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ADSORPTION OF ZINC AND IRON IONS FROM AQUEOUS SOLUTION USING WASTE MATERIAL AS ADSORBENT

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Abstract. Reducing or eliminating ions of toxic heavy elements such as iron and zinc from aqueous solutions has been adopted in this research. The batch process is used to remove metal ions using a cheap adsorbent material that is called hawthorn nucleus. In addition, the influences of contact time, pH, metal ions concentration, and adsorbent dose on the removal percentage have been studied. This study showed that adsorption or removal efficiency increases over time and the quantity of the adsorbent material, as well as pH showed that the equivalent and negative charges category is preferred for adsorption by the hawthorn nucleus. The highest removal efficiency was found to be 91% for zinc and 95% for iron. In such conditions, *i.e*., 120 minutes time, the metal concentration is 25 ppm, the amount of the adsorbent material is 5 g/L and pH is 10 for zinc and 7 for iron .Adsorption isotherm and kinetics were also investigated for both metal ions. The results showed that the adsorption findings followed Langmuir isotherm and the pseudo-second-order kinetic for adsorption isotherm and kinetics, respectively.

Keywords: adsorption, waste material, heavy metal ions, adsorbent, hawthorn.

1. Introduction

Wastewater released by industrial processes is frequently polluted by an assortment of poisonous or in any case unsafe substances, which negatively affect the water condition.[1] Urbanization and industrialization have brought about the exponential release of industrial effluents and poisonous substantial metals into water bodies. Essential metals such as iron, chrome, zinc, and lead which are toxic and harmful to organisms, though in small quantities.[2] These specific minerals are biodegradable and can be assembled in life forms, and then pose a significant health threat to humans, plants, and animals. Despite the fact that humans have no immediate difficulty with these toxins, human health can be affected casually by different behaviors, especially in drinking water and the evolving lifestyle. Furthermore, in agriculture, significant contamination of minerals in the soil can cause enormous damage to crop development and quality. In this manner, the elimination of heavy metals, from normal waters or soils, has pulled in significant considerations.[3]

Different methods have been utilized for the treatment of heavy metals, including ion exchange, precipitation, reverse osmosis, and adsorption. Precipitation is generally relevant among these methods and viewed as the most economical. In any case, this procedure creates a huge quantity of precipitate sludge that needs more treatment. Ion exchange and reverse osmosis can adequately decrease metal particles, however, their utilizations were restricted because of various detriments, for example, high cost for material and operation in addition to the restricted pH run for the ion exchange resin.[4]

Thereafter, it has been noted that the use of adsorption as an alternative method to other methods is better and is increasingly being used as a useful process and providing a clean environment. Recently important considerations have been given to this method.[5] One of these considerations or reinforcements that helped to use this method is that it is possible to use simple or cheap materials or plant residues as a possible adsorbent for heavy elements.[6, 7] The most common substances utilized as adsorbents are clays, zeolites, carbons, polymeric, and biomass substances. Research has shown that these materials have little adsorbability and are limited to heavy element ions. Furthermore, there was difficulty in separating them. Consequently, extensive attempts are still required for the advancement of recently materials that can be utilized as adsorbents in purification implementations.[8]

Complex natural materials, natural macromolecules, and rotting biomass of microorganisms can be utilized as biosorbents. These are, much of the time, wastes of natural matters. Lignocellulosic waste materials are appropriate sorbents for the elimination of heavy metal ions from wastewater as they are inexpensive and furthermore the treating is easy and economical. Tree leaves, wood bark, nut or walnut wastes, and other lignocellulosic

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substances were considered as the sorbents for heavy metal ions from water solutions.[9]

The aim of the present work is to study the activity of hawthorn waste as an adsorbent for zinc and iron ions adsorption using batch operation, the effect of time, initial concentration, pH, and the amount of the adsorbent in addition to adsorption isotherm and kinetic approach.

2. Experimental

2.1 Materials

Zinc sulfate heptahydrate [$ZnSO_4 \cdot 7H_2O$] and iron nitrate nonahydrate [$Fe(NO3)_3 \cdot 9H_2O$], which were purchased from Fluka Chemika, were used as Zn and Fe precursors. Sulfuric acid and potassium hydroxide were used to adjust the pH solution. Hawthorn kernel waste material was collected, washed, and dried in the oven at 373 K overnight. Then, the materials were crushed and used as biosorbents.

2.2 Experimental procedure

A stock solution of 250 ppm heavy metal was prepared by dissolving an appropriate quantity of zinc sulfate or iron nitrate in 1000 mL of distilled water at neutral pH. The required concentrations were attained by diluting the stock solution in distilled water. The initial concentrations of the experimental solutions were 15, 25, 35, 50, and 100 ppm. Briefly, 100 mL of the prepared solution was put in a 250 mL beaker. An appropriate amount of biosorbent was then weighed and added to the solution. The solution was mixed using a magnetic stirrer for 2 h. Samples were taken at different time intervals and then analyzed by atomic absorption spectrophotometry. The removal percentage for heavy metals was calculated according to Eq. (1):

$$\% \text{ removal efficiency} = \frac{C_{initial} - C_{at\ any\ time}}{C_{initial}} * 100 \quad (1)$$

where $C_{initial}$ and $C_{at\ any\ time}$ (mg L^{-1}) are concentrations at initial and any time, respectively.

3. Results and Discussion

3.1. Atomic Force Microscope

Fig. 1 shows AFM of the hawthorn surface three-dimensional profile. It's clear from this figure that the average particle diameter of the biosorbent was found to be 58 nm. Also, it is observed that the material surface has crystalline structure, the layer development of hawthorn kernel crystal, and the height of the terraces.

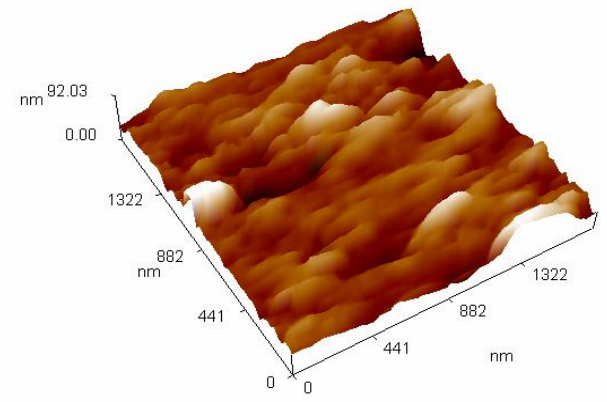


Fig. 1. AFM for hawthorn kernel

3.2. Scanning electron microscopy

The morphology of hawthorn material was performed using the SEM technique. In Fig. 2, SEM images of the hawthorn powder are presented at two different magnitudes: 500 nm and 2 μm. The SEM images reveal that the sample presents morphology of stretched structure and agglomeration is formed due to their nanometric size.

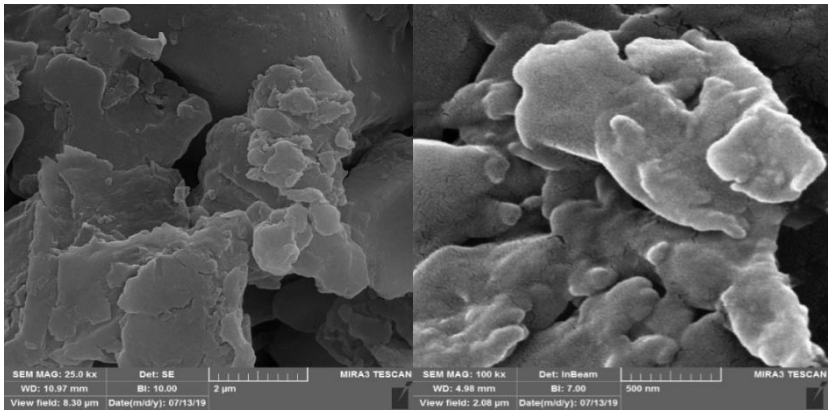


Fig. 2. SEM images of hawthorn kernel

3.3. Effect of time and pH

The time course of Zn and Fe ions adsorption on hawthorn is presented in Figs. 3 and 4, respectively, at metal concentration 25 ppm and adsorbent dose of 5 g/L. The adsorption removal for Zn increases from 30 to 68 % and from 80 to 95% for Fe as time increases from 30 to 120 min at 7 pH. Different pH values are also shown in these figures. This variant has a noticeable effect on the adsorption process, the lowest removal efficiency obtained was 23% for zinc and 6% for iron at the lowest pH equal to 3. After 120 minutes, when increasing pH to 7, the removal efficiency is 68% for zinc and 95% for iron. When pH increases further to 10, we get the highest 91% removal efficiency of the two elements, but when this pH induces hydrolysis of ions or deposition of hydroxide ions. When pH has a low hydrogen ion concentration, this leads to the rejection or dissonance of positive charges. This prevents it from reaching the surface of the hawthorn nucleus. This behavior is in agreement with Sciban and Klasnja.[9]

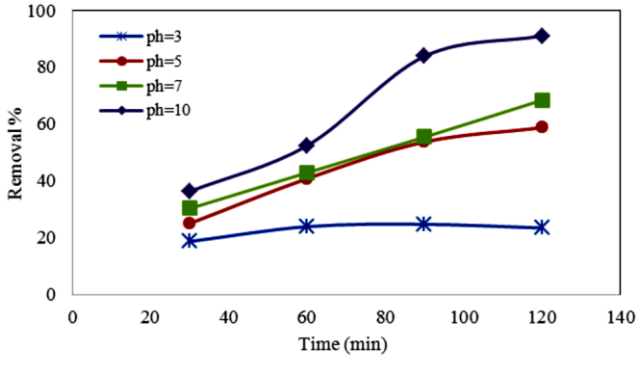


Fig. 3. pH effect on adsorption of Zn at the concentration of 25 ppm and adsorbent dose of 5 g/L

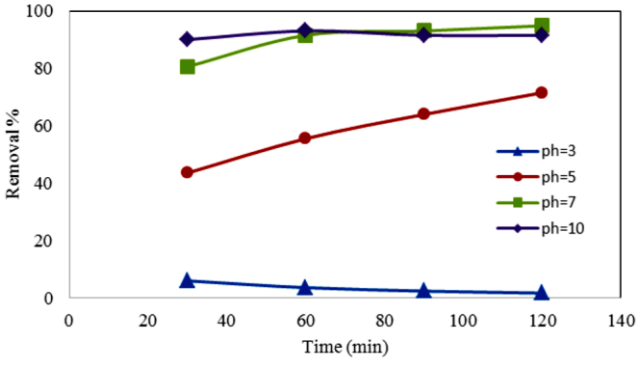


Fig. 4. pH effect on adsorption of Fe at the concentration of 25 ppm and adsorbent dose of 5 g/L

3.4. Effect of initial metal concentration

Zinc and iron adsorption are greatly affected by the initial concentration of their ions in aqueous solutions. In this study, different initial concentrations of 25, 50, 75, and 100 ppm were tested while maintaining the adsorbent amount of 5 g/L and pH=7. The results were shown in Figs. 5 and 6 for zinc and iron removal percentages, respectively. As depicted from the figures, with the increase in the metal concentration from 25 to 100 ppm, the removal percentage for zinc and iron decreases from 59 to 27% and 95 to 48% respectively after 120 min. This can be described by the fact that the adsorbent has a limited number of active sites that have become saturated above a certain concentration and the rate of metal capture causes the movement of ions from outside to inside the place of the adsorbent. This behavior is consistent with Arabyarmohammadi *et al.*[10] and Deivasigamani *et al.*[11]

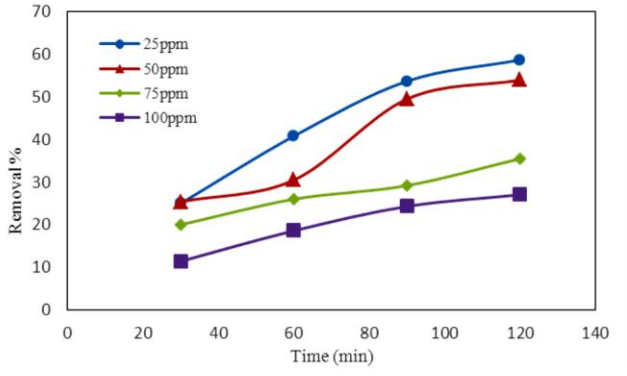


Fig. 5. Effect of zinc concentration on adsorption at pH=7 and adsorbent dose of 5 g/L

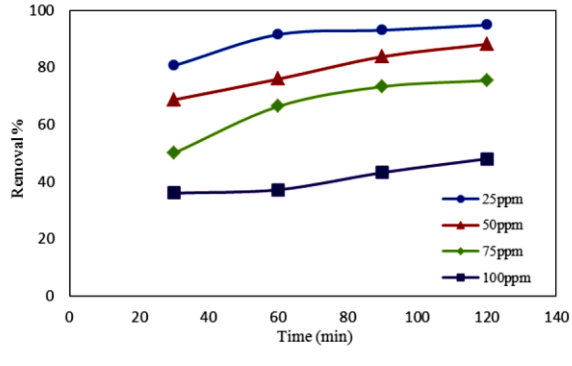


Fig. 6. Effect of iron concentration on adsorption at pH=7 and adsorbent dose of 5 g/L

3.5. Effect of adsorbent dose

The influence of variation of adsorbent mass on the adsorption of Zn and Fe is shown in Figs. 7 and 8, respectively. As the adsorbent mass increases, the amount of metal ions adsorbed increases due to the increment in the number of binding sites for the ions. To achieve the maximum removal efficiency of the biosorbent for Zn and Fe, the biomass concentration was varied from 1 to 10 g/L and it was found that the concentration of 5 g/L was sufficient for maximum ions removal of 59 and 95% for Zn and Fe ions, respectively, at a constant metal concentration of 25 ppm, pH=7, and time of 120 min. The adsorption increased from 25 to 59% and from 62 to 95% for zinc and iron, respectively, as the adsorbent dose increased from 1 to 5 g/L after 120 min and this is attributed to the increase in the surface area and adsorption sites available for reduction.[12,13] It is seen from Fig. 7 that a further increase in biomass to 10 g/L leads to a decrease in sorption percentage greatly, which is in agreement with the literature data.[14] This phenomenon shows that the adsorbed sites remain unsaturated during the adsorption process and that a number of sites are ready to accommodate higher adsorption by increasing the amount of the adsorbent.[15]

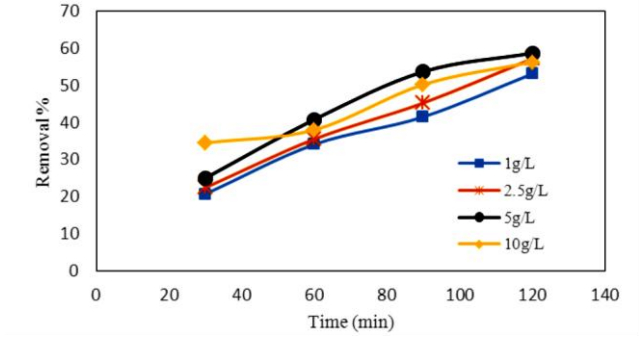


Fig. 7. Effect of adsorbent concentration at pH=7 and zinc concentration of 25 ppm

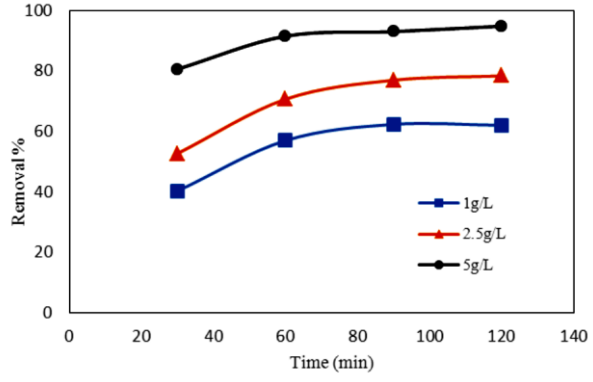


Fig. 8. Effect of adsorbent concentration at pH=7 and iron concentration of 25 ppm

3.6. Adsorption Isotherm

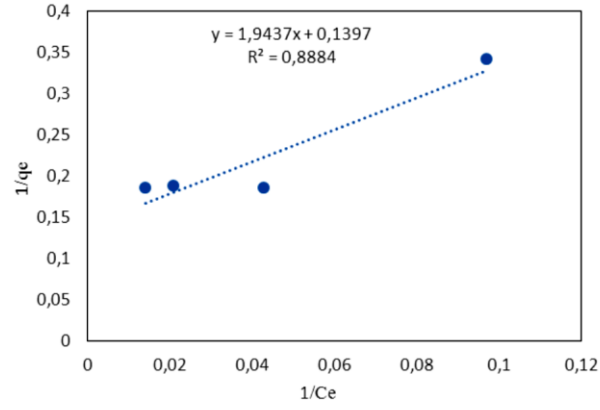
Adsorption isotherm is a significant tool to test the interaction between adsorbates adsorbent. As shown in Figs. 9 and 10, the experimental data acquired from the batch process were fitted well using Freundlich and Langmuir isotherm equations. Langmuir isotherm model is represented by Eq. (2).[16]

$$\frac{C_e}{q_e} = \frac{1}{q_m\, b} + \frac{1}{q_m} C_e \qquad (2)$$

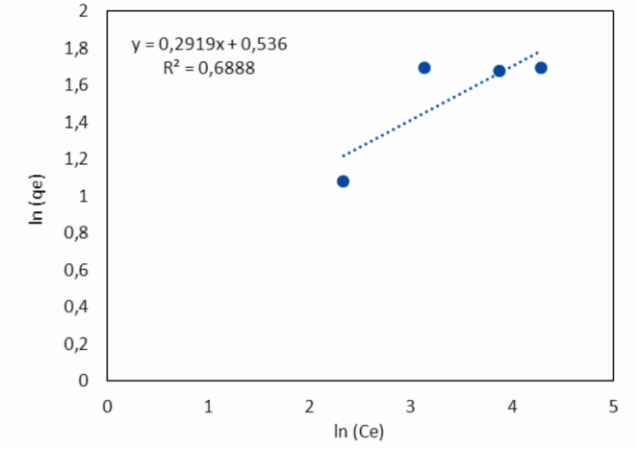
where C_e (mg/L) is the concentration of the adsorbate at equilibrium, q_e (mg/g) is the quantity of adsorbate adsorbed per unit mass of adsorbent and calculated from Eq. (2a), q_m and b are the Langmuir constant, which can be calculated graphically from the intercept and the slope of linear plotting of (C_e/q_e) against C_e.

$$q_e = (C_0 - C_e)V/m \qquad (2.a)$$

where C_0 (mg/L) is the initial concentration of metal, *Ce* (mg/L) is the equilibrium concentration, *V* (L) is the metal solution volume, and *m* (g) is the mass of adsorbent.



a)



b)

Fig. 9. Linearization of (a) Langmuir (b) Freundlich model for zinc adsorption

However, the Freundlich model is explaining by Eq. (3):[17,18]

$$\text{Log } q_e = \frac{1}{n} \text{Log } C_e + \text{Log } K_f \quad (3)$$

where K_f and $1/n$ are empirical constants. They can be obtained by plotting log q_e *vs.* log C_e, and the slope of the line acquired is the value of $1/n$ while log K_f is *y*-intercept of line.

By comparing R^2 and error results for zinc and iron adsorption, a good agreement was found with the Langmuir model for both heavy metals as shown in Figs. 9 and 10. The R^2 values for the Langmuir model of zinc and iron were 0.88 and 0.98, respectively. Also, the error results were 0.019 and 0.005 for zinc and iron adsorption, respectively.

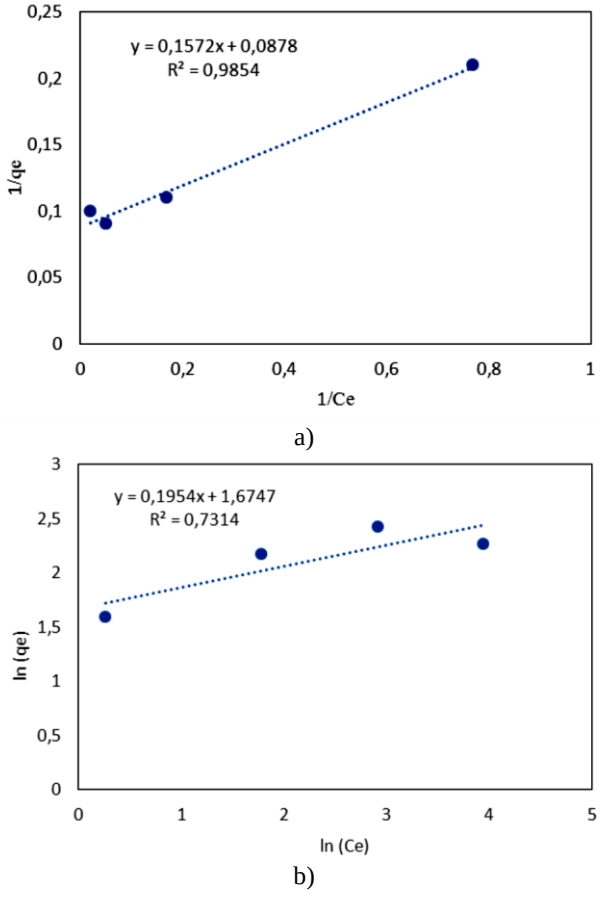


Fig. 10. Linearization of (a) Langmuir (b) Freundlich model for iron adsorption

3.7. Kinetics of Adsorption

To evaluate the mechanism of dominating rate within the adsorption of zinc and iron, kinetic studies were carried out. The kinetics of adsorption onto the hawthorn were examined with the pseudo-first-order, second-order, and intra-particle diffusion models as illustrated in Figs. 11–13 for zinc metal and Figs. 14–16 for iron metal. The equations for these models can be expressed as follows:

$$ln\ q_t = lnq_e - k_1\ t \quad (4)$$

$$\frac{t}{q_t} = \frac{1}{k_2\ q_e^2} + \frac{t}{q_e} \quad (5)$$

$$q_t = k_p\ t^{1/2} + C \quad (6)$$

where q_t and q_e represent the quantities of heavy metals adsorbed (mg/g) at any time t (min) and equilibrium. k_1 is the adsorption rate constant and its magnitude is determined from the slope of ln q_t against t.

For the pseudo-second-order, k_2 is the adsorption rate constant. In this type, linear regression was achieved from the graph t/q_t against t. The value of k_2 can be calculated from the intercept of the graph. While for intra diffusion, k_p (mg/ g $min^{1/2}$) is the rate constant for this model, and C is a constant that can be obtained by plotting q_t *vs* $t^{1/2}$. The results showed that R^2 for both Zn and Fe were higher in the pseudo-second-order model compared with the other two models but the error was lower in this model. The R^2 in the pseudo-second-order was 0.9869 and 0.9996 for both Zn and Fe. While the error was 0.117 for zinc and 0.019 for iron.

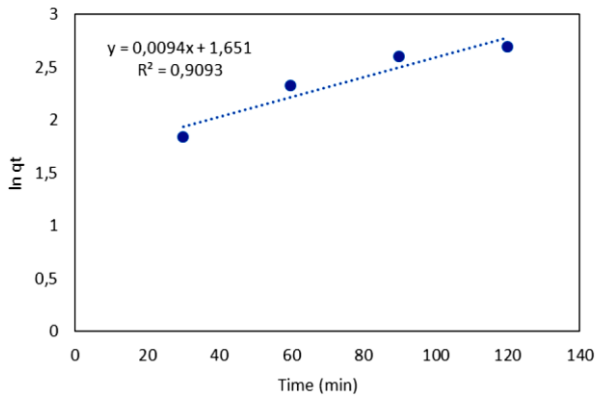


Fig. 11. Pseudo-first-order kinetics for zinc adsorption

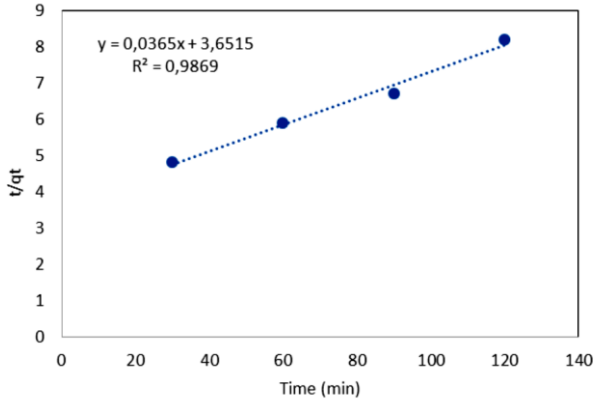


Fig. 12. Pseudo-second-order kinetics for zinc adsorption

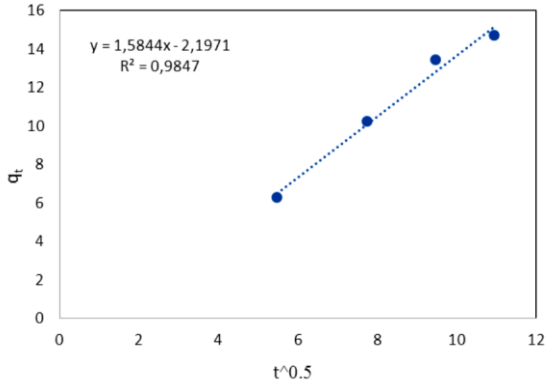


Fig. 13. Intra diffusion kinetics for zinc adsorption

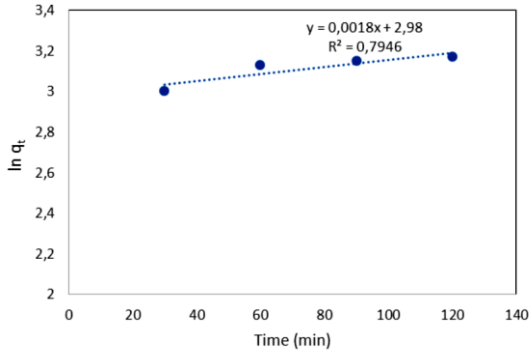


Fig. 14. Pseudo-first-order kinetics for iron adsorption

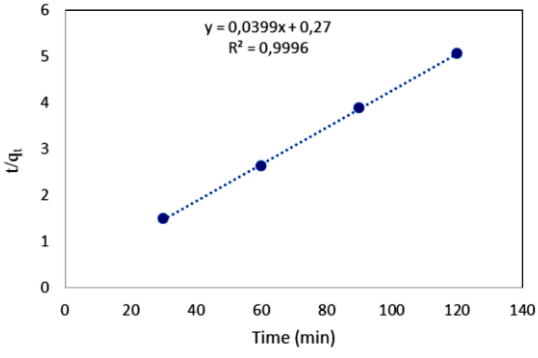


Fig. 15. Pseudo-second-order kinetics for iron adsorption

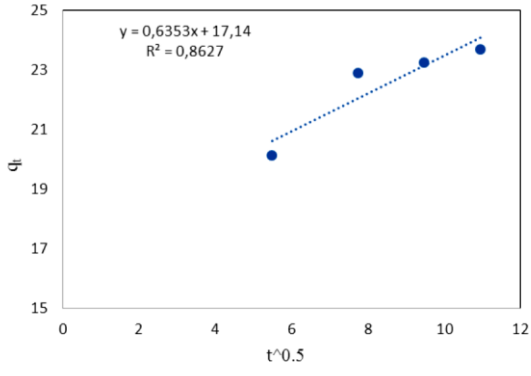


Fig. 16. Intra diffusion kinetics for iron adsorption

4. Conclusions

The removal efficiency for both zinc and iron increased as pH increased from 3 to 7. As the initial concentration of the metal increased, the removal efficiency decreased. However, as the amount of hawthorn kernel increased, the removal percent increased, whereas at high adsorbent amount of 10 g/L the removal efficiency decreased. For adsorption isotherm, the Langmuir model applies for both zinc and iron ions while for adsorption kinetics the pseudo-second-order model applies for both metals. Hawthorn kernel shows good adsorption removal efficiency for iron ions compared to zinc ions, 95% for iron and 68.5% for zinc were removed at pH=7, metal concentration of 25 ppm, adsorbent amount of 5 g/L, and time of 120 min.

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АДСОРБЦІЯ ІОНІВ ЦИНКУ ТА ФЕРУМУ З ВОДНОГО РОЗЧИНУ З ВИКОРИСТАННЯМ ВІДХОДІВ ЯК АДСОРБЕНТУ

Анотація. *У цій роботі досліджено зменшення вмісту або вилучення іонів токсичних важких елементів, таких як ферум і цинк, з водних розчинів. Для вилучення іонів металів використано періодичний процес із використанням дешевого адсорбційного матеріалу, який називається ядром глоду. Також було вивчено вплив часу контакту, pH, концентрації іонів металів і дозування адсорбенту на відсоток видалення. Це дослідження показало, що ефективність адсорбції або вилучення зростає з часом і кількістю адсорбуючого матеріалу, а також pH показало, що категорія еквівалентних і негативних зарядів є кращою для адсорбції ядром глоду. Встановлено, що найвища ефективність вилучення становить для цинку - 91% і феруму - 95%. За таких умов, тобто за тривалості 120 хвилин, концентрація металу становить 25 м.ч., кількість матеріалу адсорбента - 5 г/л, а pH - 10 для цинку і 7 для феруму. Ізотерма та кінетика адсорбції також були досліджені для іонів обох металів. Результати показали, що отримані дані з адсорбції відповідають ізотермі Ленгмюра та кінетиці псевдодругого порядку для ізотерми та кінетики адсорбції, відповідно.*

Ключові слова: *адсорбція, відходи, іони важких металів, адсорбент, глід.*