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Abstract

In this study, fish scales (Pomadasys kaakan's scales) were used as new biosorbent for removing Ni^{2+} and Cu^{2+} ions from wastewater. The effects of electric and magnetic fields on the absorption efficiency were also investigated. The effects of sorbent content, ion concentration, contact time, pH, electric field (EF), and magnetic field (MF) on absorption efficiency were assertained. In addition, the isotherm of absorption was studied in this work. This study revealed that electric field and magnetic field have significant effects on the absorption efficiency of ions from wastewater. An increase in the electric field enhanced the removal percentage of the ions and accelerated the absorption process by up to 40% in comparison with the same condition without an electric field

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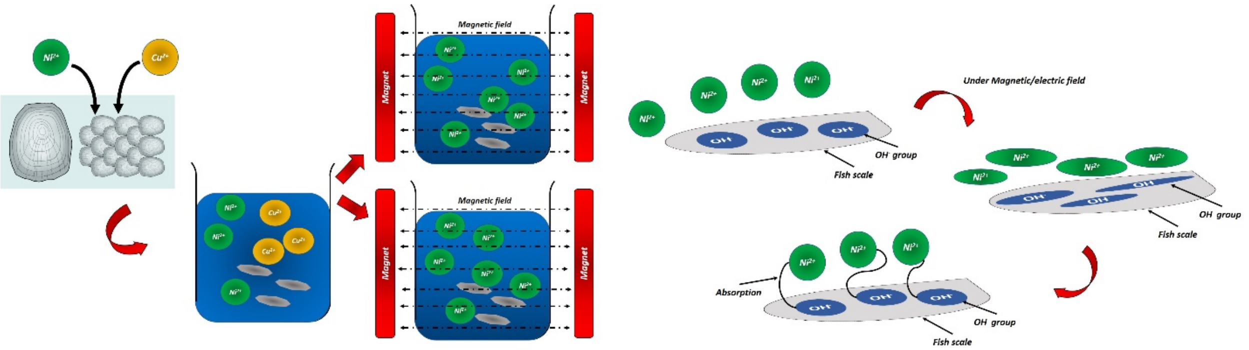
or a magnetic field. By increasing contact time from 10 to 120 minutes, the removal of Ni^{2+} ions was increased from 1% to 40% and for Cu^{2+} ions, the removal increased from 20% to almost 95%, respectively. In addition, increasing pH, ion concentration and scales dose increased removal percentage effectively. The results indicated that using fish scales for Cu^{2+} ions absorption is ideal due to the very high removal percentage (approximately 95%) without using either an electric or magnetic field.

Keywords: FISH SCALES, BIOSORBENT, ADSORPTION, WASTE-WATER, IONS REMOVAL, ELECTRIC_MAGNETIC FIELD.

Graphical abstract



1. Introduction

Nowadays, water pollution is one of the most important concerns due to the contamination of water sources by heavy metals in wastewater from industries. Industrial wastewaters normally contain metal ions such as: Ni^{2+}, Cu^{2+}, Co^{3+}, Pb^{2+}, Ag^{2+}, etc. Using an absorbent for removing these ions from wastewater is a subject of numerous research investigations (Demirbas et al., 2005; Vasseghian et al., 2022; Liu et al., 2022).

These ions and other contaminations are harmful to the environment and humankind. According to World Health Organization (WHO), the maximum safe amounts of Ni^{2+} ions in potable water is 0.02 mg/L and for Cu^{2+} ions in drinking water and industrial effluent is 2 mg/L and 0.05-1.5 mg/L, respectively. Long time exposure to Ni^{2+} causes chronic bronchitis, reduced lung function, and cancer of the lungs and Cu^{2+} leads to stomachache, irritation of the nose, mouth, eyes, and headache (Ahmaruzzaman, 2011).

Various methods such as adsorption, ion exchange (Demirbas et al., 2005), electrochemical techniques (Rakhmania et al., 2022; Devlin et al., 2018; Dubrawski et al., 2013), floatation, precipitation and chemical reaction (Sadrnourmohamadi and Gorczyca, 2015a, 2015b) are applied to remove ions from wastewater and reduce the risk of pollution of water sources. Adsorption is an effective method for wastewater treatment because of its low cost and environmental friendly behavior (Vafakhah et al., 2014; Wu et al., 2022; Zhang et al., 2022; Vasseghian et al., 2022). Adsorption is the process in which an adsorbent is introduced to wastewater which then adsorbs contaminations and purifies the wastewater. Ion removal may occur by chemical bonding, physical bonding, ion exchange or a mixture of these phenomena.

Adsorbents can be selected from various materials which have the capacity for wastewater treatment. Among the adsorbents, agricultural waste is under wide attention for use as biosorbents for removing contaminants. Not only do they have a large capacity for the removal of ions but they are very low cost. Adsorption of ions by biosorbents has been investigated using a wide range of agriculture wastes, for instance, lemon peel (Bhatnagar et al., 2010), corncob (Leyva-Ramos et al., 2005; Vafakhah et al., 2014), corn stalk (Vafakhah et al., 2014), almond integument (Hosseini et al., 2013), hydroxyapatite (Corami et al., 2008; Plec et al., 2006), chitosan (Baroni et al., 2008; Bazargan-lari et al., 2014; Taylor et al., n.d.), peanut hull (Contribution, 1995), bagasse fly ash (Gupta et al., 2003), rice husk (Ajmal et al., 2003) and sawdust (Yu et al., 2000) along with the optimization of different conditions on the adsorption process of biosorbent.

Fish are one of the most numerous species in the sea. Fish skin and fish scale form a major part of sea waste but have not been used for any application. Fish scales have a remarkable capacity for removing ions from wastewater and are generally a low-cost waste product from seafood manufacturing. According to (Crona et al.,2020), China is one of the largest producers and consumers of seafood in the world and the total amount of fishery production of China was approximately 62.7 million tonnes in 2014.

Fish scales have minerals, aligned type I collagen fibrils and generally have 2 different layers: the external layer and the internal layer. The alignment of these fibrils is different in the layers. The internal layer contains randomly oriented collagen fibrils with diameters of 20-30 nm. However, the external layer contains type I collagen fibrils with 70-120 nm diameters range in the shape of micro-order thickness composed of aligned collagen fibrils (Okuda et al., 2011) and this arrangement makes a plywood structure for fish scales (Gil-duran et al., 2016).

Since all chemical bonds have some natural electric or magnetic properties, because of the interaction between atoms and electrons, it is proposed that a magnetic field or an electric field might have an influence on the absorption process. However, these effects have not been investigated yet, as far as the present authors know, and it remains to be answered.

Among the researchers who have worked on the effect of electric field on hydrogen bonding (Dannenberg and Haskamp, 1999; Jissy and Datta, 2012; Mata et al., 2009; Suresh et al., 2006), proton transfer (Zhou et al., 2011) and chemical bonding (Sowlati-hashjin and Matta, 2014), Akkarapattiakal et al. (Jissy and Datta, 2012) worked on the effect of electric field on H-bonding in Guanine aggregates. They showed that the electric field along the perpendicular axis increases the dipole moments of the guanine dimer, trimer, and quartet, and also H-bonds become longer and weaker with increasing external electric field. Suresh et al. (Suresh et al., 2006) investigated the effect of an electric field on hydrogen bonds in water by developing a theoretical framework for understanding the behavior of water in an external electric field. They concluded that an electric field can only enhance the H-bond structure of water and not disrupt it at any of the field strengths. They also concluded that H-bonds can stabilize molecules with their dipoles lying perpendicular to that of the field, although the fraction of such molecules is relatively small. Mata et al. (Mata et al., 2009) investigated the effect of external electric field parallel to the hydrogen bond in FH····FH dimer by theoretical methods. They showed that an electric field in the opposite direction to the dipole moment of the system strengthens the interaction due to a larger mutual polarization between both molecules and increases the covalent character of the hydrogen bond, while an external field in the opposite direction has the inverse effect. Zhou et al. (Zhou et al., 2011) worked on the effect of electric field on proton transfer from acid (HCl) to base (NH_3/H_2O) by proposing a physical method for external electric field (E_{ext}) to drive the proton transfer from acid to base. They showed that when E_{ext} along the proton-transfer direction achieves the critical electric field (E_c), the proton transfer occurs and the degree of proton transfer can be controlled by modulating the strength of E_{ext}.

Although the effect of an electric field on bonding has been studied, the effect of an electric field on the adsorption process of ions has not been investigated. The main aim of this study was to investigate and examine the capability of Pomadasys kaakan's scale as a new absorbent for removing Ni^{2+} and Cu^{2+} ions from wastewater and more importantly to investigate the effect of the electric field (EF) and magnetic field (MF) on the adsorption process and removal efficiency of the fish scales for removing ions. Finally, an equilibrium study using Langmuir and Freundlich models was performed and the surface morphology of the scales using a scanning electron microscope was conducted.

2. Materials and methods

2.1. Preparation of adsorbent

Raw fish scales with approximately 1cm * 1 cm were collected from a local fish market in Shiraz, Iran. Firstly, the damaged and unequal scales, regarding their sizes, were removed. Then, these scales were washed with double distilled water many times to remove any contaminations and then put in an oven at 80 ºC for 2 hours in order to dry.

2.2. Solutions

Solutions were prepared from $NiNO_3.6H_2O$ and $CuNO_3.3H_2O$ stock solutions for Ni^{2+} and Cu^{2+} ions sources, respectively. Stock solutions were prepared by dissolving nickel nitrate and copper nitrate in deionized water. NaOH and H_2SO_4 solutions were also used to adjust the pH of the solutions.

2.3. Electric and magnetic fields

In order to study the effect of an electric field on the adsorption process, the main vessel which contained fish scales, and the solution was put in another vessel that contained 5%wt NaCl solution. A copper cathode and a graphite anode were set in the outer vessel which produced a uniform electric field for the inner vessel as shown schematically in Figure 1(a). The electric field was produced by using a direct current (DC) and by changing the current density of the electric field, the power of the electric field was changed and the effect of this parameter on the adsorption process was studied. NaCl was added to the outer solution to increase the conductivity of the water and hence preventing the temperature from rising and the overvoltage between the cathode and the anode increasing. Two magnets with 5 cm * 15 cm* 3 cm dimensions were used to produce a uniform magnetic field. In order to investigate the effect of the magnetic field on the absorption process, the vessel was placed between two magnets as shown in Figure 1(b). The top view of setups is also shown in Figure 2(a) and (b) for a better understanding of how the electric and magnetic fields were produced.

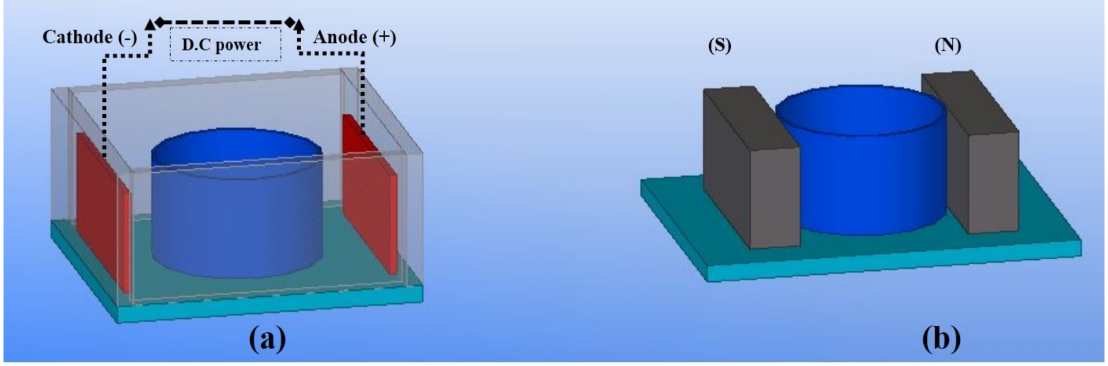


Figure 1. Schematic setup for producing uniform (a) electric and (b) magnetic fields.

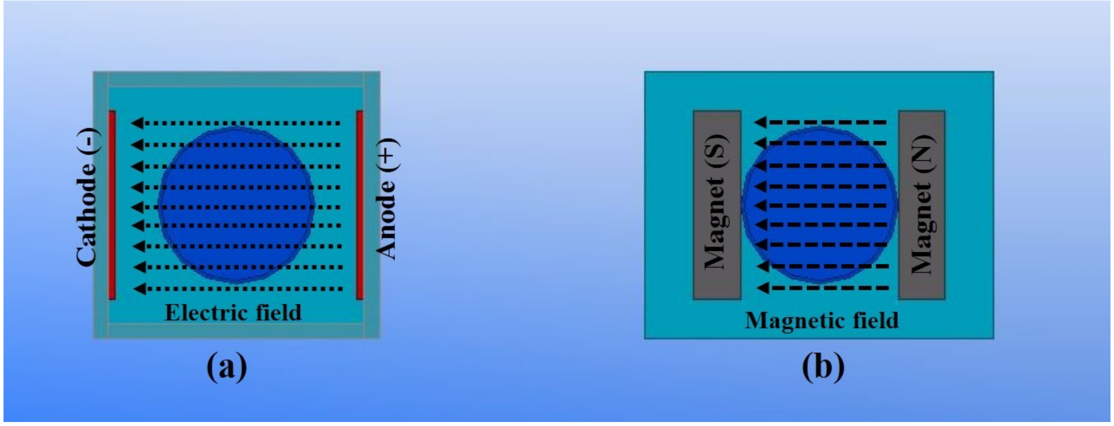


Figure 2. Top view of the setup for producing (a) an electric field and (b) a magnetic field.

2.4 Adsorption studies and isotherms

To determine the removal percentage of Ni^{2+} and Cu^{2+} ions by fish scales, the following equation is used:

$$\mathrm{Re}\,moval(\%) = \frac{(C_0 - C_f)}{C_0} \times 100 \qquad (1)$$

Where C_0 is the initial concentration of ions and C_f is the final concentration of ions after the adsorption process. To determine the amount of ions which is adsorbed by fish scales, the following equation is used:

$$q_e = \frac{(C_0 - C_e)}{M} \times V \qquad (2)$$

Where q_e is the adsorption capacity per unit mass of fish scales (mg/g), C_0 is the initial concentration of nickel or copper ions (mg/L), C_e is the equilibrium concentration of nickel or copper ions after the adsorption process (mg/L), V is the volume of solution (L) and M is the mass of biosorbent (g), respectively.

Langmuir and Freundlich isotherms are the most well-known models for the investigation of adsorption isotherms. The Langmuir isotherm assumes that adsorption takes place with a monolayer sorbent surface with a finite site of adsorption (all sites are equal) and that each site can contain only one molecule of adsorbate (Demirbas, 2008; Li et al., 2013). The linearized form of Langmuir isotherm is:

$$\frac{C_e}{q_e} = \frac{1}{q_m . k_L} + \frac{1}{q_m} C_e \qquad (3)$$

Where q_e is the adsorption capacity of adsorbent at equilibrium (mg/g adsorbent), C_e is a concentration of the remaining metal ions in the solution after the adsorption process (mg/L), k_L is a constant which is related to the net enthalpy and q_m is the maximum adsorption capacity of the adsorbent (mg/g). The values for q_m and k_L can be calculated from the plot of C_e/q_e versus C_e (Singanan and Peters, 2013).

One of the important dimensionless factors of Langmuir isotherm is R_L which is called the separation factor and evaluates the suitability of this isotherm for adsorption processes which are defined by the following equation:

$$R_L = \frac{1}{1 + k_L C_0} \tag{4}$$

If R_L is less than unity, it shows that the adsorption process of Ni^{2+} or Cu^{2+} ions by fish scales is optimum and favourable. Table 1 shows the optimum range of R_L. (Bazargan-lari et al., 2014)

Table 1. Ranges of R_L

R_L	Type of isotherm
$R_L > 1$	Unfavourable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L < 0$	Irreversible

Freundlich model assumes that adsorption takes place in heterogeneous mode and considers no surface saturation which is defined in the following equation:

$$q_e = K_F C_e^{1/n} \tag{5}$$

Where K_F and $1/n$ are constants and indicate the behavior of the adsorption capacity of adsorbent and adsorption intensity, respectively (Qada et al., 2006). Freundlich model can be rewritten in the linear form as follows:

$$\ln q_e = \frac{1}{n} \ln C_e + \ln K_F \tag{6}$$

Where K_F and $1/n$ can be determined from the intercept and the slope of the plot of $\ln(q_e)$ versus

$\ln(C_e)$, respectively. The values of 1/n less than unity represent favourable adsorption (Bouguerra et al., 2007).

Effect of Ni^{2+} and Cu^{2+} ions concentrations (15, 25, 30, and 35 mg/L), scales contents (10, 20, 30, and 40 g/L), contact times (10, 30, 60, 90, and 120 minutes), pH values (2, 4, 6, 8, 10 and 12), electric field current densities (2, 4, 6 and 8 A/dm^2) and magnetic field on the adsorption process were studied in this research. Firstly, the effect of adsorption parameters (e.g. ion concentration, scale content, contact time, and pH) on the adsorption process of Ni^{2+} and Cu^{2+} was studied. Consequently, optimum conditions were chosen to investigate the effects of electric and magnetic fields on the absorption process. It is necessary to note that, as shown later in the results, the adsorption of Cu^{2+} ions by fish scales is very efficient (up to 95% removal) and leads to the fact that the effects of electric and magnetic fields on the absorption process of ions become negligible. For this reason, the effects of electric and magnetic fields on the adsorption of Ni^{2+} ions were studied only the results might be generalized to other ions.

TESCAN-Vega 3 scanning electron microscopy was used to study the fish scales morphology and structure and AVATAR-Thermo FTIR analyzer was used to investigate the absorption process. In addition, an AAS-680 atomic absorption spectrophotometer was used to determine the concentrations of the ions before and after the adsorption process. It is necessary to note that each test was repeated 3 times to ensure the rigour of the data.

3. Results and discussion:

3.1. Sorbent morphology and structure

Fish scales morphology and structure are shown in Figure 3. As shown in Figure 3(a) wave-like structure of the surface and the internal plywood structure (Figure 3(b) and 3(d)) are clear which is in agreement with Gil-Duran et al. (Gil-duran et al., 2016) and Okuda et al. (Okuda et al., 2011) studies. Furthermore, as shown in Figure 3(c), collagen fibrils that have semi-parallel orientation are easily recognized.

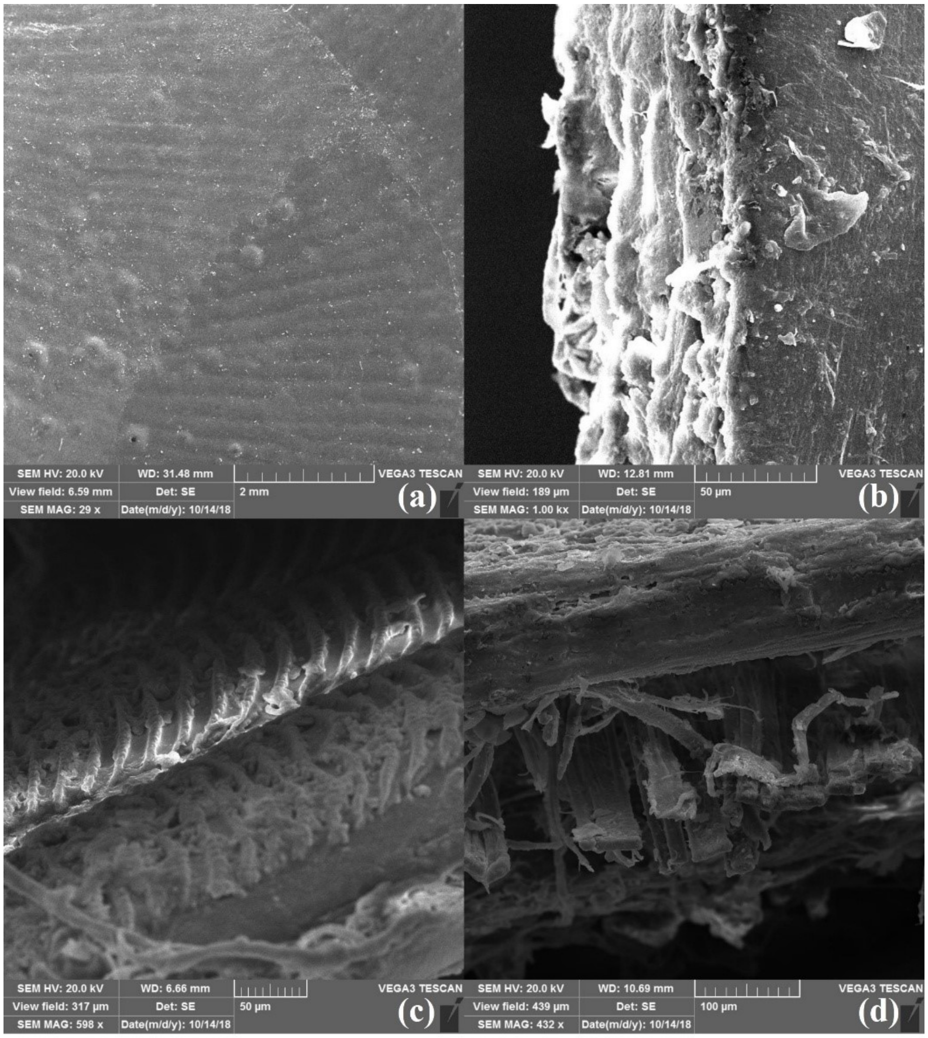


Figure 3. SEM images of (a) The scale's surface,(b) Edge of the scale, (c) and (d) torn cross section of the scale.

3.2. Effect of contact time

Effect of contact time on adsorption process of ions by using fish scales biosorbent was performed in the following conditions: sorbent content: 20 g/L, ions concentration: 15 mg/L, pH: 8, and contact times: 10, 30, 60, 90, and 120 minutes at room temperature. The effect of contact time on the adsorption of Ni^{2+} and Cu^{2+} ions is shown in Figure 4.

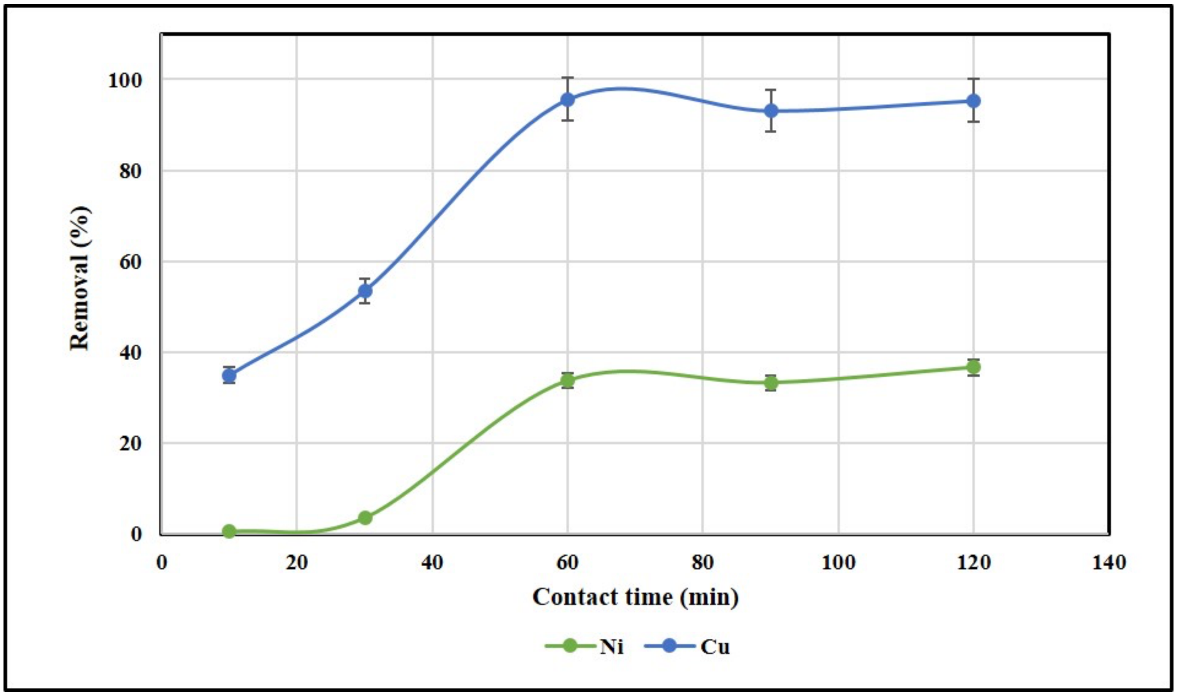


Figure 4. Effect of contact time on the removal of Ni^{2+} and Cu^{2+} ions.

As observed in Figure 4, the adsorption of both Ni^{2+} and Cu^{2+} ions increased with increasing contact time. For Ni^{2+} ions, by increasing contact time from 10 to 120 minutes, the removal efficiency was increased from approximately 2% to 36% and for Cu^{2+} ions, the removal efficiency was increased from 34% to 95%, respectively. This behavior has been reported by other researchers. However, the removal efficiency was much higher for Cu^{2+} ions than Ni^{2+} ions and reached approximately 95% for copper absorption. This may be due to better chemical absorption of Cu^{2+} ions and better compatibility between Cu^{2+} ions and scales surface. Finally, 120 minutes of contact time was chosen for investigating other parameters.

3.2 Effect of pH

The effect of the pH of the bath on the removal efficiency of the ions was carried out in the following conditions: contact time: 120 minutes, sorbent content: 20 g/L, and initial concentration: 15 mg/L as shown in Figure 5.

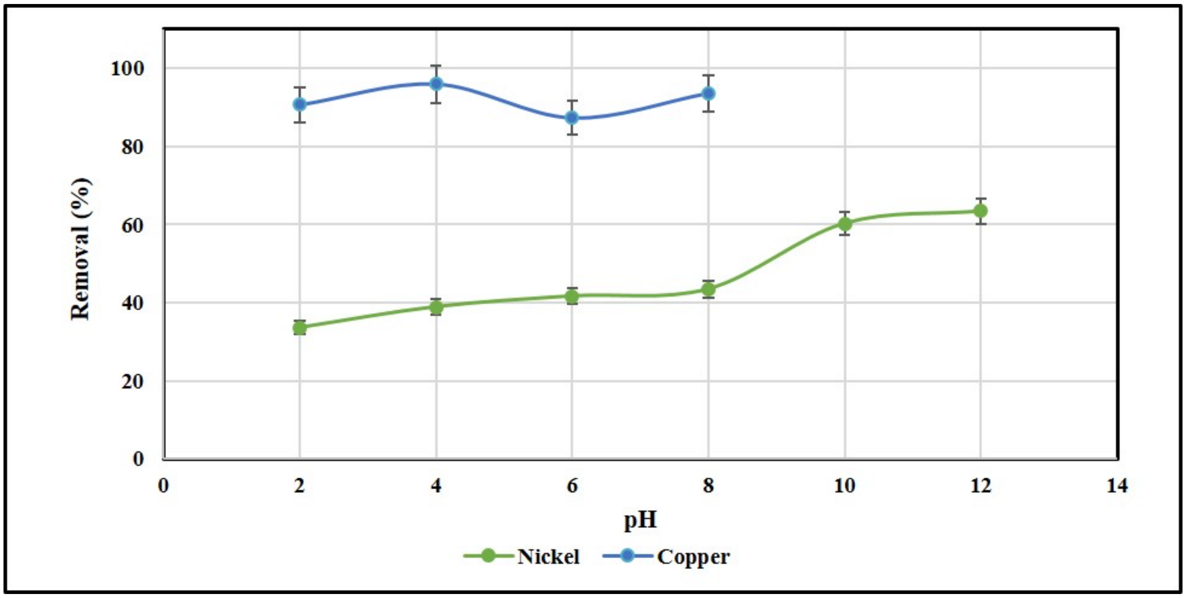


Figure 5. Effect of pH on the removal of Ni^{2+} and Cu^{2+} ions.

As shown in Figure 5, by increasing pH from 2 to 12 in the nickel adsorption, the removal of ions was increased from 33% to 63%, and for copper by increasing the pH from 2 to 8, the removal efficiency of the ion was almost the same for all pH values and the ion removal fluctuated around 90%. This shows that pH is not an important parameter in the copper adsorption process. It is necessary to note that, by increasing pH above 8 for copper adsorption, the Cu^{2+} ions formed precipitates in the bath due to the increasing of hydroxyl groups and produce $Cu(OH)_2$, and hence a bluish precipitate was formed at the bottom of the vessel. As a result, the effect of pH on copper adsorption was investigated only in the range of pH= 2 to pH= 8. It is important to note that by measuring the pH of the solution before and after the tests, the pH was decreased by 1, even at high pH values, i.e., higher than 8. This indicates that hydroxyl groups have an important role in the adsorption of these ions by fish scales. Fourier-transform infrared spectroscopy (FTIR) spectra of the fish scales after adsorption tests for Ni^{2+} and Cu^{2+} ions are shown in Figure 6.

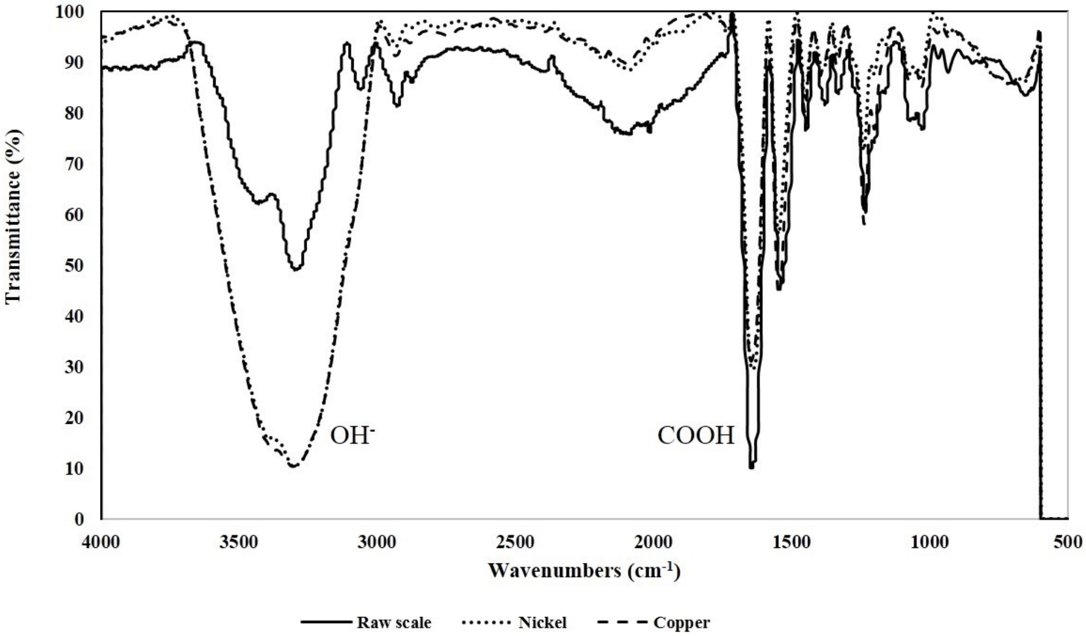


Figure 6. FTIR spectra of the raw scale and after adsorption of Ni^{2+} and Cu^{2+} ions.

As observed in Figure 6, a broad peak in the 3400 cm^{-1} wavenumber is due to hydroxyl groups and a sharp peak in the 1646 cm^{-1} wavenumber is due to carboxylic acid groups (Thomas Cairns, Ian G McWilliam, Robert L Pecsok, 1976). As shown in Figure 6, after the adsorption process, the hydroxyl peak became broader and sharp which indicates that OH^- ions in the bath made complex compounds with ions and carboxylic groups in fish scales. Consequently, the solution pH was decreased after absorption tests. As shown before by many researchers, collagen is a copolymer of hydroxyproline, proline, and glycine and all of them contain carboxylic acid (MAYNE and BURGESON, 1987; Silver et al., 2018). Finally, the hydroxyl group may make a complex and by this phenomenon, the adsorption of ions increased suggesting that the adsorption process of ions by fish scales biosorbent is a chemical process and not just a physical attraction between the ions and scales. According to FTIR spectra, the absorption process of these ions by scales changes the bonding of the scales surfaces. Overall, the pH=10 and pH=8 were chosen for further nickel and copper adsorption study, respectively.

3.3 Effect of initial concentration

The effect of initial concentration on the adsorption of nickel and copper ions which was performed in the following conditions is shown in Figure 7: contact time: 120 minutes, sorbent content: 20 g/L, pH= 10 for nickel adsorption, pH=8 for copper adsorption and ions concentration: 15, 25, 30 and 35 mg/L.

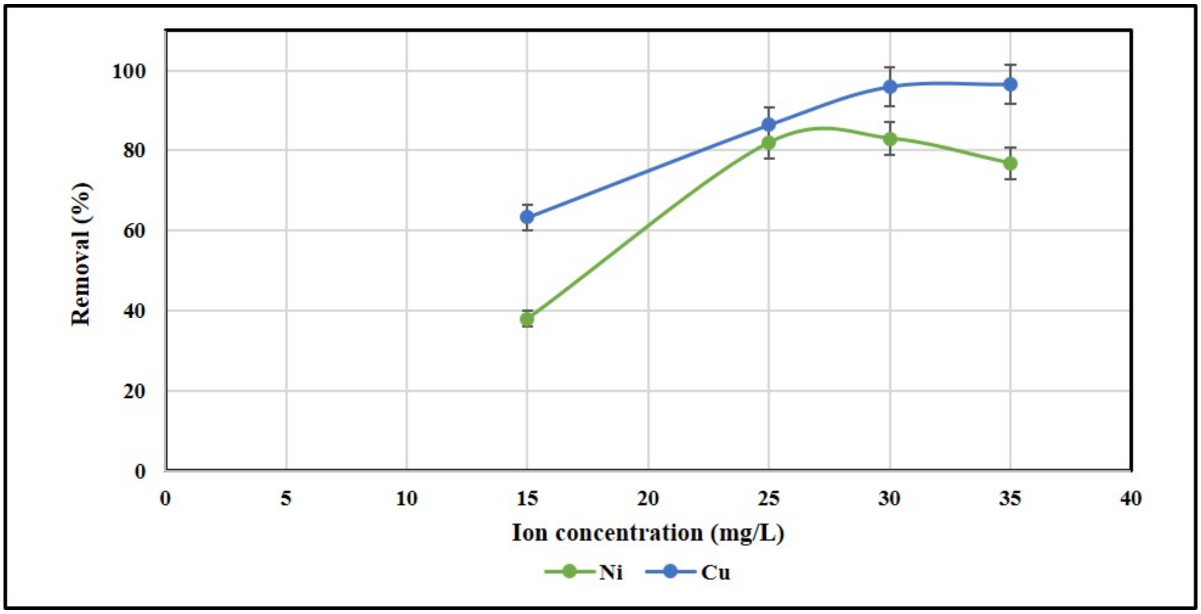


Figure 7. Effect of initial ions concentration on the removal efficiency.

As shown in Figure 7, by increasing the ion concentration, the removal efficiency of nickel adsorption increased from 38% to 76% and copper adsorption increased from 63% to 96%. This revealed that in the 25 mg/L nickel concentration, scales have free adsorption sites and by increasing the nickel concentration in the bath, the removal was increased. Similar behavior was observed for copper adsorption but until a copper concentration of 30 g/L was reached. By further increasing the concentration, the scales sites were saturated and hence no more adsorption occurred. This behavior is in agreement with the work of Hosseini et al.(Hosseini et al., 2013) and Periasamy et al.(Contribution, 1995).

3.4 Effect of scales content

The effect of sorbent content on the adsorption of nickel and copper ions which was carried out in the following conditions is shown in Figure 8: contact time: 120 minutes, pH=10 and pH=8 for nickel and copper respectively, initial concentration: 15 mg/L and sorbent content: 10, 20, 30 and 40 g/L.

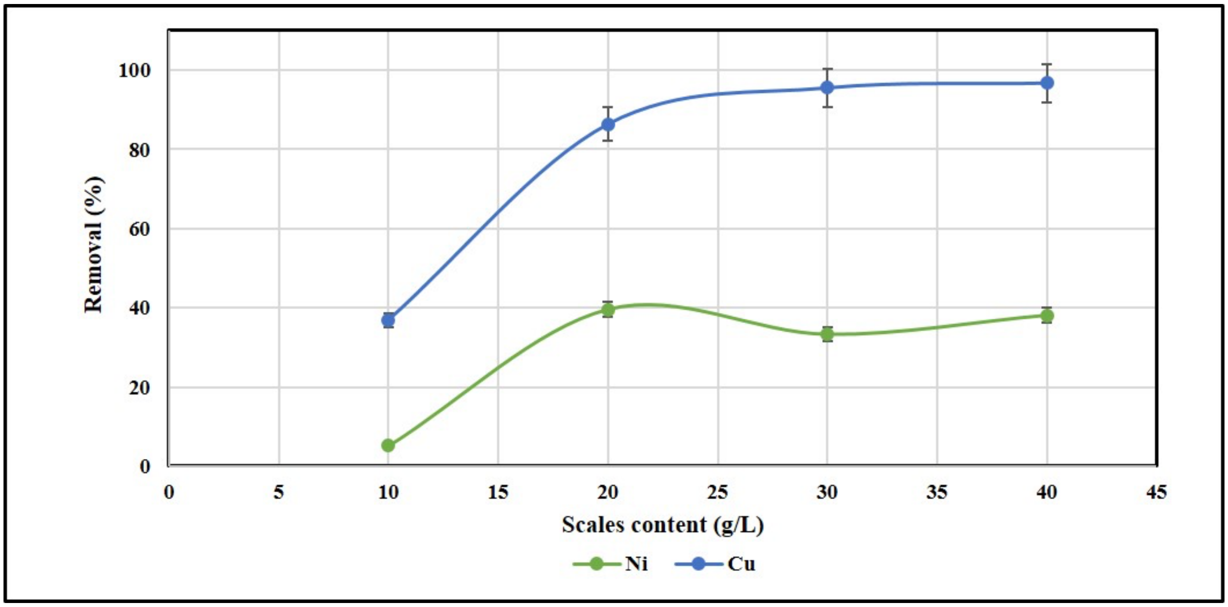


Figure 8. Effect of sorbent content on the removal efficiency of Ni^{2+} and Cu^{2+} ions.

As observed in Figure 8, by increasing sorbent content in the bath, the removal of ions increased from 5% to 38% and from 36% to 96% for nickel and copper ions, respectively. This is due to the increase of adsorption sites by increasing sorbent content in the vessel (Zhao et al., 2010).

However, after 20 g/L sorbent content, the adsorption reached saturation and as a result, the removal efficiency was constant.

3.5 Adsorption isotherms

The Langmuir isotherm of copper and nickel ions removal are shown in Figure 9(a) and b, respectively. Values for q_m and K_L calculated from the plots and Eq. 3 are shown in Table 2. The values of R_L for Ni^{2+} and Cu^{2+} ions are 0.29 and 0.037, respectively. R_L is obtained from Eq. 4 and shows that the absorption of Ni^{2+} and Cu^{2+} ions by the fish scale is favourable.

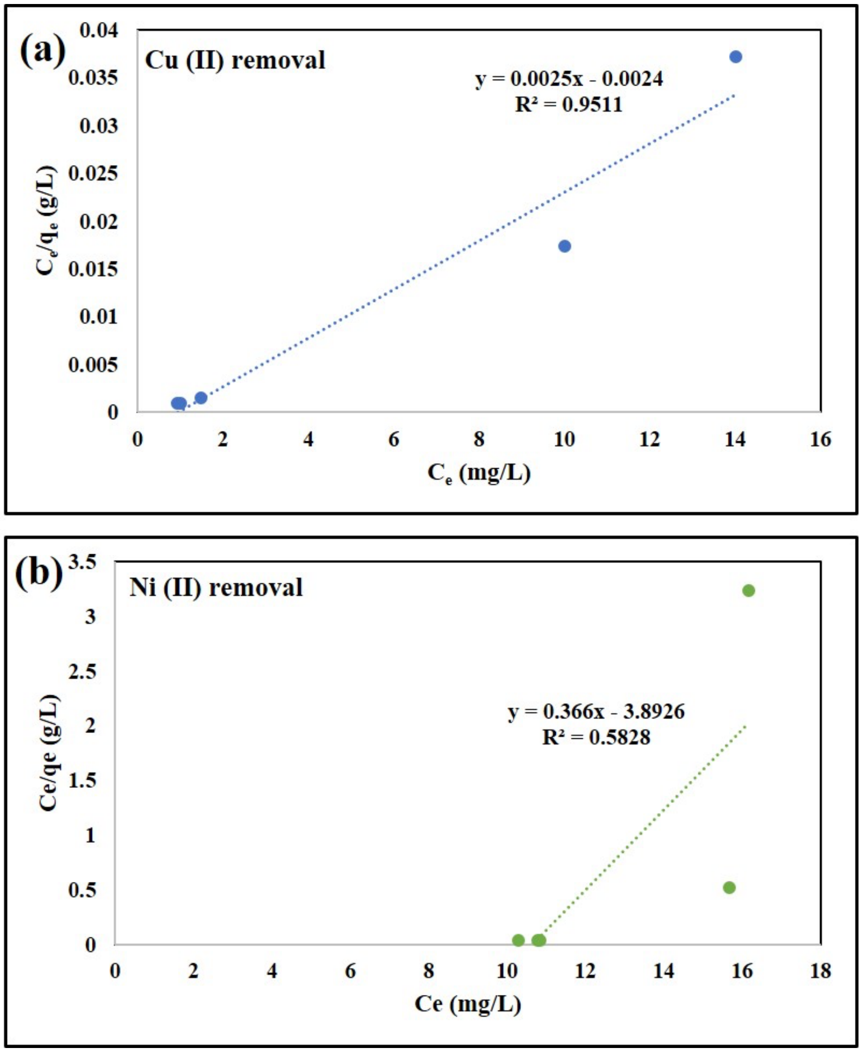


Figure 9. Langmuir isotherm model for removal of (a) Cu(II) and (b) Ni(II).

The Freundlich isotherm of Cu^{2+} and Ni^{2+} ions removal are shown in Figure 10(a) and b, respectively. The values for q_m and K_F were obtained from the plots and Eq. 6. They can also be found in Table 2. As shown in Figures 9(a) and 11(a), the value of R^2 for Langmuir and Freundlich isotherms for copper absorption are 0.9511 and 0.9292, respectively. Consequently, the Langmuir isotherm is more favourable and this model is fitted for copper absorption very well. On the other hand, the R^2 value for Langmuir and Freundlich isotherms of nickel removal are 0.5828 and 0.9068, respectively and thus, Langmuir isotherm is not a good model for nickel absorption and the Freundlich model shows better alignment for nickel absorption from wastewater treatment by fish scales.

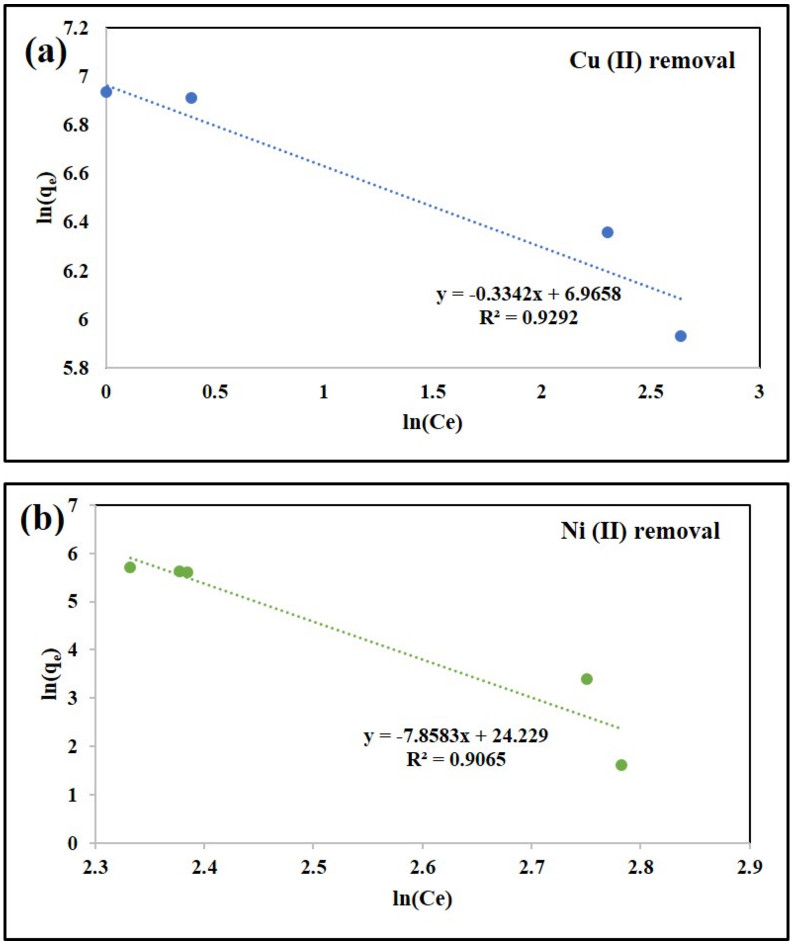


Figure 10. Freundlich isotherm model for removal of (a) Cu(II) and (b) Ni(II).

Table 2. The Langmuir and Freundlich parameters for removal of Ni^{2+} and Cu^{2+} ions.

Metals	Langmuir parameters	Freundlich parameters
Ni(II)	q_{max} = 2.73 (mg/g) K_L = 0.094 (L/mg) R^2 = 0.5828	$K_f = 3.3*10^{10}$ R^2 = 0.9065
Cu(II)	q_{max} = 400 (mg/g) K_L = 1.041 (L/mg) R^2 = 0.9511	K_f = 1059 R^2 = 0.9292

3.6 Effects of electric and magnetic fields

As observed before, the adsorption efficiency of Cu^{2+} ions by fish scales is very high and near 100%, and the optimum condition for nickel adsorption was: contact time: 120 minutes, pH: 10, ion concentration: 25 mg/L and sorbent content: 20 g/L and in this condition the removal efficiency was approximately 82% which for both nickel and copper are very high and acceptable. However, to investigate the effects of electric and magnetic fields and better interpretation of these effects and to prevent overlapping high efficiency of adsorption with the effect of electric and magnetic fields on the adsorption process, adsorption tests for Ni^{2+} ions were performed in the following condition: pH=10, sorbent content: 20 g/L, Ni^{2+} ions concentration: 25 mg/L, electric field current density: 8 A/dm^2 and contact time: 10, 30 and 60 minutes. Effects of electric and magnetic fields were investigated for nickel only. This was due to the fact that copper adsorption by fish scales had very high efficiency and the effect of the electric field on the copper adsorption would be very difficult to determine. Furthermore, the effect of an electric field on the adsorption process was tested in this study as a new technique for increasing adsorption efficiency and since the efficiency of the copper adsorption was already nearly 100% it was clear that this approach would have little effect of the removal of Cu^{2+} ions. The effect of the electric field on the adsorption efficiency of nickel ions is shown in Figure 11.

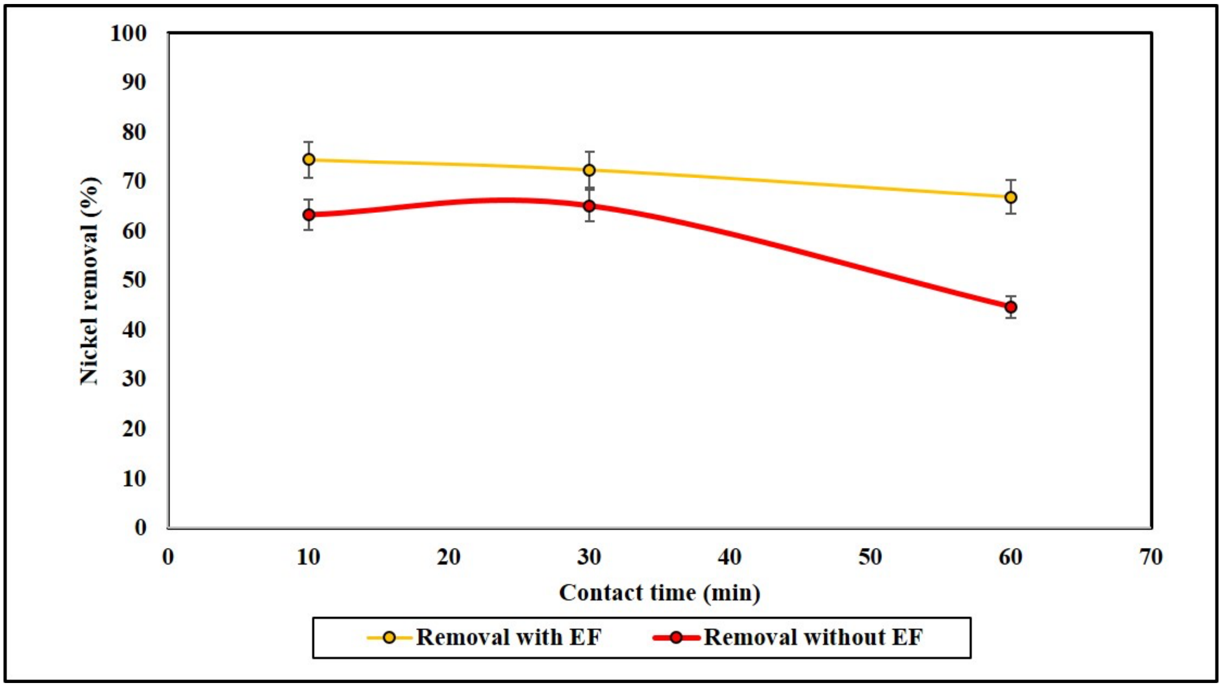


Figure 11. Effect of electric field on the removal efficiency of nickel ions.

As shown in Figure 11, the electric field increased the removal efficiency of the ions in all contact times and improved the efficiency up to 10% for 10 and 30 minutes and 20% for 60 minutes of contact time, respectively. This finding might be due to the increase of polarity of the hydroxyl group in the bath (pH=10) and on the surface of fish scales. Hence, the tendency of the hydroxyl group for the adsorption of Ni^{2+} ions to reach saturation was increased, and finally, the adsorption efficiency was enhanced. FTIR spectra of fish scales adsorption with and without the presence of an electric field in the bath are shown in Figure 12.

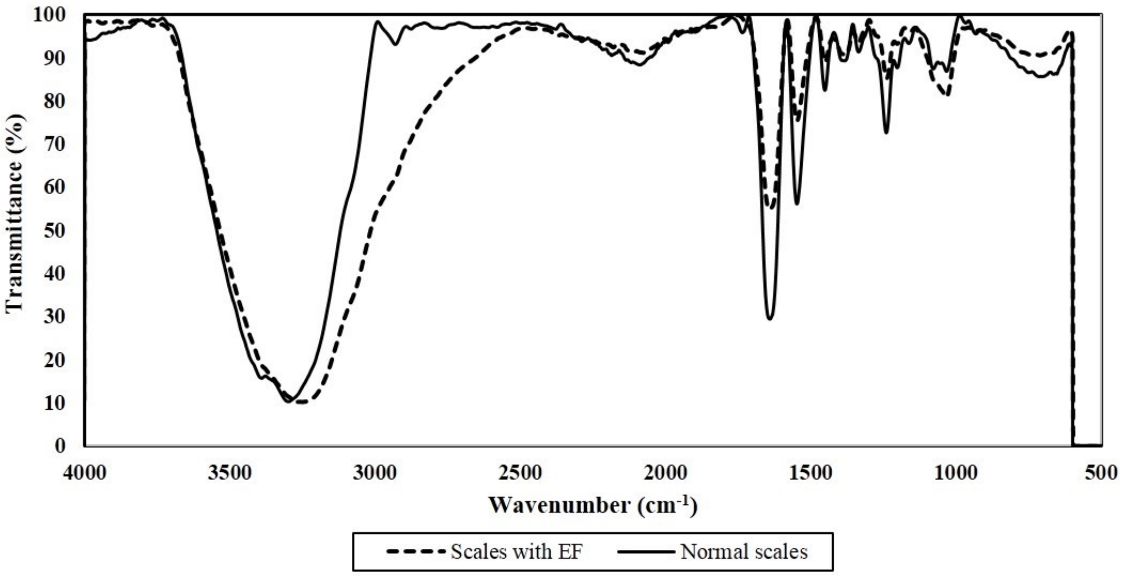


Figure 12. FTIR spectra of the fish scale in normal adsorption process and in the presence of an electric field in the adsorption process.

As observed in Figure 12, the hydroxyl peak is broader in the presence of an electric field and the broadening of peaks in the FTIR spectroscopy is related to the increase of polarity of chemical groups. In fact, in the hydroxyl group, oxygen and hydrogen atoms have partial negative and positive charges, respectively and these charges produce dipole moments in each hydroxyl group as shown schematically in Suplementary 1(a). Therefore, when an electric field is applied to the adsorption process, these dipole moments in hydroxyl groups, in the aqueous solution and on the surface of fish scales, become elongated (S1(b)) and compressed (S1(c)) depending on the directions of the electric field and the dipole moments.

Finally, by applying an electric field in the adsorption process, the electric field affects the dipole moments of hydroxyl groups and hence increase the adsorption efficiency of the ions. Overall, the contact time: 60 minutes was chosen for further study of electric and magnetic fields for a better understanding of these effects.

Wisseroth and Braune(Wisseroth et al., 1977) have studied the effect of the electric field on thermodynamic equilibrium and chemical parameters (e.g. enthaloy and entropy) of some simple reactions. They showed that a strong electric field can change the direction of the reactions and consequently change the product of the reaction in comparison with the reactions in the absence of an electric field. Sowlati-Hashjin and Matta (Sowlati-hashjin and Matta, 2014) have investigated the chemical bonds of diatomic molecules in an external electric field. They also demonstrated that changing either the direction or strength of the external electric field can change the bond length of the molecules. Finally, according to the studies which were mentioned above and also in section 1, it can be concluded that an electric field can affect the electric dipole moment and shift the electron cloud around the hydroxyl groups and change their affinity and hence enhance the removal efficiency of the Ni^{2+} ions from wastewater. It is necessary to note that in the present work, the bath was agitated during experiments in all tests, and thus all of the scales, ions, and hydroxyl groups were stirred during the experiments and when the electric field was applied, the direction of dipole moments with respect to the electric field was not fixed. Thus, these dipole moments experienced some oscilations and their bond lengths changed permanently during the experiments. However, these changes enabled an increase in the removal efficiency of Ni^{2+} ions from wastewater.

Effects of different current densities of electric fields, on the removal efficiency of Ni^{2+} ions adsorption which were performed in the following condition, is shown in Figure 13: contact time: 60 minutes, pH=10, sorbent content: 20 g/L, Ni^{2+} ions concentration: 25 mg/L and electric field current density: 2, 4, 6 and 8 A/dm^2.

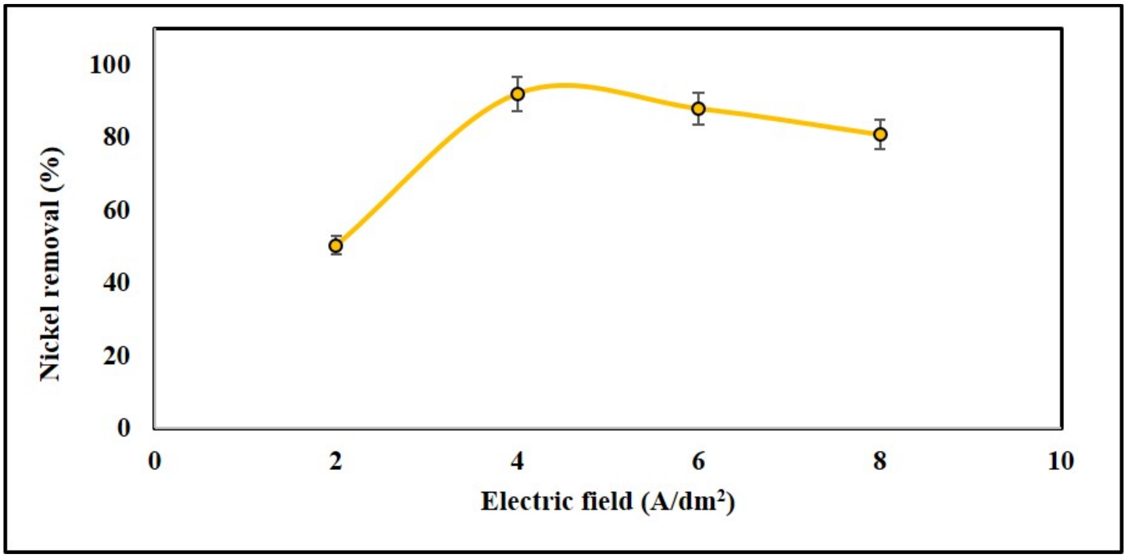


Figure 13. Effect of different electric field strength on the removal efficiency of Ni^{2+} ions.

As observed in Figure 13, by increasing the electric field current density, the removal efficiency was increased up to approximately 92% at 4 A/dm^2 as well. This may be due to the polarity of hydroxyl groups increasing and hence the tendency for the adsorption to rise and consequently improve adsorption. In comparing Figures 5, 11, and 13, the effect of the electric field is revealed due to the fact that the removal efficiency of Ni^{2+} ions without an electric field was approximately equal to 60% in 120 minutes of contact time, 45% in the same condition but in 60 minutes contact time and 92% with 4 A/dm^2 electric field. These results indicate that an electric field can reduce the contact time of adsorption to 60 minutes and increase adsorption efficiency 2 times higher at the same contact time. In fact, by using an electric field in the adsorption process for 60 minutes, the removal efficiency was increased approximately to the same removal percentage that occurred after 120 minutes without the presence of an electric field condition.

The effect of the magnetic field on the removal efficiency of nickel ions which was performed in the following conditions is shown in Figure 14: contact time: 60 minutes, pH: 10, sorbent content: 20 g/L, and Ni^{2+} ions concentration: 25 mg/L.

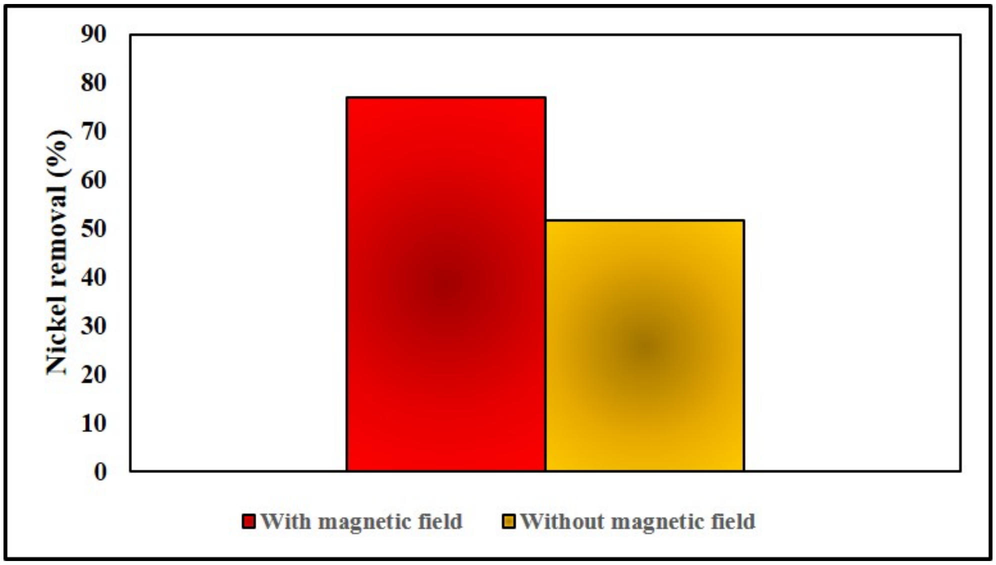


Figure 14. Effect of magnetic field on the removal efficiency of Ni^{2+} ions.

As shown in Figure 14, by applying a magnetic field during the adsorption process, the removal efficiency of nickel ions was increased by 26% (from 51% to 77%). By considering magnetic dipoles in hydroxyl groups and Ni^{2+} ions, the magnetic field can affect these magnetic dipole moments and hence increase the removal efficiency of the ions. This phenomenon is similar to the effect of the electric field on the hydroxyl groups and nickel ions but by compressing and stretching the magnetic dipole moments instead of the electric dipole moments. FTIR spectra of fish scales in the magnetic and electric fields are shown in Figure 15. It is clear that both the magnetic and electric fields have similar effects on the hydroxyl groups of fish scales. In fact, by applying either a magnetic field or an electric field during the adsorption process, the polarity of the ions and hydroxyl groups are affected, and hence these ions and hydroxyl group bond together to reach equilibrium, and hence the removal efficiency is increased.

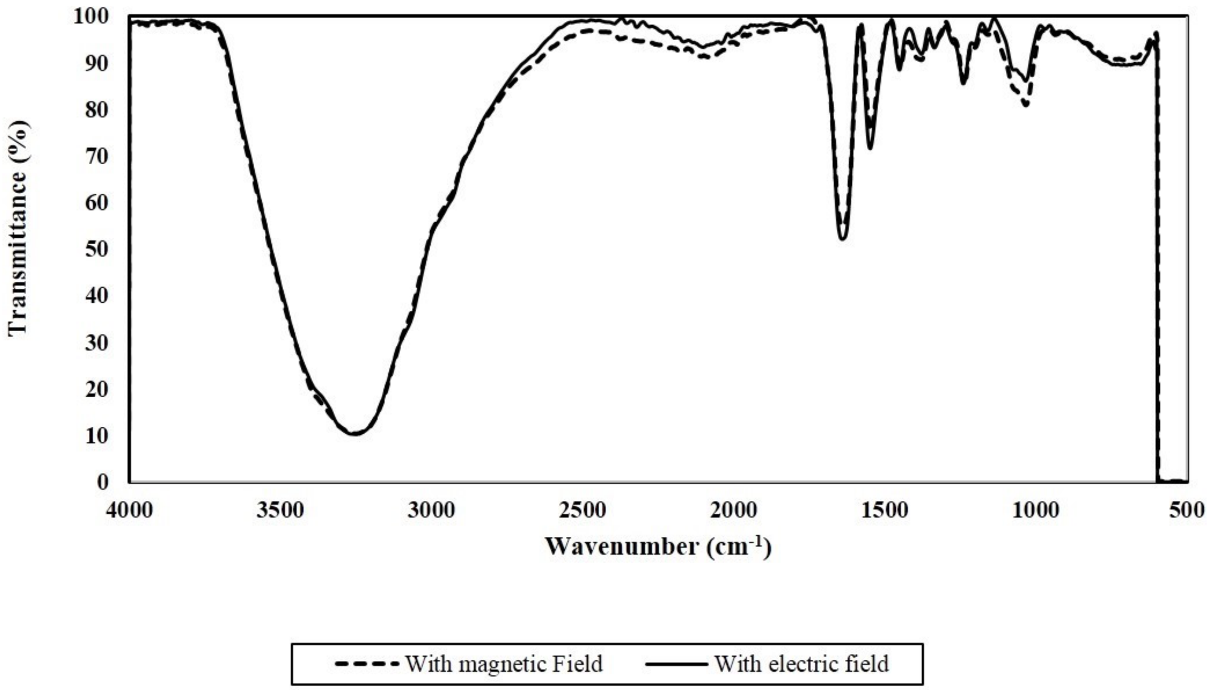


Figure 15. Comparison of FTIR spectra of fish scales in the presence of electric and magnetic fields.

Finally, a comparison of scales adsorption without any field and with the presence of electric and magnetic fields is shown in Figure 16. It was found that, by applying 4 A/dm^2 current density, the removal efficiency was increased by more than 40%, and by applying a magnetic field, the removal efficiency was increased by more than 20 % in comparison with normal conditions. It is necessary to note that after the adsorption process, the fish scales became bluish in all conditions and this is evidence of the chemical absorption of these ions by fish scales.

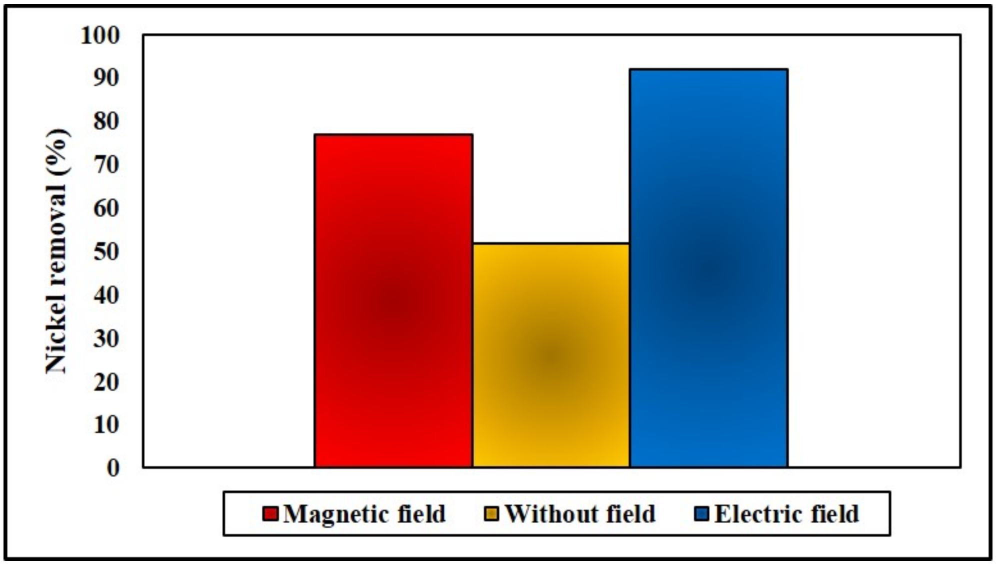


Figure 16. Comparison of adsorption of nickel ions in normal condition and presence of electric and magnetic fields.

4. Conclusions

The absorption process of Ni^{2+} and Cu^{2+} ions from wastewater by using fish scales (Pomadasys Kaakan's scales) and the effect of an electric field or a magnetic field on the absorption process were investigated. The results showed that increasing the absorption parameters (e.g. sorbent content, pH, and contact time) increases the removal efficiency of ions. Electric and magnetic fields also increase the removal efficiency of the Ni^{2+} ions from wastewater. In addition adsorption of Cu^{2+} ions by fish scales is approximately 95% which is very high. It must be mentioned that this study revealed the effect of sea contamination on sea creatures and more importantly harmful consequences on human health because of using these species as a source of food. In other words, this study not only showed the capability of fish scales as a biosorbent for wastewater treatment but, on the other hand, it revealed that fishes can adsorb seawater contamination through their scales which consequently, will be consumed by humans and affect their health.

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