

# Kinetic Studies of Heavy Metal Removal from Industrial Wastewater by Using Natural Zeolite

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## Abstract

The present work involves the study of the removal of Cu<sup>2+</sup>, Fe<sup>3+</sup>, Pb<sup>2+</sup> and Zn<sup>2+</sup> from synthetic metal solutions using natural zeolite. Laboratory experiments were used to investigate the efficiency of adsorbents in the uptake of heavy metals from industrial wastewater. The kinetic study was used to identify the effect of parameters that affect the rate of adsorption and evaluated their impact on the efficiency of the zeolite in the removal of heavy metals from industrial wastewater. Natural zeolite (clinoptilolite) as adsorbent contacted with multi-component synthetic solutions containing Cu<sup>2+</sup>, Fe<sup>3+</sup>, Pb<sup>2+</sup> and Zn<sup>2+</sup> ions without any pre-modifications and every hour 15 ml of the samples were filtered and taken for metal ion concentration analysis using the ICP-OES. The pH values were monitored and adjusted regularly. The results showed that the capacity of the adsorbents for the removal of heavy metals increased with a greater mass of adsorbent, increased initial solution pH, increased agitation speed and higher solution concentration.

**Keywords:** Kinetic studies, Heavy metals, Wastewater, Natural zeolite, Adsorption.

## 1. Introduction

Zeolites are well-known aluminosilicate minerals that are used in wastewater purification processes and environmental pollution control. The reduction of heavy metal contamination in aquatic systems is a global problem (Peng et al., 2009). In the meantime, the treatment of industrial wastewater contaminated by heavy metals has become a major challenge. According to Bish and Ming (2001) the wastewater collected from municipalities, communities and industry needs to be treated then returned back to aquatic systems or to the land (Kalló et al., 2001). The main sources of heavy metal pollution occur in wastewater from various sources such as metal plating facilities, battery manufacturing processes, mining operations, nuclear power generation, over use of pesticides, vehicle emissions, the ceramic and glass industries, paints, and treated timber and microplastics. Andras et al. (2012) proved that over limit heavy metals are recognized as toxic elements and their discharge into the water system affects both human health and the natural ecosystem (Andras et al., 2012) Since they are not biodegradable, and cause numerous diseases and disorders (Pandey et al., 2009; Tchobanoglous & Burton 1991). In order to achieve the above goal, adsorption, ion exchange can be used to remove or reduce heavy metals from wastewaters. According to Panayotova and Velikov (2003) the advantage of using clinoptilolite is being relatively cheap, abundant in supply, sustainable and it is environmentally friendly.

Kinetic studies were carried out in order to investigate the behaviour of adsorbents and understand the removal mechanisms involved in the adsorption process. Kinetic studies are critical processes that are used to obtain information about the process dynamics such as the adsorption rate, contact time and mass transfer parameters including external mass transfer coefficients and intraparticle diffusivity (Connors, 1998). Margeta et al. (2013) have divided the process

of diffusion in the zeolite system into four phases: (I) Diffusion in solution, (II) Diffusion through the film, (III) Diffusion in pores, and (IV) Ion exchange. These parameters are important in the design and to optimise the operation of any adsorption experiment in wastewater treatment. Therefore, kinetic studies were used in this work to evaluate the suitability of natural zeolite for removing heavy metal cations from solution. Kinetic studies also supply information about the nature of the ionic transport mechanisms that control the exchange rate (Harland, 1994). Factors and their effect on the efficiency of natural zeolite in removing  $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Pb}^{2+}$  and  $\text{Zn}^{2+}$  from solution were investigated in detail.

## 2. Experimental: Materials and Methods

Natural zeolite (clinoptilolite) was used as “as-received” without any pre-modifications and originally mined in Anaconda and supplied by the Anaconda mining company, Denver Colorado, USA. It is 97% pure. Synthetic multi-component solutions of  $\text{Fe}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Zn}^{2+}$  ions were prepared from analytical grade iron (III) chloride hexahydrate ( $\text{H}_2\text{Cl}_3\text{FeO}_6$ ), copper (II) chloride dehydrate ( $\text{H}_4\text{Cl}_2\text{CuO}_2$ ), Lead(II) acetate trihydrate ( $\text{C}_4\text{H}_{12}\text{O}_7\text{Pb}$ ) and zinc acetate dehydrate ( $\text{C}_4\text{H}_{10}\text{O}_6\text{Zn}$ ). The pH values were monitored and adjusted using a pH meter (Microprocessor pH Meter – pH 211-HANNA instruments). The pH was adjusted to 2, 4, and  $6 \pm 0.1$  by adding hydrochloric acid (HCl) or bases sodium hydroxide (NaOH). To observe the effect of agitation speed; agitation in a beaker was obtained by using a magnetic stirrer (stuart-SB162) at a speed of 100 rpm, 150 rpm and 200 rpm. Zeolite samples with masses 2 g, 4 g and 8 g were contacted with constant volume (100 ml) of multi - component synthetic solutions containing  $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Pb}^{2+}$  and  $\text{Zn}^{2+}$  ions. They were agitated at agitation speeds of 100, 150 and 200 rpm for agitation times of 60, 120, 180, 240, 300 and 360 minutes in a magnetic stirrer at room temperature. Two different sizes of zeolite particles were selected  $<125 \mu\text{m}$  and  $<250 \mu\text{m}$ . The effect of the initial solution concentration on the adsorption process was determined using multi-component solution concentrations in the range of (50, 100, 200 and 400) mg/l. Every hour 15 ml of the samples were filtered and taken for metal ion concentration analysis using the ICP-OES. The pH values were monitored and adjusted regularly.

The experiments were duplicated three times in order to examine the reproducibility of the results, while the mean value was used for all taken data. The deviation between the duplicate samples in analysing the cations was  $\pm 6.4\%$ , 6.3%, 5.6% and 6.4% for  $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Pb}^{2+}$  and  $\text{Zn}^{2+}$  ions respectively.

## 3. Kinetic Study Results

The results show that the highest adsorption rate of  $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Pb}^{2+}$  and  $\text{Zn}^{2+}$  ions took place in the first hours followed by a slower adsorption rate later on. The first hour is an initial stage of adsorption when higher rates of adsorption take place; this may be due to the availability of more adsorption sites and the fact that the metal ions exchange easily on the surface of the zeolite grains (Inglezakis et al., 2002). The driving force for adsorption is very high in the initial stage of the adsorption process and this also results in a higher initial adsorption rate. After that, a slower adsorption rate follows due to slower diffusion of the metal ions into the interior channels. Consequently, these metal ions occupy the exchangeable positions within the crystal structure of the natural zeolite (Amarasinghe & Williams 2004; Myroslav et al., 2006).

The data obtained from the kinetic adsorption tests were used to determine the removal capacity,  $q_e$  (mg/g) of the different adsorbents using the following equation:

$$q_e = (C_o - C_e) \times V / m \quad (1)$$

The percentage removal of metal ions from solution was also determined using the equation below:

$$\text{Percentage Adsorbed (\% removal)} \quad q_e = \{(C_o - C_e) \times 100\} / C_o \quad (2)$$

When:

$q_e$  amount of adsorbate adsorbed per unit weight of adsorbent (mg/g)

$C_o$  and  $C_e$  are the initial and final metal ion concentrations in solution (mg/l) respectively,  $V$  is the solution volume (l) and  $m$  is the weight of the zeolite used (g).

### 3.1 Factors that affect the rate of adsorption

A number of parameters that affect the rate of adsorption were studied and described in detail. These include: effect of adsorbent mass, effect of adsorbent particle size, effect of initial solution pH, effect of initial solution concentration and effect of agitation speed of adsorbent.

#### 3.1.1. Effect of adsorbent mass

Kinetic experiments were carried out using three different adsorbent masses, 2 g, 4 g and 8 g. The results in Table 1 clearly show that when the adsorbent mass was increased, this resulted in an increase in the adsorption of the heavy

metal ions. The main reason for this is that as the adsorbent mass increases more adsorption sites are available per mass of adsorbent surface and thus the total amount of metal that is removed increases.

Table 1. The effect of natural mass on the removal of heavy metals from solution zeolite.

Heavy metal ions	Adsorbent Mass (g)	Percentage Adsorbed (%)
Copper	2g	62.51
	4g	92.85
	8g	99.02
Iron	2g	99.88
	4g	99.98
	8g	100.00
Lead	2g	99.70
	4g	99.91
	8g	99.99
Zinc	2g	41.02
	4g	69.14
	8g	98.02

This result indicates that the mineral mass in the solution can affect the adsorption capacity for the removal of heavy metals as it determines the availability of adsorption sites. The removal of  $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Pb}^{2+}$  and  $\text{Zn}^{2+}$  ions mostly occurs in the early stage, while the percentage of adsorbed  $\text{Fe}^{3+}$  and  $\text{Pb}^{2+}$  reached 90% in the first hour Figure 1.

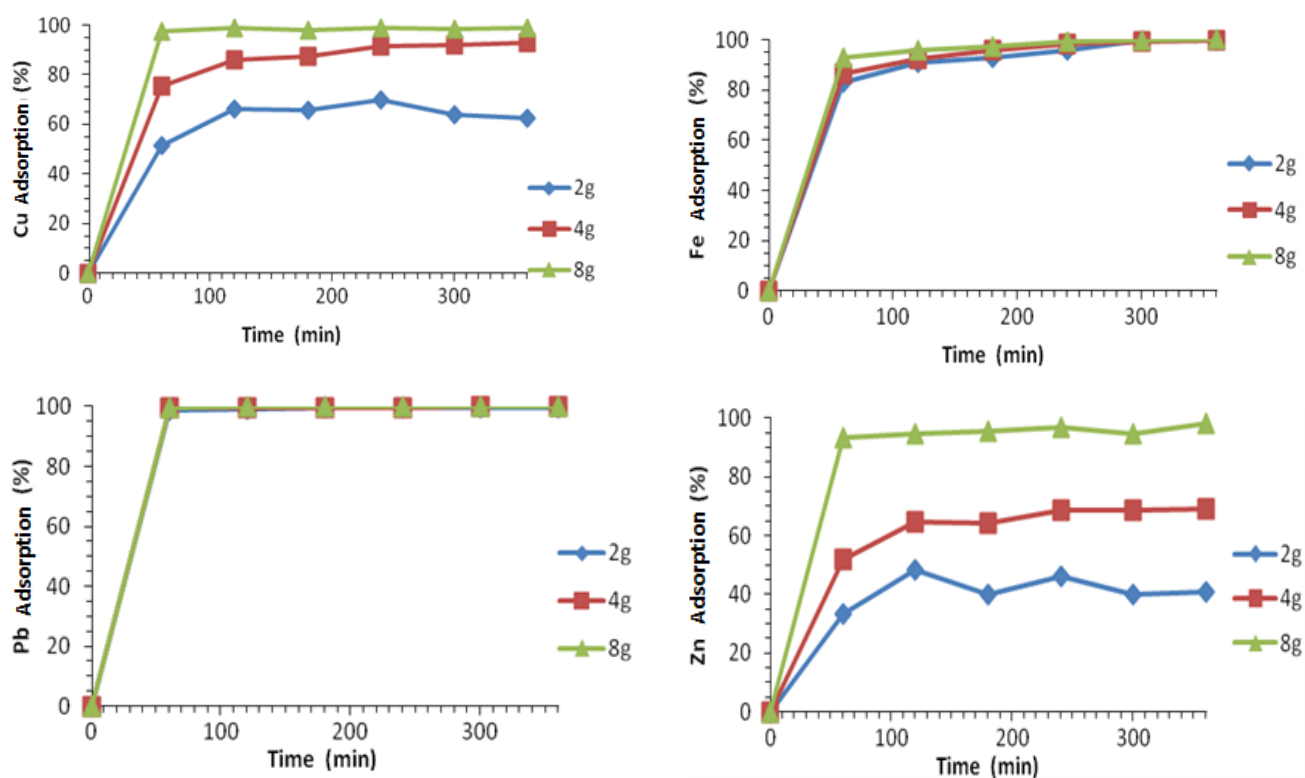


Figure 1. The effect of the mass of natural zeolite on the adsorption of copper, iron, lead and zinc from solution.

### 3.1.2. Effect of adsorbent particle size

The effect of adsorbent particle size on adsorption capacities from solutions was investigated by using two different sizes of  $<125\ \mu\text{m}$  and  $<250\ \mu\text{m}$ . It was observed that the smaller particle sized samples adsorbed more of the  $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Pb}^{2+}$  and  $\text{Zn}^{2+}$  ions. This indicates that any decrease in adsorbent particle size causes an increase in the adsorption

of the heavy metals ions Figure 2. This is because as the adsorbent particles get smaller more adsorption sites are available for metal uptake and more contacts are taking place. On the other hand smaller particle sizes result in the shortening of the diffusion distance that ions have to travel in order to get to an active site; thus adsorption is enhanced and requires a shorter time to reach equilibrium. This is in agreement with the results obtained by Sprynskyy et al. (2006) and Inglezakis et al. (2004). They concluded that the larger particle size adsorbent had lower adsorption capacities than the smaller particle sizes.

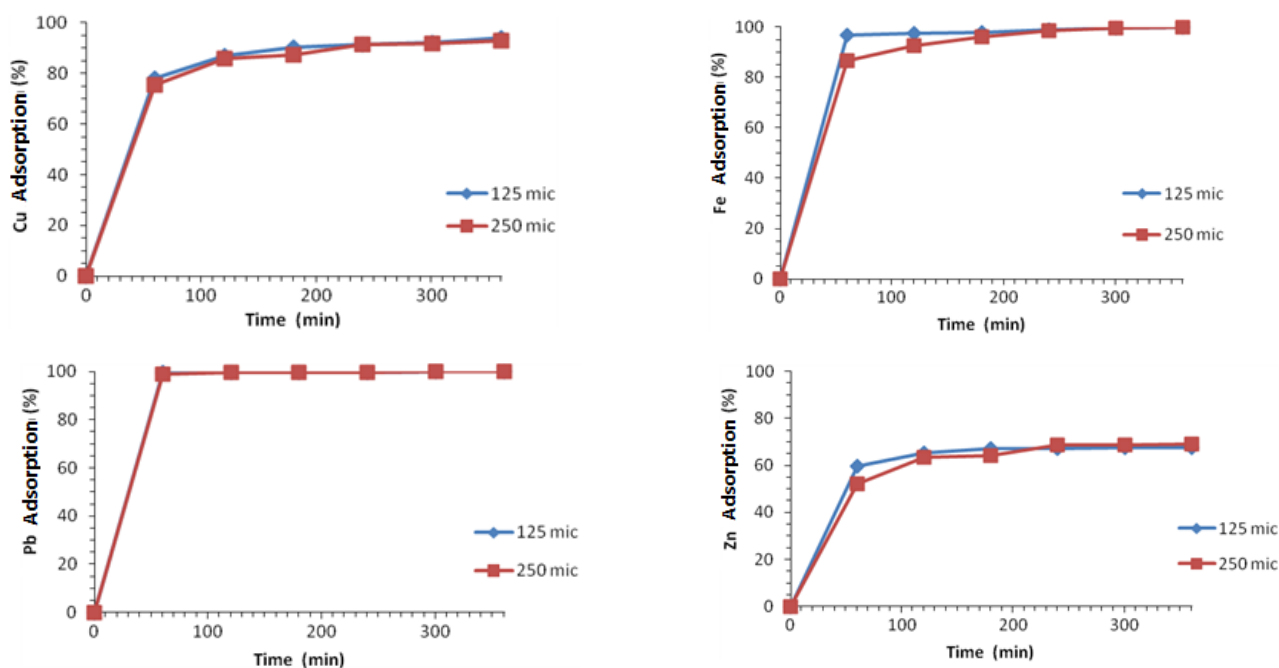


Figure 2. The effect of particle size on the adsorption of iron, copper, lead and zinc from solution.

Although particle size can affect the adsorption capacity mostly at the initial stage, as the contact time increases there is a decrease in the level of the effect of particle size on adsorption and the adsorption process gets slower. The same results were found by Malliou et al. (1994) and Erdem et al. (2004). The use of very fine particles can also cause some operational problems such as difficulty in the filtration of the zeolite from solution in batch studies (Inglezakis et al., 2001).

### 3.1.3. Effect of initial solution pH

Initial solution pH is a critical parameter for adsorption experiments. This parameter has a significant impact the heavy metal removal processes since it can influence and impact the adsorbent ability to remove metals and is connected with the competition of hydrogen ( $H^+$ ) ions with heavy metal cations for active sites on the adsorbent surface (Dimirkou, 2007; Inglezakis et al., 2003; Hui et al., 2005). An acidic solution can impact both the character of the exchanging ions and the character of the adsorbent.

Solutions with different pH values were used as follows: 2, 4 and  $6 \pm 0.1$  for the multi-component solutions. The results obtained are presented in Figure 3.

The results show that as the solution pH increases, the heavy metal removal efficiency also increases. This is due to the competition between the hydrogen ions and heavy metal cations for the same exchange sites and electrostatic repulsion between the heavy metal cations in solution; as more hydrogen ions are adsorbed, the number of protonated zeolite surfaces increases (Hui et al., 2005). Figure 3 shows how the initial solution pH influences the adsorption capacity of natural zeolite. Thus an increase in the initial pH resulted in an increase in the adsorption efficiency of natural zeolite for  $Cu^{2+}$ ,  $Fe^{3+}$ ,  $Pb^{2+}$  and  $Zn^{2+}$  ions. Moreno et al. (2001) and Alvarez-Ayuso et al. (2003) observed the same behaviour using clinoptilolite and stated that the efficiency of metal adsorption depends on the solution pH levels. However, metal precipitates at high pH values above pH7 and low values below pH2 inhibit the contact of metal ions with the adsorbent.

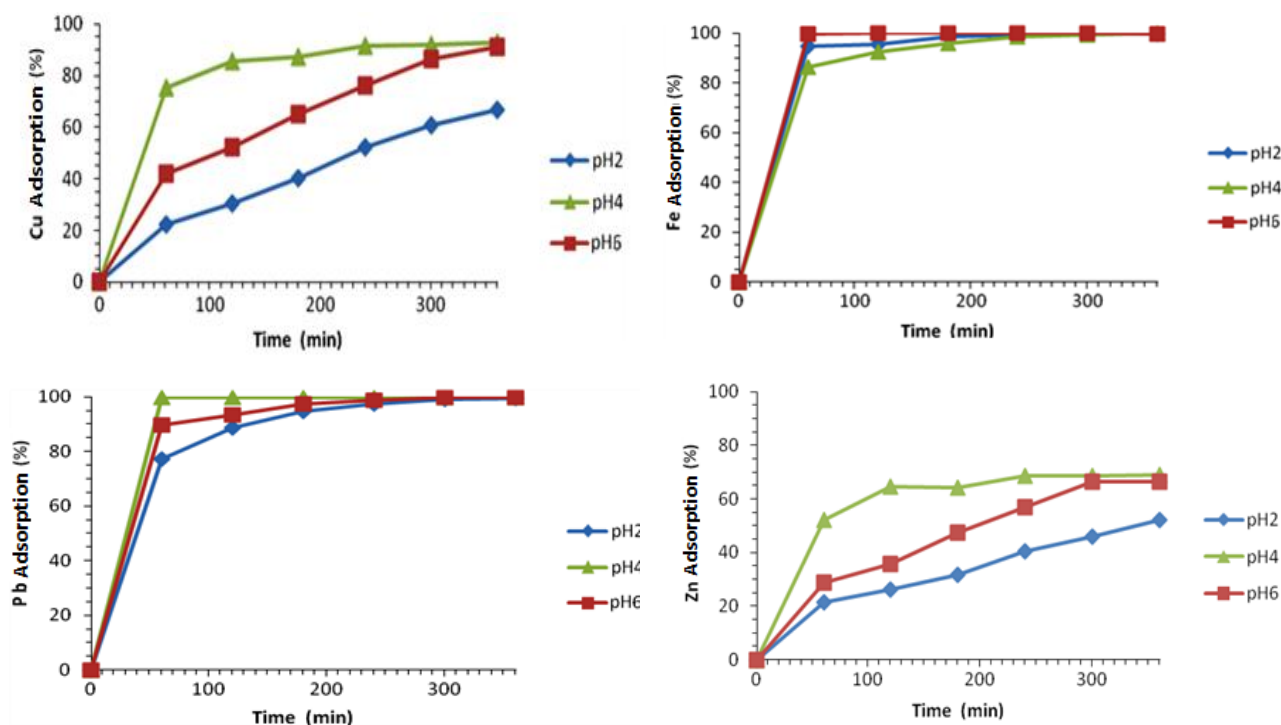


Figure 3. The effect of initial solution pH on the adsorption of copper, iron, lead and zinc from solution.

The results show that the ion exchange process increases with an increase in pH up to a maximum value and the best heavy metal removal efficiency value was obtained between pH values of 4 and 6, while pH values below pH4 or above pH6 decreased the heavy metal removal efficiency, as shown in Figure 4.

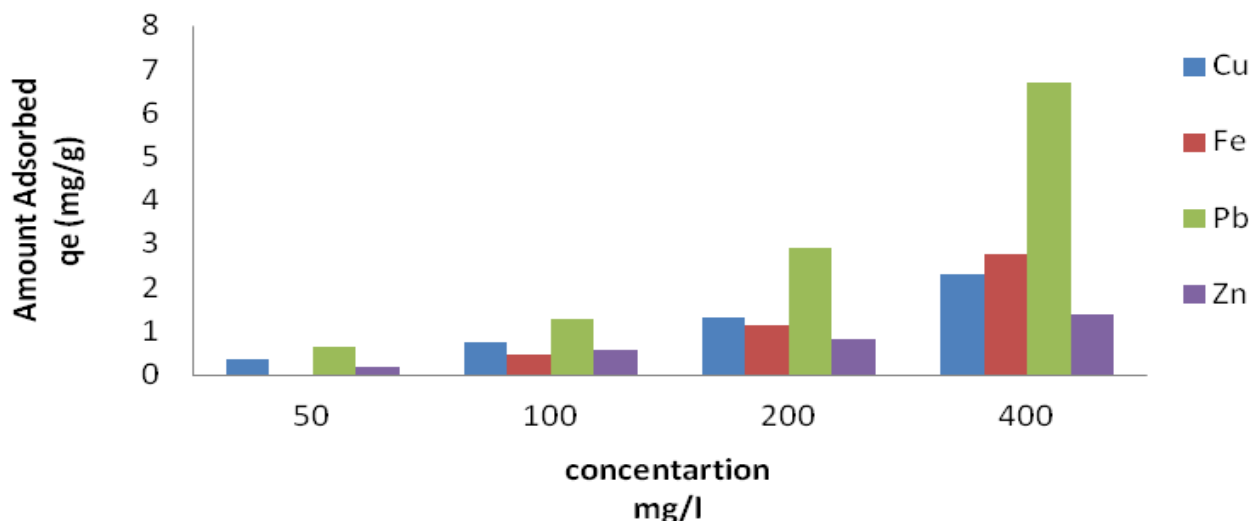


Figure 4. The effect of initial solution concentration and the amount of heavy metals adsorbed  $q_e$  (mg/g) by natural zeolite.

A low pH value ( $< 4$ ) solution can cause dissolution of the zeolite crystal structure and at higher pH values ( $> 7$ ) the zeolite structure can be affected and this can result in the reduction of the ion exchange process. This was the same

result achieved by Oren & Kaya (2006) when they assumed that pH values between pH4 and pH6 are fundamental in the ion exchange process.

### 3.1.4. Effect of initial solution concentration

The effect of the initial solution concentration on the adsorption process was determined using multi-component solution concentrations in the range of (50, 100, 200 and 400) mg/l. The initial solution concentration of the solution significantly impacts the heavy metal removal process. The results in Table 2 show that generally any increase in the initial solution concentration results in an increase in the heavy metal removal efficiency and the rate of adsorption, as shown in Figure 4. This may be a result of the concentration driving force since it is responsible for overcoming the mass transfer resistance associated with the adsorption of metals from solution by the zeolite (Oren & Kaya 2006). Therefore, as the initial concentration **increases**, the driving force also increases, resulting in improved efficiency of the heavy metal removal process. Then after the system reaches saturation point, the initial solution concentration does not show any significant change in the amount adsorbed due to a decrease in the number of active sites (Panayotova & Velikov 2003).

Table 2. The effect of initial solution concentration on the adsorption capacity of natural zeolite.

Heavy Metals	Initial Concentration (mg/l)	Amount Adsorbed, $q_e$ (mg/g)
Copper	50	0.37
	100	0.76
	200	1.30
	400	2.30
Iron	50	0.0
	100	0.46
	200	1.13
	400	2.78
Lead	50	0.62
	100	1.29
	200	2.89
	400	6.68
Zinc	50	0.19
	100	0.56
	200	0.80
	400	1.37

### 3.1.5. Effect of agitation speed

The effect of agitation speed on the removal of the cations from the solution was determined using a magnetic stirrer at speeds of 100, 150 and 200 rpm. The results of the effect of agitation are shown in Figure 5.

The results show that the metal removal efficiency increased as the speed of agitation increased. This is in agreement with the results obtained by Ören & Kaya, (2006). They concluded that an increase in the speed of agitation resulted in higher adsorption capacities. The agitation helps in overcoming the external mass transfer resistance, which controls the rate of adsorption. Hence, an increase in the speed of agitation generally results in an increase in ion mobility in the solution and reduces the mass transfer resistance. At high agitation speed, the external diffusion coefficient increases and the boundary layer becomes thinner, which usually improves the rate of solute diffusion through the boundary layer (Barrer 1982). Agitation of the mixture also results in abrasion and the production of more broken natural zeolite particles. This means that fresh smaller size zeolite particles are produced and more activate sites are available on the surface. So this mechanical procedure leads to an increase in the surface area, which significantly improves the efficiency of the heavy metal removal from solution (Trgo & Peric 2003).

## 4. Conclusions

The performed work leads to the following conclusions:

- The study indicated the suitability of the zeolite used for the removal of  $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Pb}^{2+}$  and  $\text{Zn}^{2+}$  ions from synthetic wastewater, while considering the economic aspects of wastewater treatment.
- The adsorbent mass, adsorbent particle size, initial solution pH, initial solution concentration and agitation speed as well as pre-treatment or modification of the adsorbent in the case of batch experiments are usually the most influential parameters.

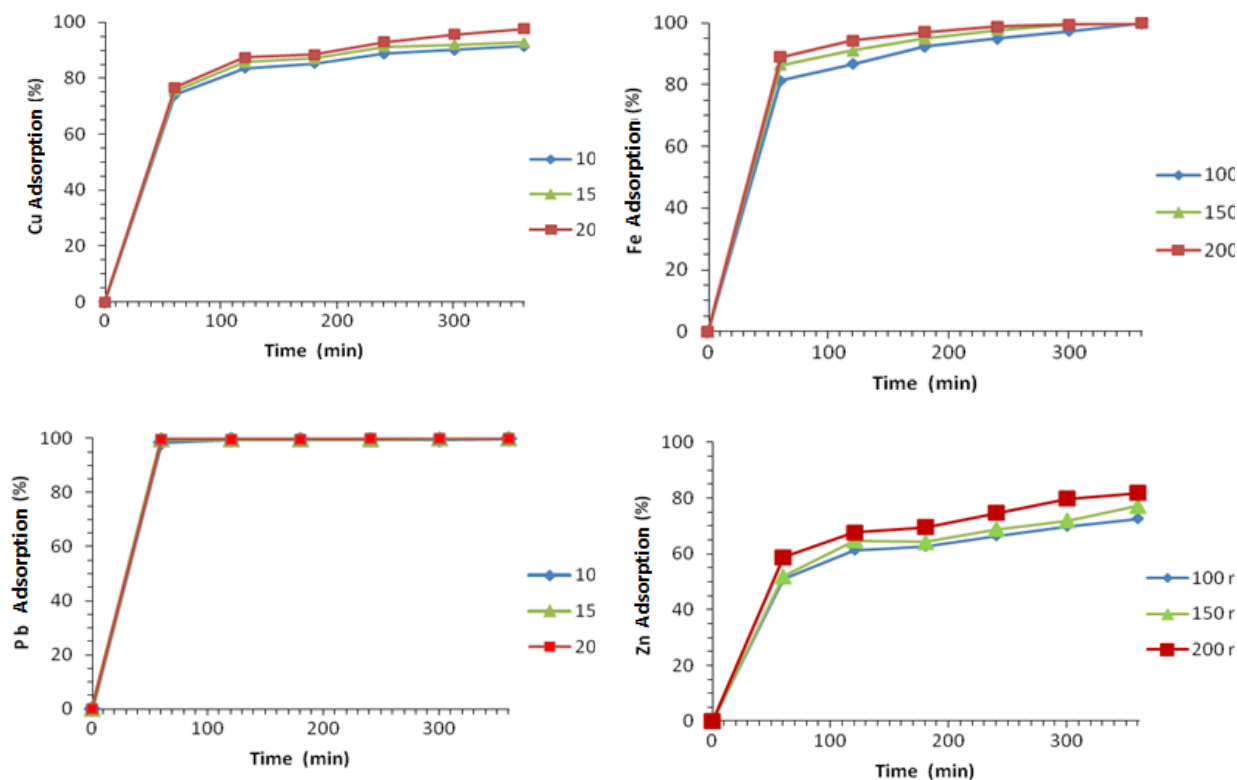


Figure 5. The effect of agitation speed on the adsorption of heavy metals by natural zeolite.

- The efficiency of heavy metal removal was enhanced and faster with increased initial solution pH, increased agitation speed, increased solution concentration, decreased particle size and greater mass of absorbent as well as the application of pre-treatments.
- Initial solution pH is the most critical parameter which has a significant impact the heavy metal removal processes compared to other parameters
- The results suggests that the adsorption of  $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Pb}^{2+}$  and  $\text{Zn}^{2+}$  ions on the selected adsorbents involves a complex mechanism and a number of possible rate controlling steps can determine the process efficiency such as boundary layer diffusion due to external mass transfer effects (external solution phase surrounding the particle), intraparticle diffusion within the exchanger itself, and chemical reaction kinetic control.
- In general the results show that adsorption is a heterogeneous process as the removal rate of  $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Pb}^{2+}$  and  $\text{Zn}^{2+}$  ions mostly occurred early on, but as the contact time increased , there was a decrease in the level of the effect of the parameters on adsorption and the adsorption process became slower.

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