

Investigation on the Effect of the Cation Counterion used on the Ion Exchange Efficiency with HZSM-5

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Abstract

In this project the efficiency of the ion exchange process of HZSM-5 with copper and zinc cations was investigated. The method utilised was found to be ineffective at the completion of this aim and no meaningful conclusions could be drawn from the data collected.

1 Aim

This project aimed to investigate how the efficiency of the ion exchange process is effected by the cation being exchanged. Specifically a comparison between the copper and zinc cation exchange processes of an HZSM-5 zeolite was attempted.

2 Introduction

Zeolites are crystalline, microporous solids used for a large number of purposes such as for catalytic cracking, air purification, water softening and desiccants.^{1,2} This project was completed using the ZSM-5 (Zeolite Socony Mobil-5)³ zeolite which has important uses in the petrochemical industry such as for the conversion of methanol to gasoline, dewaxing of distillates, separation of organic products (such as separating para-xylene from its isomers), the interconversion of hydrocarbons.⁴⁻⁶

2.1 Structure

Each zeolite is comprised of a finite or infinite number of unique unit cells each of which is made from a constant, integral number of the same type of secondary building unit (SBU) with each vertex in the SBU being a tetrahedron of either $[\text{SiO}_4]$ or $[\text{AlO}_4]^-$ (which are themselves the primary building units).^{2,7-10} Each aluminium tetrahedron in a SBU introduces a negative charge – since aluminium has a 3+ oxidation state compared the 4+

oxidation state of silicon – which is balanced by the presence of cationic counterions.^{2,9-11} The ZSM-5 zeolite used is a pentasil^{4,10} zeolite (constructed of eight five-membered rings) with an SBU containing twelve AO_4 tetrahedra which form a pair of five-one units^{4,7,12} as shown in figure 1 (A-O-A bridges are shown as straight lines to increase the clarity of the images and since the A-O-A bond angle is around $140-150^\circ \approx 180^\circ$ for silicas and aluminosilicates and the A atoms are represented by the vertices).⁷

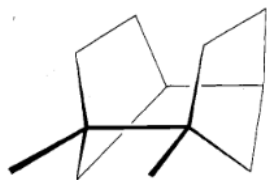


Figure 1: Secondary building unit for ZSM-5 zeolite.⁴

These SBUs then form long chains (figure 2) which then themselves interconnect to form layers hence giving a unit cell containing eight SBUs figure 3.⁴ In 3 one of the chains (shown in figure 2) is highlighted to demonstrate how the chains interconnect to form layers.



Figure 2: Chain building unit for ZSM-5 zeolite.⁴

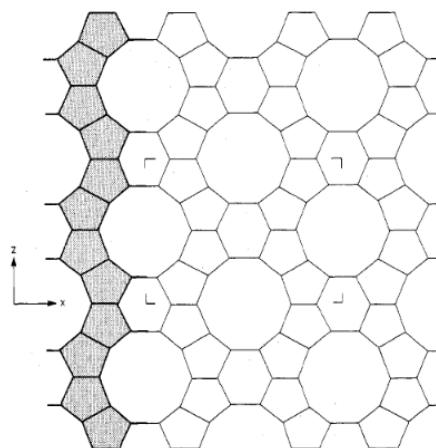


Figure 3: Layer of ZSM-5 zeolite.⁴

Since there are eight SBUs of twelve tetrahedra per unit cell there are $8 \times 12 = 96$ A atoms and there are two oxygen atoms per individual A atom in the cell¹³ so per unit

cell there are $2 \times 96 = 192$ oxygen atoms.⁷ This gives the unit cell formula given in 2.1.1 where X is a cation with a charge of q , hence $\frac{1}{q}$ of these cations are required per negative charge.¹⁴



2.2 Ion-Exchange

These X^{q+} cations can be exchanged with other ions in a process called ion-exchange. Changing the counterion of the ZSM-5 zeolite can alter the acidity, hydrophobicity, reaction selectivity and other properties of the zeolite.^{5,9,15}

The copper exchanged form of ZSM-5 is known to be one of the best forms of ZSM-5 for the selective catalytic reduction of NO by C₂–C₄ hydrocarbons.^{14,16,17} This is an important use case since large amounts of NO are produced in vehicle and industrial boiler emissions and NO is known to cause air pollution and acid rain.¹⁸

Similarly the zinc exchanged form of ZSM-5 is currently subject to much research since it has been found to be effective at selectively converting methanol to use aromatic species such as benzene, toluene and xylene (important for the manufacture of polyester fibers, dyes, pesticides and medicines) as an alternative method to petroleum processing.^{19,20} Specifically ZnZSM-5 has – so far – been the best choice of cation for this purpose since it is cheap, non-toxic and highly effective at the aforementioned aromatization process.²¹

A ZSM-5 zeolite with a SiO₂/AlO₃ ratio of 23 was used since this maximised the number of sites which were available for ion-exchange due to the higher aluminium content. In addition this increased the efficiency of the ion-exchange process since zeolites with a high Si/Al ratio are hydrophobic^{9,22,23} hence the cation solution does not spontaneously enter the zeolite nanopores so ion-exchange happens only at sites close to the pore entrance.^{9,23} This will thus reduce the percentage uncertainties in the values recorded.

3 Experimental

Standard solutions of Cu²⁺ and Zn²⁺ (50.00 cm³) were made using CuSO₄ · 5 H₂O and ZnSO₄ · 7 H₂O with concentration $2.008 \times 10^{-3} \text{ mol dm}^{-3}$ and $2.02 \times 10^{-3} \text{ mol dm}^{-3}$ respectively. The absorbance of the standard copper sulphate solution was taken at 806 nm (0.484) then 20.00 cm³ of the standard solutions were added to 0.4810 g (for the copper solution) and 0.5274 g (for the zinc solution) of HZSM-5 zeolite with an AlO₃:SiO₂ ratio of 23 – forming an opaque white suspension – before heating both solutions (with stirring) at 70 °C for one hour. Centrifugation was completed on part of the resultant copper mixture, however time constraints prevented the completion of this process. The

two mixtures were thus stored in a fridge for one week until the following laboratory session.

After one week the zeolite had settled in the bottom of the solutions. The clear solution was decanted and the remainder was centrifuged for 30 minutes before the supernatant was reintroduced to the initially decanted solution producing a slightly cloudy copper solution and a moderately cloudy zinc solution. The solutions were made up to 100.00 cm³ before the absorbance of the copper solution at 806 nm was determined (0.110) and 20.00 cm³ aliquots of the zinc solution was titrated against a standard EDTA solution (batch A: 0.4993 mol dm⁻³) with 2 cm³ of a pH 10 buffer solution and eriochrome black T as the indicator (colour change from red to light blue).

4 Results

4.1 Copper-Exchanged Zeolite

Table 1: Masses used in CuZSM-5 preparation.

Substance	Mass / g
CuSO ₄ · 5 H ₂ O	0.5014
HZSM-5	0.4810

Table 2: Spectrophotometric results.

Substance	Absorbance
Standard Solution	0.484
Post-Reaction Solution	0.110

4.2 Zinc-Exchanged Zeolite

Table 3: Masses used in preparation of ZnSO₄ standard solution.

Substance	Mass / g
ZnSO ₄ · 7 H ₂ O	0.4587

The reaction which occurred during the titrations between the EDTA and Zn²⁺ ions is given in equation 4.2.1.



Due to time constraints the standardisation of the EDTA solution was not fully completed, hence the accurate titre volume ($V_{\text{EDTA, std.}}$) has been assumed to be the titre

Table 4: Masses used in ZnZSM-5 preparation.

Substance	Mass / g
ZnSO ₄ · 7 H ₂ O	0.6331
HZSM-5	0.5274

Table 5: Titration results from standardisation of EDTA solution with standard zinc sulphate solution.

Run	Start Volume / cm ³	End Volume / cm ³	Titre Volume / cm ³
1	1.45	33.70	32.25
2	2.25	34.20	31.95

volume from the second titre (see table 5) in the absence of additional available titrations to confirm this.

$$V_{\text{EDTA}_{std.}} = 31.95 \text{ cm}^3 \quad (4.2.2)$$

The average titre volume for the titration with the post ion-exchange solution ($V_{\text{EDTA}_{prod.}}$) was determined from the second and third runs (see table 6) since the first run was a rough titration and the fourth run can be clearly seen be be anomalous.

$$V_{\text{EDTA}_{prod.}} = \frac{26.65 \text{ cm}^3 + 26.60 \text{ cm}^3}{2} = 20.63 \text{ cm}^3 \quad (4.2.3)$$

5 Calculations

5.1 Calculation of Maximum Theoretical Number of Ion Exchanges

The SiO₂/Al₂O₃ ratio in the zeolite used was 23. In this ratio there are two Al atoms per Si, so Si/Al = $\frac{23}{2} = 11.5$.

Table 6: Titration results between zinc solution after ion-exchange process and standardised EDTA solution.

Run	Start Volume / cm ³	End Volume / cm ³	Titre Volume / cm ³
1	2.40	29.10	26.70
2	2.90	29.55	26.65
3	1.40	28.00	26.60
4	11.35	37.70	26.35

Using the unit cell general formula (equation 2.1.1) letting the Si/Al ratio be r and with n being the number of aluminium atoms per unit cell:

$$r = \frac{\text{Number of Si per unit cell}}{\text{Number of Al per unit cell}} = \frac{96 - n}{n}$$

$$nr + n = 96$$

$$\therefore n = \frac{96}{r + 1}$$

Hence for $r = 11.5$ there are $n = \frac{96}{11.5+1} = 7.68$ Al per unit cell. Letting q be the cation charge and x be the number of water molecules for unit cell:

$$Mr_{\text{unit cell}} = \frac{7.68}{q} Mr_{\text{cation}} + (11.5(26.982) + (96 - 7.68)(28.085) + 192(15.999) + x(2(1.008) + 15.999)) \text{g mol}^{-1}$$

$$= \frac{7.68}{q} Mr_{\text{cation}} + 5759.4692 \text{g mol}^{-1} + x(450.375 \text{g mol}^{-1})$$

Thus for HZSM-5 where the cation is H^+ and $x \approx 25$.²⁴

$$Mr_{\text{HZSM-5 unit cell}} = \frac{7.68}{1} \times 1.008 \text{g mol}^{-1} + (5759.4692 + 25(450.375)) \text{g mol}^{-1}$$

$$= 6217.6134 \text{g mol}^{-1}$$
(5.1.1)

Let: q be the cation charge; $n_{\text{max. cation}}$ be the theoretical maximum amount of cation which can be exchanged and n_{cation} , m_{cation} and Mr_{cation} be the actual amount, mass and Mr of the cation exchanged respectively.

$$n_{\text{HZSM-5 unit cell}} = \frac{m_{\text{HZSM-5}}}{Mr_{\text{HZSM-5 unit cell}}}$$

$$n_{\text{max. cation}} = \frac{7.68}{q} n_{\text{HZSM-5 unit cell}}$$

$$= \frac{7.68}{q} \frac{m_{\text{HZSM-5}}}{Mr_{\text{HZSM-5 unit cell}}}$$

$$\% \text{ Exchanged} = \frac{n_{\text{cation}}}{n_{\text{max. cation}}} \times 100 \%$$

$$= \frac{q Mr_{\text{HZSM-5 unit cell}} n_{\text{cation}}}{7.68 m_{\text{HZSM-5}}} \times 100 \%$$
(5.1.2)

5.2 Calculations for Copper Solution

5.2.1 Determination of Molar Extinction Coefficient

Let $V_{\text{Cu}_{\text{std.}}}$ be the volume and $[\text{CuSO}_4]_{\text{std.}}$ be the concentration of the standard Cu^{2+} solution.

$$\begin{aligned}n_{\text{CuSO}_4} &= \frac{m_{\text{CuSO}_4 \cdot 5\text{H}_2\text{O}}}{Mr_{\text{CuSO}_4 \cdot 5\text{H}_2\text{O}}} \\ [\text{CuSO}_4]_{\text{std.}} &= \frac{n_{\text{CuSO}_4}}{V_{\text{Cu}_{\text{std.}}}} \\ &= \frac{m_{\text{CuSO}_4 \cdot 5\text{H}_2\text{O}}}{V_{\text{Cu}_{\text{std.}}} Mr_{\text{CuSO}_4 \cdot 5\text{H}_2\text{O}}\end{aligned}\quad (5.2.1)$$

Rearranging the Beer-Lambert law (equation 5.2.2) for the molar extinction coefficient:

$$A = \epsilon cl \quad (5.2.2)$$

$$\epsilon = \frac{A}{cl} \quad (5.2.3)$$

Hence using equations 5.2.1 and 5.2.3 with $A_{\text{Cu}_{\text{std.}}}$ being the absorbance of the standard CuSO_4 solution:

$$\begin{aligned}\epsilon_{\text{CuSO}_4} &= \frac{A_{\text{Cu}_{\text{std.}}}}{[\text{CuSO}_4]_{\text{std.}} l} \\ &= \frac{A_{\text{Cu}_{\text{std.}}} V_{\text{Cu}_{\text{std.}}} Mr_{\text{CuSO}_4 \cdot 5\text{H}_2\text{O}}{l m_{\text{CuSO}_4 \cdot 5\text{H}_2\text{O}}}\end{aligned}\quad (5.2.4)$$

This hence gives:

$$\begin{aligned}\epsilon_{\text{CuSO}_4} &= \frac{0.484 \times 50.00 \times 10^{-3} \text{ dm}^3 \times (63.546 + 32.066 + 4(15.999) + 5(2(1.008) + 15.999)) \text{ g mol}^{-1}}{1.0 \text{ cm} \times 0.5014 \text{ g}} \\ &= \frac{0.484 \times 50.00 \times 10^{-3} \text{ dm}^3 \times 249.677 \text{ g mol}^{-1}}{1.0 \text{ cm} \times 0.5014 \text{ g}} = 12.05 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}\end{aligned}\quad (5.2.5)$$

5.2.2 Determination of Percentage of Cu^{2+} Exchanged Compared to the Theoretical Maximum

By rearranging the Beer-Lambert Law (equation 5.2.2) for concentration:

$$c = \frac{A}{\epsilon l} \quad (5.2.6)$$

Letting $[\text{CuSO}_4]_{\text{prod.}}$ be the concentration, $A_{\text{Cu}_{\text{prod.}}}$ be the absorbance, $n_{\text{Cu}_{\text{prod.}}}$ be the amount of Cu^{2+} ions and $V_{\text{Cu}_{\text{prod.}}}$ be the volume of the solution after the ion-exchange reaction while using equation 5.2.6:

$$\begin{aligned} [\text{CuSO}_4]_{\text{prod.}} &= \frac{A_{\text{Cu}_{\text{prod.}}}}{\epsilon_{\text{CuSO}_4} l} \\ n_{\text{Cu}_{\text{prod.}}} &= [\text{CuSO}_4]_{\text{prod.}} V_{\text{Cu}_{\text{prod.}}} \\ &= \frac{A_{\text{Cu}_{\text{prod.}}} V_{\text{Cu}_{\text{prod.}}}}{\epsilon_{\text{CuSO}_4} l} \end{aligned} \quad (5.2.7)$$

Substituting equation 5.2.4 into 5.2.7:

$$n_{\text{Cu}_{\text{prod.}}} = \frac{A_{\text{Cu}_{\text{prod.}}} V_{\text{Cu}_{\text{prod.}}} m_{\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}}{A_{\text{Cu}_{\text{std.}}} V_{\text{Cu}_{\text{std.}}} Mr_{\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}} \quad (5.2.8)$$

Using equations 5.2.1 and 5.2.8 to determine the amount of copper which was exchanged into the zeolite ($n_{\text{Cu}_{\text{ex.}}}$) letting $V_{\text{Cu}_{\text{react.}}}$ be the volume of the standard solution added to the HZSM-5.

$$\begin{aligned} n_{\text{Cu}_{\text{ex.}}} &= [\text{CuSO}_4] V_{\text{Cu}_{\text{react.}}} - n_{\text{Cu}_{\text{prod.}}} \\ &= \frac{m_{\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}} V_{\text{Cu}_{\text{react.}}}}{V_{\text{Cu}_{\text{std.}}} Mr_{\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}}} - \frac{A_{\text{Cu}_{\text{prod.}}} V_{\text{Cu}_{\text{prod.}}} m_{\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}}}{A_{\text{Cu}_{\text{std.}}} V_{\text{Cu}_{\text{std.}}} Mr_{\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}}} \\ &= \frac{m_{\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}} (A_{\text{Cu}_{\text{std.}}} V_{\text{Cu}_{\text{react.}}} - A_{\text{Cu}_{\text{prod.}}} V_{\text{Cu}_{\text{prod.}}})}{A_{\text{Cu}_{\text{std.}}} V_{\text{Cu}_{\text{std.}}} Mr_{\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}}} \end{aligned} \quad (5.2.9)$$

Substituting equation 5.2.9 into equation 5.1.2 and setting $q = 2$ hence gives:

$$\% \text{ Cu}^{2+} \text{ Exchanged} = \frac{2Mr_{\text{HZSM-5 unit cell}} m_{\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}} (A_{\text{Cu}_{\text{std.}}} V_{\text{Cu}_{\text{react.}}} - A_{\text{Cu}_{\text{prod.}}} V_{\text{Cu}_{\text{prod.}}})}{7.68m_{\text{HZSM-5}} A_{\text{Cu}_{\text{std.}}} V_{\text{Cu}_{\text{std.}}} Mr_{\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}}} \times 100 \% \quad (5.2.10)$$

Using 5.2.10 with:

$Mr_{\text{HZSM-5 unit cell}} = 6217.6134 \text{ g mol}^{-1}$ from equation 5.1.1

$m_{\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}} = 0.50140 \pm 0.00005 \text{ g}$ from table 1

$A_{\text{Cu}_{\text{std.}}} = 0.484$ from table 2

$V_{\text{Cu}_{\text{react.}}} = 20.00 \pm 0.06 \times 10^{-3} \text{ dm}^3$ from method (section 3)

$A_{\text{Cu}_{\text{prod.}}} = 0.110$ from table 2

$V_{\text{Cu}_{\text{prod.}}} = 100.00 \pm 0.20 \times 10^{-3} \text{ dm}^3$ from method (section 3)

$m_{\text{HZSM-5}} = 0.48100 \pm 0.00005 \text{ g}$ from table 1

$V_{\text{Cu}_{\text{std.}}} = 50.00 \pm 0.06 \times 10^{-3} \text{ dm}^3$ from method (section 3)

$Mr_{\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}} = 249.577 \text{ g mol}^{-1}$ from equation 5.2.5

$$\begin{aligned} \% \text{ Cu}^{2+} \text{ Exchanged} &= \frac{2 \times 6217.6134 \text{ g mol}^{-1} \times 0.50140 \text{ g} (0.484 \times 20.00 - 0.110 \times 100.00) 10^{-3} \text{ dm}^3}{7.68 \times 0.4810 \text{ g} \times 0.484 \times 50.00 \times 10^{-3} \text{ dm}^3 \times 249.577 \text{ g mol}^{-1}} \\ &\quad \times 100 \% \\ &= -18 \% \end{aligned}$$

5.2.3 Error Propagation

Let the percentage of Cu^{2+} exchanged be v_{Cu} in the error propagation below:

$$\begin{aligned} \delta v_{\text{Cu}} = v_{\text{Cu}} &\left(\left(\frac{\delta Mr_{\text{HZSM-5 unit cell}}}{Mr_{\text{HZSM-5 unit cell}}} \right)^2 + \left(\frac{\delta m_{\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}}}{m_{\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}}} \right)^2 + \left(\frac{\delta (A_{\text{Cu}_{\text{std.}}} V_{\text{Cu}_{\text{react.}}} - A_{\text{Cu}_{\text{prod.}}} V_{\text{Cu}_{\text{prod.}}})}{A_{\text{Cu}_{\text{std.}}} V_{\text{Cu}_{\text{react.}}} - A_{\text{Cu}_{\text{prod.}}} V_{\text{Cu}_{\text{prod.}}}} \right)^2 \right. \\ &\quad \left. + \left(\frac{\delta m_{\text{HZSM-5}}}{m_{\text{HZSM-5}}} \right)^2 + \left(\frac{\delta A_{\text{Cu}_{\text{std.}}}}{A_{\text{Cu}_{\text{std.}}}} \right)^2 + \left(\frac{\delta V_{\text{Cu}_{\text{std.}}}}{V_{\text{Cu}_{\text{std.}}}} \right)^2 + \left(\frac{\delta Mr_{\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}}}{Mr_{\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}}} \right)^2 \right)^{1/2} \end{aligned} \quad (5.2.11)$$

Let $S = A_{\text{Cu}_{\text{std.}}} V_{\text{Cu}_{\text{react.}}} - A_{\text{Cu}_{\text{prod.}}} V_{\text{Cu}_{\text{prod.}}}$, thus:

$$\begin{aligned}
\delta S &= \left((\delta (A_{\text{Cu}_{\text{std.}}} V_{\text{Cu}_{\text{react.}}}))^2 + (\delta (A_{\text{Cu}_{\text{prod.}}} V_{\text{Cu}_{\text{prod.}}}))^2 \right)^{1/2} \\
&= \left(\left(A_{\text{Cu}_{\text{std.}}} V_{\text{Cu}_{\text{react.}}} \left(\left(\frac{\delta A_{\text{Cu}_{\text{std.}}}}{A_{\text{Cu}_{\text{std.}}}} \right)^2 + \left(\frac{\delta V_{\text{Cu}_{\text{react.}}}}{V_{\text{Cu}_{\text{react.}}}} \right)^2 \right)^{1/2} \right)^2 \right. \\
&\quad \left. + \left(A_{\text{Cu}_{\text{prod.}}} V_{\text{Cu}_{\text{prod.}}} \left(\left(\frac{\delta A_{\text{Cu}_{\text{prod.}}}}{A_{\text{Cu}_{\text{prod.}}}} \right)^2 + \left(\frac{\delta V_{\text{Cu}_{\text{prod.}}}}{V_{\text{Cu}_{\text{prod.}}}} \right)^2 \right)^{1/2} \right)^2 \right)^{1/2} \\
&= \left(A_{\text{Cu}_{\text{std.}}}^2 V_{\text{Cu}_{\text{react.}}}^2 \left(\left(\frac{\delta A_{\text{Cu}_{\text{std.}}}}{A_{\text{Cu}_{\text{std.}}}} \right)^2 + \left(\frac{\delta V_{\text{Cu}_{\text{react.}}}}{V_{\text{Cu}_{\text{react.}}}} \right)^2 \right) \right. \\
&\quad \left. + A_{\text{Cu}_{\text{prod.}}}^2 V_{\text{Cu}_{\text{prod.}}}^2 \left(\left(\frac{\delta A_{\text{Cu}_{\text{prod.}}}}{A_{\text{Cu}_{\text{prod.}}}} \right)^2 + \left(\frac{\delta V_{\text{Cu}_{\text{prod.}}}}{V_{\text{Cu}_{\text{prod.}}}} \right)^2 \right) \right)^{1/2} \tag{5.2.12}
\end{aligned}$$

Hence substituting equation 5.2.12 into 5.2.11 gives:

$$\begin{aligned}
\delta v_{\text{Cu}} &= v_{\text{Cu}} \left(\left(\frac{\delta Mr_{\text{HZSM-5 unit cell}}}{Mr_{\text{HZSM-5 unit cell}}} \right)^2 + \left(\frac{\delta m_{\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}}}{m_{\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}}} \right)^2 \right. \\
&\quad \left. + \frac{A_{\text{Cu}_{\text{std.}}}^2 V_{\text{Cu}_{\text{react.}}}^2 \left(\left(\frac{\delta A_{\text{Cu}_{\text{std.}}}}{A_{\text{Cu}_{\text{std.}}}} \right)^2 + \left(\frac{\delta V_{\text{Cu}_{\text{react.}}}}{V_{\text{Cu}_{\text{react.}}}} \right)^2 \right) + A_{\text{Cu}_{\text{prod.}}}^2 V_{\text{Cu}_{\text{prod.}}}^2 \left(\left(\frac{\delta A_{\text{Cu}_{\text{prod.}}}}{A_{\text{Cu}_{\text{prod.}}}} \right)^2 + \left(\frac{\delta V_{\text{Cu}_{\text{prod.}}}}{V_{\text{Cu}_{\text{prod.}}}} \right)^2 \right)}{(A_{\text{Cu}_{\text{std.}}} V_{\text{Cu}_{\text{react.}}} - A_{\text{Cu}_{\text{prod.}}} V_{\text{Cu}_{\text{prod.}}})^2} \right. \\
&\quad \left. + \left(\frac{\delta m_{\text{HZSM-5}}}{m_{\text{HZSM-5}}} \right)^2 + \left(\frac{\delta A_{\text{Cu}_{\text{std.}}}}{A_{\text{Cu}_{\text{std.}}}} \right)^2 + \left(\frac{\delta V_{\text{Cu}_{\text{std.}}}}{V_{\text{Cu}_{\text{std.}}}} \right)^2 + \left(\frac{\delta Mr_{\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}}}{Mr_{\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}}} \right)^2 \right)^{1/2} \tag{5.2.13}
\end{aligned}$$

Substituting values into equation 5.2.13 thus yields:

$$\delta v_{\text{Cu}} = \pm 0.00 \%$$

So the percentage of Cu^{2+} exchanged is $-18 \pm \%$.

5.3 Calculation of Ion-Exchange Efficiency for Zinc Solution

5.3.1 Standardisation of EDTA Solution (Batch A)

Letting $V_{\text{Zn}_{\text{std.}}}$ be the volume, $[\text{ZnSO}_4]_{\text{std.}}$ be the concentration and $m_{\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}_{\text{std.}}}$ be the mass of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ used for the preparation of the ZnSO_4 standard solution used to standardise the EDTA solution.

$$[\text{ZnSO}_4]_{\text{std.}} = \frac{m_{\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}_{\text{std.}}}}{Mr_{\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}} V_{\text{Zn}_{\text{std.}}}} \quad (5.3.1)$$

From equation 4.2.1 there is a 1:1 stoichiometric ratio between the Zn^{2+} and EDTA^{4-} ions hence letting $[\text{EDTA}^{4-}]$ be the concentration of the EDTA solution $n_{\text{Zn}_{\text{std. analyte}}}$ be the amount and $V_{\text{Zn}_{\text{std. aliquot}}}$ be the volume of Zn^{2+} ions in the analyte.

$$[\text{EDTA}^{4-}] = \frac{n_{\text{Zn}_{\text{std. analyte}}}}{V_{\text{EDTA}_{\text{std.}}}} = \frac{[\text{ZnSO}_4]_{\text{std.}} V_{\text{Zn}_{\text{std. aliquot}}}}{V_{\text{EDTA}_{\text{std.}}}} \quad (5.3.2)$$

Thus substituting equation 5.3.1 into equation 5.3.2 gives:

$$[\text{EDTA}^{4-}] = \frac{m_{\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}_{\text{std.}}} V_{\text{Zn}_{\text{std. aliquot}}}}{Mr_{\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}} V_{\text{Zn}_{\text{std.}}} V_{\text{EDTA}_{\text{std.}}}} \quad (5.3.3)$$

5.3.2 Determination of Percentage of Zn^{2+} Exchanged Compared to the Theoretical Maximum

Let $[\text{ZnSO}_4]_{\text{std. orig.}}$ be the concentration of, $m_{\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}_{\text{orig.}}}$ be the mass of zinc sulphate used and $V_{\text{Zn}_{\text{std. orig.}}}$ be the volume of the standard zinc sulphate solution created for the ion exchange process.

$$[\text{ZnSO}_4]_{\text{std. orig.}} = \frac{m_{\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}_{\text{orig.}}}}{Mr_{\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}} V_{\text{Zn}_{\text{std. orig.}}}} \quad (5.3.4)$$

Using equation 5.3.4 with $V_{\text{Zn}_{\text{orig.}}}$ as the volume of the standard solution used in the ion-exchange process.

$$\begin{aligned} n_{\text{Zn}_{\text{orig.}}} &= [\text{ZnSO}_4]_{\text{std. orig.}} V_{\text{Zn}_{\text{orig.}}} \\ &= \frac{m_{\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}_{\text{orig.}}} V_{\text{Zn}_{\text{orig.}}}}{Mr_{\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}} V_{\text{Zn}_{\text{std. orig.}}}} \end{aligned} \quad (5.3.5)$$

Using equation 5.3.3 the amount of zinc remaining in solution after the ion-exchange ($n_{Zn_{prod.}}$) can be calculated with $V_{Zn_{prod.}}$ being the volume of this resultant solution and $V_{Zn_{prod.} \text{ aliquot}}$ being the volume of the aliquot titrated.

$$\begin{aligned} n_{Zn_{prod.}} &= \frac{V_{EDTA_{prod.}} [EDTA^{4-}] V_{Zn_{prod.}}}{V_{Zn_{prod.} \text{ aliquot}}} \\ &= \frac{V_{EDTA_{prod.}} m_{ZnSO_4 \cdot 7H_2O_{std.}} V_{Zn_{std.} \text{ aliquot}} V_{Zn_{prod.}}}{V_{Zn_{prod.} \text{ aliquot}} Mr_{ZnSO_4 \cdot 7H_2O} V_{Zn_{std.}} V_{EDTA_{std.}}} \end{aligned} \quad (5.3.6)$$

Using equations 5.3.5 and 5.3.6 to calculate the amount of Zn^{2+} ions exchanged with the HZSM-5 ($n_{Zn_{ex.}}$):

$$\begin{aligned} n_{Zn_{ex.}} &= n_{Zn_{orig.}} - n_{Zn_{prod.}} \\ &= \frac{m_{ZnSO_4 \cdot 7H_2O_{orig.}} V_{Zn_{orig.}}}{Mr_{ZnSO_4 \cdot 7H_2O} V_{Zn_{std.} \text{ orig.}}} - \frac{V_{EDTA_{prod.}} m_{ZnSO_4 \cdot 7H_2O_{std.}} V_{Zn_{std.} \text{ aliquot}} V_{Zn_{prod.}}}{V_{Zn_{prod.} \text{ aliquot}} Mr_{ZnSO_4 \cdot 7H_2O} V_{Zn_{std.}} V_{EDTA_{std.}}} \\ &= \frac{V_{Zn_{prod.} \text{ aliquot}} V_{Zn_{std.}} V_{EDTA_{std.}} m_{ZnSO_4 \cdot 7H_2O_{orig.}} V_{Zn_{orig.}}}{V_{Zn_{std.} \text{ orig.}} V_{Zn_{prod.} \text{ aliquot}} Mr_{ZnSO_4 \cdot 7H_2O} V_{Zn_{std.}} V_{EDTA_{std.}}} \\ &\quad - \frac{V_{Zn_{std.} \text{ orig.}} V_{EDTA_{prod.}} m_{ZnSO_4 \cdot 7H_2O_{std.}} V_{Zn_{std.} \text{ aliquot}} V_{Zn_{prod.}}}{V_{Zn_{std.} \text{ orig.}} V_{Zn_{prod.} \text{ aliquot}} Mr_{ZnSO_4 \cdot 7H_2O} V_{Zn_{std.}} V_{EDTA_{std.}}} \end{aligned} \quad (5.3.7)$$

Hence substituting equation 5.3.7 into 5.1.2 and setting $q = 2$ gives:

$$\begin{aligned} \% \text{ Zn Exchanged} &= \frac{2Mr_{HZSM-5 \text{ unit cell}}}{7.68m_{HZSM-5} V_{Zn_{std.} \text{ orig.}} V_{Zn_{prod.} \text{ aliquot}} Mr_{ZnSO_4 \cdot 7H_2O} V_{Zn_{std.}} V_{EDTA_{std.}}} \\ &\quad \times (V_{Zn_{prod.} \text{ aliquot}} V_{Zn_{std.}} V_{EDTA_{std.}} m_{ZnSO_4 \cdot 7H_2O_{orig.}} V_{Zn_{orig.}} \\ &\quad - V_{Zn_{std.} \text{ orig.}} V_{EDTA_{prod.}} m_{ZnSO_4 \cdot 7H_2O_{std.}} V_{Zn_{std.} \text{ aliquot}} V_{Zn_{prod.}}) \times 100 \% \end{aligned} \quad (5.3.8)$$

Using equation 5.3.8 with:

$$\begin{aligned}
Mr_{\text{HZSM-5 unit cell}} &= 6217.6134 \text{ g mol}^{-1} \text{ from equation 5.1.1} \\
V_{\text{Zn}_{\text{prod. aliquot}}} &= 20.00 \pm 0.06 \times 10^{-3} \text{ dm}^3 \text{ from method (section 3)} \\
V_{\text{Zn}_{\text{std.}}} &= 100.00 \pm 0.20 \times 10^{-3} \text{ dm}^3 \text{ from method (section 3)} \\
V_{\text{EDTA}_{\text{std.}}} &= 31.95 \pm 0.20 \times 10^{-3} \text{ dm}^3 \text{ from equation 4.2.2} \\
m_{\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}_{\text{orig.}}} &= 0.63310 \pm 0.00005 \times 10^{-3} \text{ g from table 4} \\
V_{\text{Zn}_{\text{orig.}}} &= 20.00 \pm 0.06 \times 10^{-3} \text{ dm}^3 \text{ from method (section 3)} \\
V_{\text{Zn}_{\text{std. orig.}}} &= 50.00 \pm 0.06 \times 10^{-3} \text{ dm}^3 \text{ from method (section 3)} \\
V_{\text{EDTA}_{\text{prod.}}} &= 26.63 \pm 0.20 \times 10^{-3} \text{ dm}^3 \text{ from equation 4.2.3} \\
m_{\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}_{\text{std.}}} &= 0.45870 \pm 0.00005 \text{ g from table 3} \\
V_{\text{Zn}_{\text{std. aliquot}}} &= 10.00 \pm 0.04 \times 10^{-3} \text{ dm}^3 \text{ from method (section 3)} \\
V_{\text{Zn}_{\text{prod.}}} &= 100.00 \pm 0.20 \times 10^{-3} \text{ dm}^3 \text{ from method (section 3)} \\
m_{\text{HZSM-5}} &= 0.52740 \pm 0.00005 \text{ g from table 4} \\
Mr_{\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}} &= (65.38 + 32.066 + 4(15.999) + 7(2(1.008) + 15.999)) \text{ g mol}^{-1} \\
&= 287.547 \text{ g mol}^{-1}
\end{aligned}$$

$$\% \text{ Zn Exchanged} = 66 \%$$

5.3.3 Error Propagation

Let the percentage of Zn^{2+} exchanged be v_{Zn} in the following error propagation:

$$\begin{aligned}
\delta v_{\text{Zn}} = v_{\text{Zn}} & \left(\left(\frac{\delta Mr_{\text{HZSM-5 unit cell}}}{Mr_{\text{HZSM-5 unit cell}}} \right)^2 + \left(\frac{\delta m_{\text{HZSM-5}}}{m_{\text{HZSM-5}}} \right)^2 + \left(\frac{\delta V_{\text{Zn}_{\text{std. orig.}}}}{V_{\text{Zn}_{\text{std. orig.}}}} \right)^2 + \left(\frac{\delta V_{\text{Zn}_{\text{prod. aliquot}}}}{V_{\text{Zn}_{\text{prod. aliquot}}}} \right)^2 \right. \\
& + \left(\frac{\delta Mr_{\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}}}{Mr_{\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}}} \right)^2 + \left(\frac{\delta V_{\text{Zn}_{\text{std.}}}}{V_{\text{Zn}_{\text{std.}}}} \right)^2 + \left(\frac{\delta V_{\text{EDTA}_{\text{std.}}}}{V_{\text{EDTA}_{\text{std.}}}} \right)^2 \\
& + \left(\frac{\delta \left(\frac{V_{\text{Zn}_{\text{prod. aliquot}} V_{\text{Zn}_{\text{std.}}} V_{\text{EDTA}_{\text{std.}}} m_{\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}_{\text{orig.}}} V_{\text{Zn}_{\text{orig.}}} - V_{\text{Zn}_{\text{std. orig.}}} V_{\text{EDTA}_{\text{prod.}}} m_{\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}_{\text{std.}}}{V_{\text{Zn}_{\text{prod. aliquot}} V_{\text{Zn}_{\text{std.}}} V_{\text{EDTA}_{\text{std.}}} m_{\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}_{\text{orig.}}} V_{\text{Zn}_{\text{orig.}}} - V_{\text{Zn}_{\text{std. orig.}}} V_{\text{EDTA}_{\text{prod.}}} m_{\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}_{\text{std.}}} \right)}{V_{\text{Zn}_{\text{std. aliquot}} V_{\text{Zn}_{\text{prod.}}}} \right)^2 \left. \right)^{1/2}
\end{aligned} \tag{5.3.9}$$

Using the same method demonstrated in section 5.2.3 in equation 5.2.12 to expand equation 5.3.9 hence gives:

$$\begin{aligned}
\delta v_{\text{Zn}} = v_{\text{Zn}} & \left(\left(\frac{\delta Mr_{\text{HZSM-5 unit cell}}}{Mr_{\text{HZSM-5 unit cell}}} \right)^2 + \left(\frac{\delta m_{\text{HZSM-5}}}{m_{\text{HZSM-5}}} \right)^2 + \left(\frac{\delta V_{\text{Znstd. orig.}}}{V_{\text{Znstd. orig.}}} \right)^2 + \left(\frac{\delta V_{\text{Znprod. aliquot}}}{V_{\text{Znprod. aliquot}}} \right)^2 \right. \\
& + \left(\frac{\delta Mr_{\text{ZnSO}_4 \cdot 7 \text{H}_2\text{O}}}{Mr_{\text{ZnSO}_4 \cdot 7 \text{H}_2\text{O}}} \right)^2 + \left(\frac{\delta V_{\text{Znstd.}}}{V_{\text{Znstd.}}} \right)^2 + \left(\frac{\delta V_{\text{EDTAstd.}}}{V_{\text{EDTAstd.}}} \right)^2 \\
& + \frac{V_{\text{Znprod. aliquot}}^2 V_{\text{Znstd.}}^2 V_{\text{EDTAstd.}}^2 m_{\text{ZnSO}_4 \cdot 7 \text{H}_2\text{Oorig.}}^2 V_{\text{Znorig.}}^2 \left(\left(\frac{\delta V_{\text{Znprod. aliquot}}}{V_{\text{Znprod. aliquot}}} \right)^2 + \left(\frac{\delta V_{\text{Znstd.}}}{V_{\text{Znstd.}}} \right)^2 \right)}{V_{\text{Znprod. aliquot}} V_{\text{Znstd.}} V_{\text{EDTAstd.}} m_{\text{ZnSO}_4 \cdot 7 \text{H}_2\text{Oorig.}} V_{\text{Znorig.}} - V_{\text{Znstd. orig.}} V_{\text{EDTAprod.}} m_{\text{ZnSO}_4 \cdot 7 \text{H}_2\text{Ostd.}}} \\
& + \left. \left(\frac{\delta V_{\text{EDTAstd.}}}{V_{\text{EDTAstd.}}} \right)^2 + \left(\frac{\delta m_{\text{ZnSO}_4 \cdot 7 \text{H}_2\text{Oorig.}}}{m_{\text{ZnSO}_4 \cdot 7 \text{H}_2\text{Oorig.}}} \right)^2 + \left(\frac{\delta V_{\text{Znorig.}}}{V_{\text{Znorig.}}} \right)^2 \right) + \frac{V_{\text{Znstd. orig.}}^2 V_{\text{EDTAprod.}}^2 m_{\text{ZnSO}_4 \cdot 7 \text{H}_2\text{Ostd.}}^2}{V_{\text{Znstd. aliquot}} V_{\text{Znprod.}}} \\
& \left. \left(\left(\frac{\delta V_{\text{Znstd. orig.}}}{V_{\text{Znstd. orig.}}} \right)^2 + \left(\frac{\delta V_{\text{EDTAprod.}}}{V_{\text{EDTAprod.}}} \right)^2 + \left(\frac{\delta m_{\text{ZnSO}_4 \cdot 7 \text{H}_2\text{Ostd.}}}{m_{\text{ZnSO}_4 \cdot 7 \text{H}_2\text{Ostd.}}} \right)^2 + \left(\frac{\delta V_{\text{Znstd. aliquot}}}{V_{\text{Znstd. aliquot}}} \right)^2 \right. \right. \\
& \left. \left. + \left(\frac{\delta V_{\text{Znprod.}}}{V_{\text{Znprod.}}} \right)^2 \right) \right)^{1/2}
\end{aligned} \tag{5.3.10}$$

Substituting values into equation 5.3.10 gives:

$$\delta v_{\text{Zn}} = \pm 0.00 \%$$

Hence the percentage of Zn^{2+} exchanged is $66 \pm \%$.

6 Analysis

Between laboratory sessions the solutions were stored in a fridge in an attempt to reduce the rate of ion exchange since some of the ZSM-5 had already been separated out of the copper solution. This is not likely to have been very effective since the temperature of the fridge is still fairly high and the samples were left for a long period of time (one week), hence both samples are likely to have reached new equilibria during this time thus effecting the results collected. It would have been better if the initial centrifugation of the copper solution was not completed since then both mixtures would have been exposed to the same conditions, hence allowing direct comparison of the ion exchange results.

Losses in the non-exchanged ions are likely to have occurred for both solutions during the centrifugation process since some metal ions will have remained within the precipitate and in the tube when the supernatant fluid was collected. To reduce this loss distilled water could be added to the centrifuge tube and additional centrifugations performed. This was not completed due to time constraints.

6.1 Copper Exchanged ZSM-5

As seen in section 5.2.1 the percentage of copper calculated to have been exchanged with the HZSM-5 was negative. This can be explained by the fact that the solution placed in the spectrophotometer still contained some suspended zeolite (seen by how the solution was slightly cloudy after the centrifugation), hence this increased the absorbance value of the sample over the true value and thus resulting in the negative yield calculated. To reduce the effect of any zeolite remaining suspended in the solution a titrimetric method to calculate the copper ion concentration would have been better such as titrating against an EDTA solution using Fast Sulphon F as the indicator.²⁵ This is also a better method since it allows a more direct comparison between the copper and zinc ion exchange processes since very similar methods are used to determine the cation concentrations which may partially compensate for unforeseen systematic errors.

6.2 Zinc Exchanged ZSM-5

From section 5.3.2 the percentage of zinc calculated to have been exchanged with the ZSM-5 zeolite was $66 \pm \%$. This value is much higher than expected since S.A. Yasnik et al. calculated an exchange efficiency of 48% for CuSO_4 ZSM-17 following contact for 48 hours at room temperature.¹⁷

The zeolite suspended in the zinc solution resulted in the aliquot volume being less than expected since the suspended zeolite displaced some of the solution when the aliquot volume was being measured, hence making it too small. This may explain the anomalous final titre volume (run 4) obtained (see table 6) since some of the solid zeolite may have

settled in the bottom of the volumetric flask, hence for this final titration the pipette contained a greater number of suspended zeolite particles thus reducing the analyte volume and resulting in the anomalously small titre volume.

Further centrifugations could have been completed to reduce the amount of suspended zeolite from the solutions. Centrifugation was used instead of filtration to separate the zeolite since small nano-scale particles ZSM-5 often block the filter paper during filtrations hence resulting in a very slow filtration.²⁶

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7 Supplementary Information