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Zeolite X</th>
<th>Zeolite X/carbon</th>
<th>Zeolite X/diatomite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight of the vitrified material (g) per 1 g of the material before vitrification</td>
<td>0.736</td>
<td>0.275</td>
<td>0.789</td>
</tr>
</tbody>
</table>

3.5.2 Geopolymerization

Figure 17 shows samples of spent ion-exchange materials solidified by geopolymers. The concentrations of Mn^{2+} ion escaped from the solidified materials are shown in Table 12. There detected concentrations of manganese ion leached to water and NaCl solution are negligible. But, the concentrations of manganese ion leached from geopolymers to H_2SO_4 solution were < 5 ppm after six months. Therefore, geopolymerization technique allows less energy used for successful immobilization of the harmful ions in spite of it converts the waste material into larger volume product.

![Figure 17: Zeolite ion-exchange materials after ion-exchange with manganese ion treated with geopolymers made of kaolin, fly ash and 50% kaolin - 50% fly ash. The samples from left to right are: X, XC and XD.](image-url)
Table 12: Concentration of Mn$^{2+}$ ions leached to water, 0.1 M NaCl solution and 0.25 M H$_2$SO$_4$ from samples encapsulated with geopolymers.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Concentration of Mn$^{2+}$ ions leached to the solutions (ppm) after one month</th>
<th>Concentration of Mn$^{2+}$ ions leached to the solutions (ppm) after six months</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O</td>
<td>0.1 M NaCl solution</td>
<td>0.25 M H$_2$SO$_4$ solution</td>
</tr>
<tr>
<td>Samples encapsulated with kaolin geopolymer</td>
<td>0.02-0.16</td>
<td>1.64-2.266</td>
</tr>
<tr>
<td>Samples encapsulated with fly ash geopolymer</td>
<td>0.07-0.45</td>
<td>1.64-2.26</td>
</tr>
<tr>
<td>Samples encapsulated with 50% kaolin - 50% fly ash geopolymer</td>
<td>0.1-0.27</td>
<td>2.65-3.88</td>
</tr>
</tbody>
</table>

4. Conclusion

In the present work, the zeolite X/carbon composite and zeolite X/diatomite composite were successfully prepared by a hydrothermal treatment. Zeolite X layer coating porous supports showed perfect attachment even when the composites were used in the ion-exchange process for Mn$^{2+}$ ion removal. All X, XC and XD showed interesting ability for manganese removal. The performance of ion-exchange materials for ion-exchange process showed the following order: XD > XC > X when the ion-exchange capacity was calculated based on the weight of zeolite present in the composites. Mn$^{2+}$ ion removal was affected by initial ion concentration, temperature and pH of manganese solution. A study of thermodynamic parameters displayed that the ion-exchange reaction of Mn$^{2+}$ ions is a spontaneous and endothermic. For all ion-exchange materials, the Freundlich isotherm model successfully agreed with the experimental data of Mn$^{2+}$ ion removal by the ion-exchange process. The kinetic study of the ion-exchange process indicated that the pseudo second order model significantly described the experimental data. The overall ion-exchange process of Mn$^{2+}$ ions is determined by a combination of ion-exchange reaction and less of both boundary layer film and intra-particle...
diffusion. Appling of composites in the ion-exchange process reduced the effect of boundary layer film and intra-particle diffusion on the overall rate of ion-exchange reaction. Encapsulation of Mn$^{2+}$ ion was successfully conducted by vitrification at 1200°C and geopolymerization. Vitrification process resulted in smaller volume solid product than geopolymerization in spite of vitrification requires more energy than required for geopolymerization.

Acknowledgement

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