FULL PAPER

Important thermodynamic variables with the kinetic study of the stage of industrial oil water treatment via ion-exchange resin

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Ion-exchange technology was used in the present work for removing sodium, sulphate, and chloride pollutants from the wastewater of the Daura refinery. Here, the batch experiments were conducted for examining the effects of mixing time and resin amount on the residual of pollutants and removal efficiency in this work. Adsorption kinetics and thermodynamics were also studied. The adsorption was feasible, spontaneous, and endothermic, according to many thermodynamic parameters such as the enthalpy ($\Delta H$), free energy ($\Delta G$), and entropy ($\Delta S$). Chloride, sulfate, and sodium have removal efficiencies of (88, 91, and 82) % respectively. For sodium and sulfate, the best mixing time is 12 minutes, and for chloride, it is 14 minutes. The pseudo-second-order kinetic model fits sulfate adsorption on lewatit well, but the pseudo-first-order kinetic model fits sodium and chloride adsorption on lewatit well.

KEYWORDS
Industrial oil water; lewatit; enthalpy; sulfate; sodium.

Introduction

As industry and technology advance, large amounts of water are utilized for industrial activities, resulting in generating considerable wastewater volumes. Different pollutants' levels are levels that are intentionally released into the environment, depending on the type of industry (Donald & Herbert, 1979) [6]. Large amounts of toxic derivatives like grease and oil, sulphides, phenols, suspended solids, cyanides, nitrogen compounds, along with heavy metals like nickel, iron, selenium, copper, molybdenum, zinc, salt (inorganic and organic), and so on, are found in wastewaters which are released via oil refineries (Graham, 1959) [8]. Yet, not all salts (i.e. contaminants) are harmful or toxic and thus do not need to be removed in order for water to be safe for drinking. The reversible interchanges of the ions between a solution and a solid ion-exchange medium is known as ion-exchange. Anions are exchanged for OH-, whereas cations are exchanged for H+ or Na+. The majority of today's exchange media are soluble synthetic polymer resins, though a few naturally-occurring minerals like Zeolite and green sand are also utilized (Mat Calf & Eddy, 1981; Hikki, 1999) (11:17). Hardness, the salts of magnesium and calcium bicarbonate (or sulfate & chloride) salts, can precipitate in boilers and on heating coils, causing the formation of the scale. They are, however, safe for consumption in drinking water. Higher-pressure boilers, for example, can necessitate extremely "pure" or de-mineralized water (water that has had minerals eliminated) (WQA, 1996) [27]. Ion-exchange is the most common method for removing unwanted ions (dissolved salts) from water. Particle size and moisture...
content are two significant properties of ion-exchange resin. For a variety of reasons, water is one of the most essential components of the ion-exchange resins. It affects the resin's porosity and selectivity because higher moisture content causes an increase in the porosity, which causes the active sites of exchange to be spaced further apart (De Silva, 1999) [5]. The degree of cross-linking is inversely proportional to the amount of water in a resin. As a result, a significant increase in water content indicates a decrease in cross-linking (Harland & Clive, 1994) [9]. Ion-exchange is influenced by particle size in 2 ways. Since the surface area available for exchange decreases as particle size increases, the rate of exchange for a resin decrease. As size of the particles decreases, head loss through ion-exchange beds increases. Thus, smaller beads have a higher chance of fracture (Crittenden et al., 2005) [4]. Conventional resin beads range in size from 300 to 1200 μm. Based on their origin, ion-exchange materials have two types, which are mineralic and organic, the latter is synthetic polymers that are available in anionic and cationic forms, and the former are materials that are only available in cation-exchange form (betonites and zeolites). Taking into consideration the nature of fixed ion-exchange sites, organic ion-exchange materials may be anionic, cationic, or combined anionic/cationic (i.e. amphoteric) exchangers (functional groups). Because ion-exchangers act similarly to traditional bases and acids, the major classes of such materials, namely anion and cation-exchangers, can be further divided into four types based on the type of functional group: Strongly basic, weakly basic, strongly acidic, and weakly acidic materials (Inamuddin & Mohammad, 2012) [13]. The purpose of the presented work was to examine the wastewater treatment (in Daura refinery) via ion-exchange resin for removing the pollutant ions of chloride, sulfate, and sodium, also to calculate the best resin weight, mixing time, studying the effects of temperature on the removal efficiency of the pollutant, studying the kinetics of the reaction, and thermodynamic parameter of ion-exchange approach throughout treatment.

Theoretical concepts

Ion-exchange Capacity

It is defined on the basis of total exchange capacity; also, capacity is specified regarding wet-volume capacity. The resin's moisture content, which depends on the resin's functional form and varies for each resin type, determines the wet-volume capacity. Wet-volume capacity is usually measured in milli-equivalents per milliliter of resin bed (meq/mL), but it can be measured as well in kilo grains as CaCo3 per cubic foot (kg/ft3) of resin, depending on the number of functional groups in resin bead.

Selectivity

In terms of cation-exchange and anion-exchange, the ion-exchange resin selectivity indicates its preference or affinity for specific anions. The functional group and moisture content of resin bead have an impact on selectivity (Crittenden et al., 2005; DeSilva, 1999) [4,5]. The resin selectivity is influenced by the atomic number and magnitude of the valence of the ion. Ion-exchange resins have greater selectivity or affinity for increasing charge ions. Selectivity has been based upon the ion’s atomic number in cases where several ions carry the same charge, with a higher atomic number being of a higher selectivity (DeSilva, 1999; Harlland and Clive, 1994) [5, 10]. The selectivity of an exchanging cation typically increases as the charge on exchanging cation increases in the following order:

\[ \text{Li}^+ < \text{H}^+ < \text{Na}^+ < \text{K}^+ < \text{Cs}^+ < \text{Rb}^+ < \text{Ag}^+ < \text{Be}^+ < \text{Mg}^{2+} < \text{Ca}^{2+} < \text{Sr}^{2+} < \text{Ba}^{2+} < \text{Ce}^{3+} < \text{La}^{3+} < \text{Th}^{4+} \]
A common selectivity series for anions is:
F⁻ < OH⁻ < HCO₃⁻ < CH₃COO⁻ < Cl⁻ < HSO₃⁻ < Br⁻ < CrO₄⁻² < NO₃⁻ < SCN⁻ < I⁻ < ClO₄⁻ < C₂O₄⁻² < SO₄²⁻

_Distribution coefficient_

The distribution coefficient is calculated by dividing an ion’s concentration in the exchanger by its concentration in solution at equilibrium. The formula for calculating the distribution coefficient (Kd) is as follows (Strelowand & Baxter, 1969) [22]:

\[ K_d = \frac{\text{amount on resin}}{\text{amount in the solution}} \times \text{mL of solution/gm of dry resin} \]

The Kd value might range from unity to fairly large powers of ten. Kd is not a constant; it is a coefficient, while its value is determined by a number of variables. The concentration of the ion to be separated is the first factor to consider. Second, Kd is affected by other ions’ concentration with the same charge in solution; the existence of competing ions reduces the target ion’s ability to bind to the exchanger.

_Kinetics of adsorption_

_Pseudo-first order reaction kinetic_

Straightforward linear equation in terms of Pseudo-first order reaction kinetic is provided as follows (Bhattacharyya & Sharma, 2004) [21]:

\[ \ln (q_e - q_t) = lnq_e K1t \]

where:

- \( k1 \) represents rate constant regarding first-order adsorption (1/min).
- \( q_e \) represents amount of adsorbed ion at saturation (mg/g).
- \( q_t \) represents amount of adsorbed ion at time \( t \) (mg/g).

Plot of \( \ln (q_e - q_t) \) versus \( t \) allows calculating rate constant \( k1 \) and \( q_e \).

_Pseudo-second order reaction kinetic_

Pseudo-second order reaction kinetic may be represented as (Mckay & Ho, 1998) [18]:

\[ \frac{t}{q_t} = \frac{1}{k2q_e^2} + \frac{t}{q_e} \]

Where:

- \( k2 \) represents the pseudo-second-order rate constant (g/mg min). Comparable to pseudo-first-order reaction kinetic, \( k2 \) and \( q_e \) might be specified from the intercepts and slope of plot \( t/q_t \) versus \( t \).

One of the studies on wastewater and water treatment was conducted by Brown _et al._ (2002) [2], using a new process of ion-exchange; it increased the chance for using either weak or strong acid cation resin for softening the generated waters at TDS levels up to 7000 mg/L to residual hardness levels not more than 0.1 mg/L. There is a possibility for eliminating the use of caustic and acid, even for WAC resins regeneration when using large dosages of high-purity brine.

**Experimental**

_Materials_

In this study, ion-exchange technical used chemicals material resin [strong basic anion Lewatit (mp 500) and strong acid cation Lewatit (S108)]. Resin material (cation and anion) is generally porous, providing a high surface area. Furthermore, the ion’s trapping happens with the accompanying releasing of other ions.

_Apparatus and methods_

The tools used in the present work are the laboratory shaker model (Heidolph Unimax 1010), UV-1100 Spectrophotometer, Chromatography column, and ion-selective. More details are shown in Saif (2017) [20].

_Methods_

Put (100) mL volume of wastewater sample in a beaker and add different weights in grams of the resin material (such as cation) in a beaker, and beaker put on the shaker apparatus, the shaker is operated at a
constant speed (200 rpm) and also of different times and filtrate the mixture. The filtrate is taken for analysis; the detailed procedure was shown in (Saif 2017) [20].

Results and discussions

Effects of weight resin on the removal efficiency of chloride, sulfate, and sodium

The resin amount is a significant parameter utilized for obtaining quantitative ion-exchange. The ion-exchange dependence on resin amount has been examined via varying the quantity of strong basic anion Lewatit (mp 500) (0.1-0.8 gm) in 100 mL of Sulfate solution, and (1-8 gm) in 100 mL of Chloride solution, and strong acid cation Lewatit (S108) (0.5-4 gm) in 100 mL of sodium solution, at pH (7) because these types of resin operate of a wide range of pH from (1 to 14), and contact times (15 min for anion, 10 min for cation). The shaker speed of 200 rpm which remained constant at temperature was maintained at room temperature. It is indicated that the removal efficiency of sulfate, chloride, and sodium ions increases with higher resin dosages as shown in Figures, the removal efficiency of an adsorbent (as ion-exchange) is subjected to an increase with the increase in the adsorbent dosage (resin), as a result of the availability of an extra vacant site of resin to be occupied by pollutants (Xing et al., 2011). As seen from the Figure 1 the optimum resin amounts are 0.7 g and 0.8 g in 100 mL of sulfate solution Ci =400 ppm given [R%=91, residual=37 ppm] and 0.8 g in 100 mL of sulfate solution Ci= 800 ppm given [R%=76, residual=194 ppm]. In Figure 2 the chloride with Ci= 350ppm) is shown, the removal efficiency achieved is [R%=88, residual=42 ppm] at dose of (8 gm) and [R%=67, residual=212 ppm] at dose (8 gm) for Ci= 650ppm), and achieve the optimum amount of resin for sodium Ci =200 ppm) at (3.5-4 gm). These amounts are given removal efficiency [R%=80-82, residual=40-36 ppm], as shown in Figure 3. This result is in agreement with some results of Ghaly and Verma (2008) [7] that studied the removal of sodium salt and found the sodium salt removal efficiency is (75.3%) A study conducted by Pepe and Caputo (2007) indicated a decrease in the contaminants of up to 99.99% by the use of series of zeolite columns based on the zeolite type, salt concentration, and valence of the salt cation.

![Figure 1](image-url) FIGURE 1 Effect of dose resin on the removal efficiency and residual of sulfate
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FIGURE 2 Effect of dose resin on the removal efficiency and residual of chloride

FIGURE 3 Effect of dose resin on the removal efficiency and residual of sodium

Effects of mix time on removal efficiency of chloride, sulfate, and sodium

The contact time effects on the ion-exchange of SO4-2, Cl- and Na+ by strong basic anion Lewatit (mp 500) and strong acid cation Lewatit (S108) exchange resin was studied by taking 0.1, 0.5 gm of resin with 100 mL of SO4-2, Cl- and Na+ solution, respectively, in various flasks. In addition, the flasks were shaken for 2-16 minutes; the pH of wastewater before treatment was 7. The shaker speed of 200 rpm remained constant at temperature was maintained at room temperature. It is apparent that the removal efficiency of sulfate and chloride ions increased with mixing time, as shown in Figures 4-6. Equilibrium time is a parameter of economical wastewater treatment (Kadirvelu et al., 2003) [15]. As seen from Figure 4, the optimum mixing time is (12 min) for sulfate solution (Ci =400 ppm) given [R%=25, residual=300 ppm] and sulfate solution (Ci =800 ppm) given [R%=19, residual=650 ppm]. In Figure 5 the chloride with Ci =350 ppm is shown; the removal efficiency achieved is [R%=23, residual= 270 ppm] at time (14 min) and [R%=18, residual=530 ppm] at time (14 min) for (Ci =650 ppm).

The time mixing effect on sodium removal remains constant after 12 min. of mixing to give [R%=45, residual=111 ppm]; this result is shown in Figure 6. In the first few minutes, there was a rapid increase in the percentage; after that, it slowly increased till reaching the equilibrium state. It has been reported that the adsorption is high at the adsorption
process’s beginning because of the large surface area of the adsorbent that is provided at the beginning for adsorption of ion-exchange. As the sites of surface adsorption become exhausted, the rate of the uptake is determined via the rate of the transportation of the adsorbate from exterior to interior sites of adsorbent particles. These notes were indicated by Acksu (2001) [1]. At a low level, fast adsorption is possible because of the gradient of the initial concentration between adsorbate in solution and the number of the available vacant sites at the beginning on the surface. The gradual increase in adsorption and thus the equilibrium attainment was because of the limited mass transfer related to adsorbate molecules from the bulk liquid to external surface of adsorbents as indicated by Acksu (2001); also the initial concentration gradient was between the adsorbate in solution and the number of the available vacant sites at the beginning on the adsorbent’s surface.

FIGURE 4 Effect of mixing time on the removal efficiency and residual of sulfate

FIGURE 5 Effect of mixing time on the removal efficiency and residual of chloride
Important thermodynamic variables with the ...

**Effects of temperature**

For the purpose of examining the temperature effect on ion adsorption onto Lewatit (MP 500) and cation Lewatit (S108) in a single component system, experimentations were conducted with initial concentration values of SO4-2, Cl- and Na+ solution (400, 350, 200 ppm), and (0.2, 5, 0.5) gm resin weight, respectively, at 10 minutes mixing time, pH 7 and using 3 temperatures (25°C, 40°C and 60°C) and a constant stirring speed of 200rpm. Results show a decrease in ion removal via increasing the system's temperature (Figure 7), which shows the removal efficiency of sulfate reduced from [R%=60 to 50], chloride from [R%=35 to 21], and sodium from [R%=68 to 62] with an increase in temperature from 25°C to 60°C, at pH=7. Furthermore, the results exhibited that the chloride removal is more than the sodium and sulfate. The removal sequence is thus Cl < SO4 < Na.

**Ion-exchange kinetic**

Kinetics of adsorption express the rate of solute uptake, thus, determining the residence time related to adsorption reaction, and it is a significant property that defines the adsorption efficiency (Zhihui et al., 2009) [27]. In this section, pseudo-first-order equation and pseudo-second-order equation were utilized for testing the experimental data of the signal component system.
FIGURE 8 pseudo-first-order for ion exchange of sulfate, chloride, and sodium

Plotting ln (qe-qt) against (t) in Figure 8 provided pseudo-first-order adsorption rate constant (k1) and (qe) values from the slope and intercept and listed in Table 1.

Figure 9 shows plotting of t/qt against t; from this figure, pseudo-second-order adsorption rate constant k2 and qe values are obtained from intercept and slope. Table 1 exhibits a comparison regarding the constants of the adsorption rate, calculated and experimental qe values for pseudo-first and second-order reaction kinetics.

FIGURE 9 pseudo-second-order for ion exchange of sulfate, chloride, and sodium

The values regarding correlation coefficient (R2) and (qe calculated) indicates a more sufficient fit of pseudo-second order model with experimental data compared with pseudo-first order model for sulfate, sodium and chloride values of the coefficient of correlation (R2), indicating a better fit pseudo-first-order model, while the regression coefficients were more than 0.945.

TABLE 1 comparison of adsorption rate constants, experimental and calculated qe values for the pseudo-first-and-second-order reaction kinetics for removal of sulfate, chloride and sodium

<table>
<thead>
<tr>
<th>Ion</th>
<th>qe experimental</th>
<th>Pseudo-first-order</th>
<th>Pseudo-second-order</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>K1</td>
<td>qe Calculated</td>
</tr>
<tr>
<td>SO₄</td>
<td>100</td>
<td>0.287</td>
<td>130</td>
</tr>
<tr>
<td>CL</td>
<td>4</td>
<td>0.0866</td>
<td>3.63</td>
</tr>
<tr>
<td>Na</td>
<td>17.8</td>
<td>0.1799</td>
<td>18.05</td>
</tr>
</tbody>
</table>
Thermo-dynamic study

The amounts of sorption regarding single ions through lewatit were conducted at temperatures of (25, 40, and 60) °C. Also, the thermo-dynamic parameters were assessed for the system via utilizing Eq. (4) (Khan et al., 1995) [16]:

\[
\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad \text{.........................(4)}
\]

Kd represents coefficient of distribution (mL/g)
\(\Delta S\) = entropy (J/mol K)
T = temperature (K)
\(\Delta H\) = enthalpy (kJ/mol).

FIGURE 10 distribution coefficient versus 1000/temperature for single component systems

\(R\) = gas constant (8.314 J/mol K).
The values of entropy and enthalpy were acquired from intercept and slope of lnKd versus 1000/T (Figure 10).

Table 2 summarizes the coefficients of the distribution from a series of the batch experiments at a variety of the temperature values. Gibbs free energy (\(\Delta G\)) were computed with the use of the well-known Eq. (5) (Khan et al., 1995) [16]:

\[
\Delta G = \Delta H _ T \Delta S \quad \text{.........................(5)}
\]

Table 3 lists the thermos-dynamic parameter values for ion sorption on lewatit. The exothermic nature of the sorption-exchange process is indicated by negative \(\Delta H\) values. As the resin leaves the hydration sphere to be undergoing the ion-exchange with ion-exchange material, it is likely to emit some energy heat for the removal of (H+, OH-) and intake of the incoming (anion cation,) with regard to dehydration and hydration; also the size regarding the hydrated ionic radii of incoming (anion, cation) are all factors that affect \(\Delta G\). (anion, cation).

Negative values of \(\Delta G\) are an indication of the fact that the process of sorption spontaneous and feasible, while a more stable level of energy is achieved after ion-exchange of metal ions (Tagami et al., 2001; Zhou et al., 2011) [23,28]. The value of \(\Delta G\) for such processes decreases as temperature rises (for chloride), indicating that sorption is less favourable at high temperatures. With increasing temperature (for sodium and sulfate), the values of \(\Delta G''\) become more negative, indicating the process's spontaneity; it also shows that sorption is better at high temperatures. Throughout the process of ion-exchange, the entropy is reflecting changes in the sphere of the hydration regarding the exchanging cation. Na and SO ions showed positive \(\Delta S\) indicating high ion randomness near the adsorbent surface because of ion-exchange and reflecting the adsorbent's affinity, yet the CI ions showed negative \(\Delta S\) values, indicating a
high uniform of ion near the surface of the adsorbent, while the sorbet ions were stable on solid surface. Immobilization, fixation, or association of chloride ions caused by adsorption occurs due to a reduction in the freedom degree of the adsorbate ions that results in negative entropy change.

**TABLE 2** distribution coefficients of sulfate, chloride and sodium at different temperatures

<table>
<thead>
<tr>
<th>Ion</th>
<th>$k_d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO$_4$</td>
<td>739</td>
</tr>
<tr>
<td>Cl</td>
<td>10.8</td>
</tr>
<tr>
<td>Na</td>
<td>415</td>
</tr>
</tbody>
</table>

**TABLE 3** thermodynamic parameters for the adsorption of ions on resin

<table>
<thead>
<tr>
<th>Ion</th>
<th>$\Delta H$ (kJ/mol)</th>
<th>$\Delta S$ (J/mol k)</th>
<th>$\Delta G$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO$_4$</td>
<td>-10.47</td>
<td>20.1</td>
<td>-16.4</td>
</tr>
<tr>
<td>Cl</td>
<td>-19.52</td>
<td>-45.1</td>
<td>-5.4</td>
</tr>
<tr>
<td>Na</td>
<td>-6.14</td>
<td>29.5</td>
<td>-14.9</td>
</tr>
</tbody>
</table>

**Conclusion**

1. When the amount of resin was increasing, the final concentration was decreasing, and the removal of efficiency was increasing.
2. The highest efficiency was 91 % when anion resin was used, and the mixing time is 12 min at neutral pH.
3. The selectivity generally increases with a higher valence charge.
4. The actual capacity of the resin was in the safety lime of the theoretical capacity.
5. The adsorption process has been feasible, spontaneous, and endothermic.
6. Sulfate adsorption on lewatit fitted well to pseudo-second-order kinetic model, yet the adsorption of sodium and chloride on lewatit behaves to pseudo-first order kinetic model.

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**References**

[12] D.T. Howe, J. Rankin, E.S. Draper, Ultrasound Obstet. Gynecol., 2012, 35, 75-82. [Crossref], [Google Scholar], [Publisher]
[21] A. Sharma, K.G. Bhattacharyya, Adsorption, 2004, 10, 327-338. [Crossref], [Google Scholar], [Publisher]
[22] F.W.E. Strelow, C. Baxter, Talanta, 1969, 16, 1145-1155. [Crossref], [Google Scholar], [Publisher]
[26] S. Xing, M. Zhao, Z. Ma, J. Environ. Sci., 2011, 23, 1497-1502. [Crossref], [Google Scholar], [Publisher]

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