Removal of Heavy Metals from Aqueous Solution using Clinoptilolite and Stilbite

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Abstract— **Heavy metals are highly toxic and they must be removed from the polluted streams. Adsorption by zeolites is currently considered to be very suitable for wastewater treatment because of its simplicity and cost effectiveness. The aim of this investigation was to compare adsorption efficiency of heavy metals (Cu, Zn, Mn and Pb) from aqueous solution using two different types of natural zeolite: clinoptilolite from Bulgaria and stilbite from Macedonia.**

The obtained information will be basis for further research for acid mine drainage treatment with zeolite.

The adsorption of Cu, Zn, Mn and Pb from aqueous solution using clinoptilolite and stilbite is effective. Copper and zinc ions are better adsorbed using stilbite, manganese ion is better adsorbed using clinoptilolite as adsorbent and for lead ion a both of used adsorbent gave a similar results. According to the maximum adsorption capacity (q_e) was determine the selectivity of clinoptilolite and stilbite, for the respective heavy metal ions. The selectivity series obtained about clinoptilolite was: $Pb^{2+} > Cu^{2+} > Zn^{2+} > Mn^{2+}$, and about stilbite was $Pb^{2+} > Cu^{2+} > Zn^{2+} > Mn^{2+}$.

From the kinetic modelling, the pseudo-second order kinetic model gave a better fits than pseudo-first order kinetic model for adsorption of Cu, Zn, Mn and Pb onto clinoptilolite and stilbite.

Keywords— copper, zinc, manganese, lead, clinoptilolite, stilbite, adsorption.

I. INTRODUCTION

Heavy metals are highly toxic and non-biodegradable, therefore they must be removed from the polluted streams in order to meet increasingly stringent environmental quality standards.

The removal of heavy metals can be accomplished by a variety of techniques. Conventional methods typically involve the use of processes such as coagulation, precipitation, ion-exchange, electro-chemical methods, membrane processes, extraction, adsorption, etc. Among these methods, adsorption is currently considered to be very suitable for wastewater treatment because of its simplicity and cost effectiveness. Some widely used adsorbents for adsorption of heavy metals include activated carbon [1], clay minerals [2], biomaterials [3], industrial solid wastes and zeolites [4-9].

Zeolite is a natural porous mineral in which the partial substitution of Si^{4+} by Al^{3+} results in an excess of negative charge. This is compensated by alkali and alkaline earth cations (Na^+, K^+, Ca^{2+} or Mg^{2+}) [8]. Zeolites have been used as adsorbents, molecular sieves, membranes, ion-exchangers and catalysts, mainly because zeolite exchangeable ions are relatively innocuous [10]. Thus, zeolites are particularly suitable for removing undesirable heavy metal ions (e.g. lead, nickel, zinc, cadmium, copper, chromium and/or cobalt), radionuclides as well as ammoniacal nitrogen [11] (ammonia and ammonium) from industrial, municipal and agricultural wastewaters.

The aim of this investigation was to compare adsorption efficiency of heavy metals (Cu, Zn, Mn and Pb) from aqueous solution using two different types of natural zeolite: clinoptilolite and stilbite. Onto clinoptilolite have made some investigation about adsorption of heavy metals from acid aqueous solution [12, 13, 20, 21], but stilbite is still new material without some important investigtion.

According to the maximum adsorption capacity (q_e) was determine the selectivity of clinoptilolite and stilbite, for the respective heavy metal ions.

The pseudo-first order and pseudo-second order kinetic models were used to describe kinetic of adsorption of Cu, Zn, Mn and Pb onto clinoptilolite and stilbite.

II. MATIRIALS AND METHODS

A. Adsorbents

Two different types of natural zeolite (clinoptilolite and stilbite) were investigate in recent study. The clinoptilolite was taken from Kardzali, Bulgaria and the stilbite is from Vetunica, Macedonia. This natural zeolites: clinoptilolite and stilbite were used as an adsorbent for adsorption of heavy metals, such as Cu, Zn, Mn and Pb. The particle size range of the natural zeolites used in this study was 0.8 to 2.5 mm.

X-Ray Difractometer 6100 from Shimadzu was used to investigate the mineralogical structure of natural zeolite samples. This technique is based on observing the scattering intensity of an X – Ray beam hitting a sample as a function of incident and scattered angle, polarization, and wavelength or energy. The diffraction data obtained are compared to the database maintained by the *International Centre for Diffraction Data*, in order to identify the material in the solid samples.

The results of XRD (Figure 1a) shown that the sample of natural zeolite from Bulgaria contained clinoptilolite in the majority and (Figure 1b) shown that the zeolite sample from Macedonia is stilbite about 57% and the rest are: albite, anorthite, kaolinite and quartz.
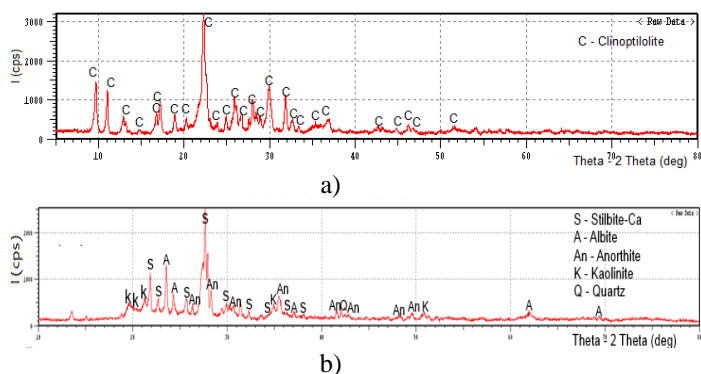
Figure 1: X–Ray diffraction of natural zeolites
a) Clinoptilolite sample and b) Stilbite sample

The surface morphology of natural zeolite samples were studied using a scanning electron microscope, VEGA3 LMU. This particular microscope is also fitted with an Inca 250 EDS system. EDS, stands for Energy Dispersive Spectroscopy, it is an analytical technique used for the elemental analysis of a sample based on the emission of characteristic X – Rays by the sample when subjected to a high energy beam of charged particles such as electrons or protons. Micrographs of natural zeolite samples obtained from SEM analysis are given in Figure 2. The micrographs clearly show a number of macro-pores and well defined crystals of clinoptilolite and stilbite in the zeolite structure in a both of samples.
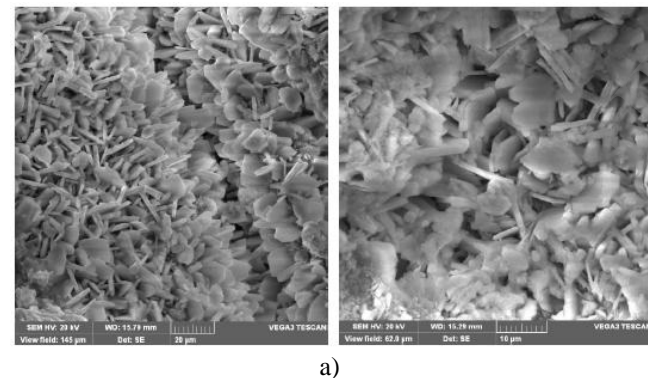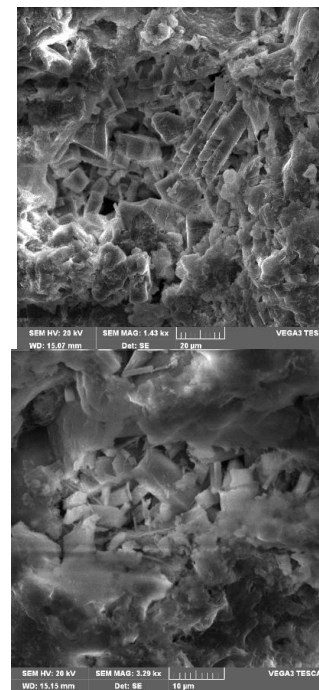
Figure 2: Micrographs of natural zeolite samples obtained from SEM analysis
a) Clinoptilolite and b) Stilbite

An electron beam was directed onto different parts of the samples in order to get a more accurate analysis. Obtained elemental composition of clinoptilolite and stilbite are presented in Table 1.

Table 1: EDS analysis showing the elemental composition for natural zeolite samples

Element	Clinoptilolite	Stilbite
O	57.56	61.62
Na	0.24	0.34
Mg	0.72	1.07
Al	5.28	8.13
Si	30.13	26.29
K	2.71	1.65
Ca	1.99	0.91
Fe	1.38	/
Total	100	100

Results of EDS analysis showed that the predominant exchangeable cations in clinoptilolite structure were K^+ and Ca^{2+}, while the predominant exchangeable cations in stilbite structure was K^+ and then follow Mg^{2+} and Ca^{2+}.

B. Adsorbate

The heavy metals, Cu, Zn, Mn and Pb were used as adsorbate in the recent investigations. Synthetic single component solutions of these metals were prepared by dissolving a weighed mass of the analytical grade salt $CuSO_4.5H_2O$, $ZnSO_4.7H_2O$, $MnSO_4.H_2O$ and $Pb(NO_3)_2$, appropriately, in 1000ml distilled water.

C. Experimental procedure

Adsorption of heavy metals ions on clinoptilolite and stilbite were performed with synthetic single component ion solutions of Cu^{2+}, Zn^{2+} Mn^{2+} and Pb^{2+} ions with initial concentration of 25 mg/l. Initial pH value 3.5 of prepared solutions was adjusted by adding 2% sulfuric acid and controlled by 210 Microprocessor pH Meter. The experiments were performed in a batch mode in a series of beakers equipped with magnetic stirrers by contacting a mass of 5g adsorbent with a volume of solution, 400ml. Adsorbent and aqueous phase were suspended by magnetic stirrer at 400 rpm. The agitation time was varied up to 360 minutes. At the end of the predetermined time, the suspension was filtered and the filtrate was analyzed. The final pH value was also measured. All experiments were performed at room temperature on $20\pm1^{o}C$. The initial and remaining concentrations of metal ions were determined by Liberty 110, ICP Emission Spectrometer, Varian. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) is an analytical technique used for the detection of trace metals. It is a type of emission spectroscopy that uses the inductively coupled plasma to produce excited atoms and ions that emit electromagnetic radiation at wavelengths characteristic of a particular element. The intensity of this emission is indicative of the concentration of the element within the sample.

The adsorption capacity was calculated by using the following expression:

$$q_e = \frac{V(C_0 - C_e)}{m}, \ (mg/g) \qquad (1)$$

where: q_e is the mass of adsorbed metal ions per unit mass of adsorbent (mg/g), C_0 and C_e are the initial and final metal ion concentrations (mg/l), respectively, V is the volume of the aqueous phase (l) and m is the mass of adsorbent used (g).

Degree of adsorption, in percentage, is calculated as:

$$AD\% = \left(1 - \frac{C_e}{C_0}\right) \cdot 100 \qquad (2)$$

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III. RESULT AND DISCUSSION

From the obtained result can be concluded that adsorption of Cu, Zn, Mn and Pb from aqueous solution using clinoptilolite and stilbite is effective, because, approximately 80-100% from metal ions are removed at equilibrium.

To determine which of tested natural zeolites have better adsorption efficiency is made comparison of each metal ion separately.

Adsorption of copper ions from aqueous solution is a more efficient using stilbite. In the first 60 minutes 97.52% of the copper ions are adsorbed by stilbite and 84.40% by clinoptilolite at same conditions (Figure 3). Equilibrium is reached at 240 min at both of adsorbents.

Regarding to the adsorption of zinc ions can be concluded the same, stilbite shows better results compared with clinoptilolite (Figure 4). Equilibrium of both adsorbents is achieved after a longer time compared with equilibrium of copper ions.

In contrast to copper and zinc ions, better efficiency of removal of manganese ions from the solution is achieved using clinoptilolite (Figure 5). Equilibrium is achieved at 360 min at both of used adsorbents. At that time the percentage of adsorbed ions by clinoptilolite is about 90% while the percentage of adsorbed ions by stilbite is about 80%.

Excellent results are obtained for adsorption of lead ions from aqueous solution using clinoptilolite and stilbite as adsorbents (Figure 6). Almost 100% effectivity in removal of lead ions is noted at shorter time for equilibrium.
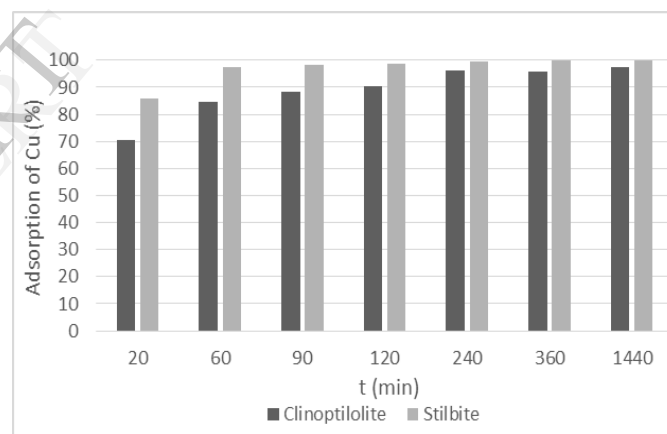

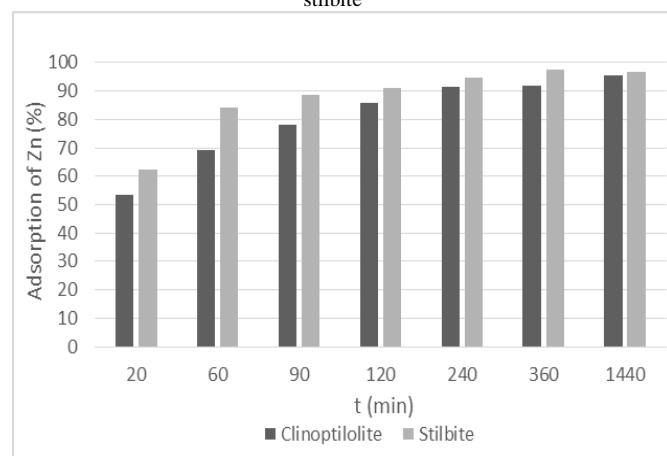Figure 3: Adsorption efficiency for removal of Cu using clinoptilolite and stilbite

Figure 4: Adsorption efficiency for removal of Zn using clinoptilolite and stilbite
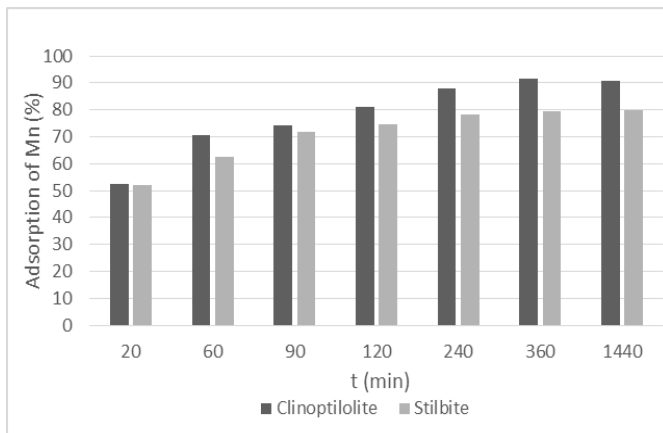
Figure 5: Adsorption efficiency for removal of Mn using clinoptilolite and stilbite
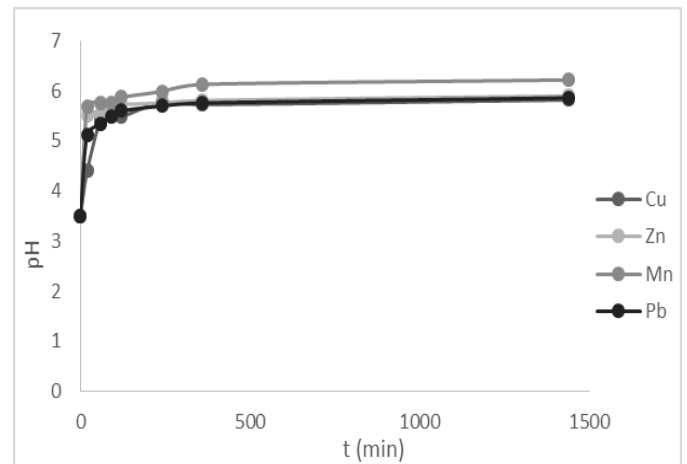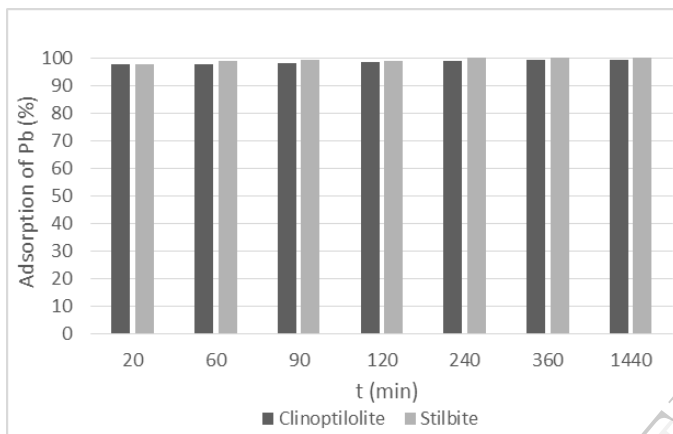

Figure 6: Adsorption efficiency for removal of Pb using clinoptilolite and stilbite

From the measurement of final pH value at all experiments can be concluded that clinoptilolite and stilbite have a buffering effect. This is in agreement with results obtained by Erdem, 2004 [8] and Motsi, 2010 [14]. The buffering effect is clearly shown on Figures 7 and 8.
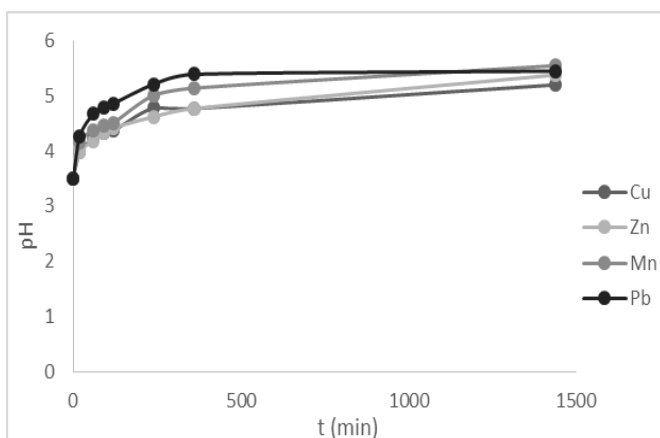

Figure 7: pH value changimg according to the time using clinoptilolite as adsorbent

Figure 8: pH value changimg according to the time using stilbite as adsorbent

According to the obtained results were determine the selectivity of used clinoptilolite and stilbite. This was done by comparing the maximum adsorption capacity (q_e) of clinoptilolite and stilbite for the respective heavy metal ion. The selectivity series obtained about clinoptilolite in single component solution was: $Pb^{2+} > Cu^{2+} > Zn^{2+} > Mn^{2+}$, and about stilbite in single component solution was $Pb^{2+} > Cu^{2+} > Zn^{2+} > Mn^{2+}$. The selectivity series obtained about clinoptilolite and stilbite were the same.

The difference in adsorption capacity of the natural zeolite for the heavy metal ions may be due to a number of factors which include hydration radii, hydration enthalpies and solubility of the cations. The hydration radii of the cations are: $r_HZn^{2+}=4.30Å$, $r_HCu^{2+}=4.19Å$, $r_HPb^{2+}=4.01Å$ and $r_HMn^{2+}=4.38Å$ [15,16]. The smallest cations should ideally be adsorbed faster and in larger quantities compared to the larger cations, since the smaller cations can pass through the micropores and channels of the zeolite structure with ease [8]. Furthermore, adsorption should be described using hydration enthalpy, which is the energy that permits the detachment of water molecules from cations and thus reflects the ease with which the cation interacts with the adsorbent. Therefore, the more a cation is hydrated the stronger its hydration enthalpy and the less it can interact with the adsorbent [14]. Because of its high Si:Al ratio, clinoptilolite has a low structural charge density. Therefore, divalent cations with low hydration energies are sorbed preferably compared to cations with high hydration energies [17]. The hydration energies of the cations are: -2010, -1955, -1760 and -1481 kJmol^{-1} for Cu^{2+}, Zn^{2+}, Mn^{2+} and Pb^{2+} respectively [15, 16]. According to the hydration radii the order of adsorption should be $Pb^{2+} > Cu^{2+} > Zn^{2+} > Mn^{2+}$, and according to the hydration enthalpies the order should be $Pb^{2+}>Mn^{2+}>Zn^{2+}>Cu^{2+}$.

The above series according to the hydration radii is same with the experimentally obtained series for clinoptilolite and stilbite, which is $Pb^{2+} > Cu^{2+} > Zn^{2+} > Mn^{2+}$.

A. Kinetic studies

The kinetic data of the adsorption of Cu, Zn, Mn and Pb onto clinoptilolite and stilbite were evaluated using pseudo-first order and pseudo-second order kinetic models. The pseudo-first order model assumes that the rate of change of solute uptake with time is directly proportional to difference in saturation concentration and amount of solid uptake with time [18].

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (3)$$

Where q_e and q_t are the amounts of metal ions adsorbed per unit mass of the adsorbent (mg/g) at equilibrium and time t, respectively and k_1 is the rate constant of adsorption (min^{-1}). When $\ln(q_e - q_t)$ was plotted against time, a straight line should be obtained with a slope of k_1, if the first order kinetics is valid.

The pseudo-second order model as developed by Ho and McKay [19] has the following form:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \qquad (4)$$

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

Where q_t and q_e are the amount of metal adsorbed per unit weight of adsorbent (mg/g) at time t, and at equilibrium respectively. k_2 is adsorption rate constant of the pseudo-second order equation (g/mg min). A plot of t/q_t versus time (t) would yield a line with a slope of $1/q_e$ and an intercept of $\frac{1}{k_2 \cdot q_e^2}$, if the second order model is a suitable expression.

a)
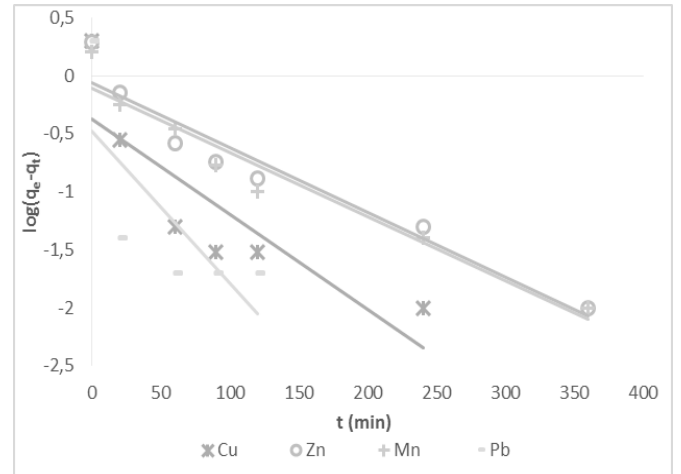
b)

Figure 9: Pseudo-first order kinetic model
a) clinoptilolite and b) stilbite
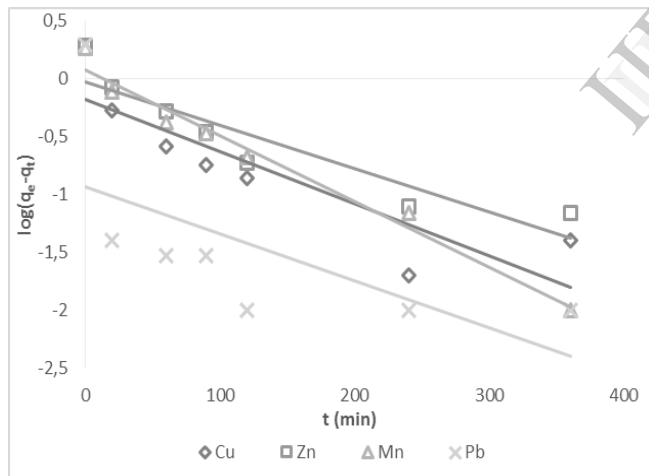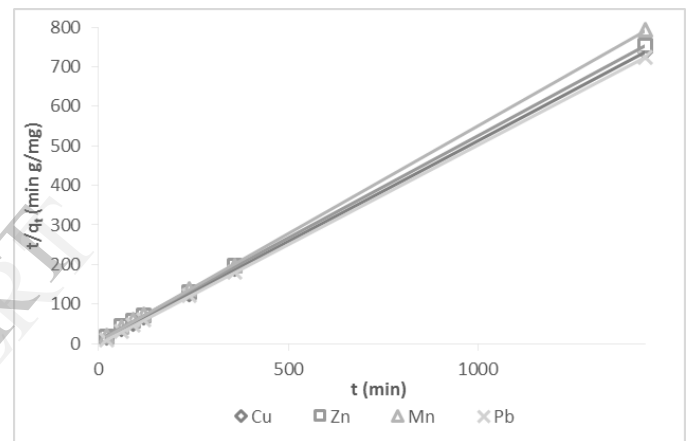
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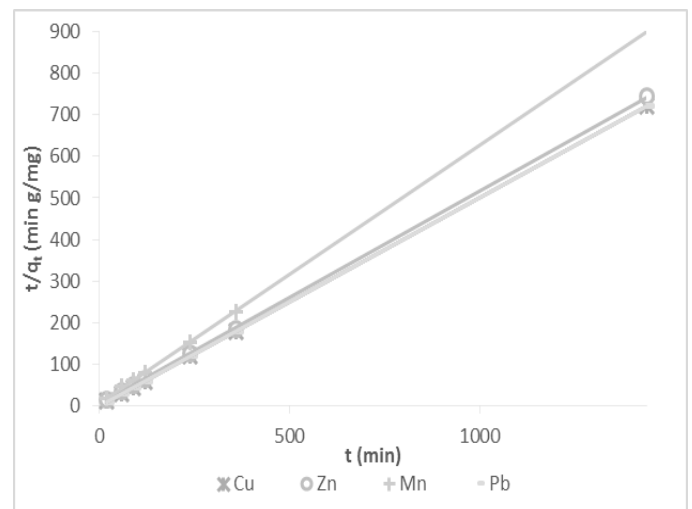
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Figure 10: Pseudo-second order kinetic model
a) clinoptilolite and b) stilbite

Table 2: Pseudo-first order and pseudo-second order kinetics rate constants for Cu, Zn, Mn and Pb on clinoptilolite and stilbite.

		Pseudo-first order kinetic model		
		q_e (mg/g)	k_1	R^2
Clinoptilolite	Cu	1.95	0.0104	0.7617
	Zn	1.91	0.0088	0.8549
	Mn	1.83	0.0131	0.9767
	Pb	1.99	0.0092	0.4131
Stilbite	Cu	2	0.0189	0.7239
	Zn	1.95	0.0129	0.931
	Mn	1.6	0.0127	0.9421
	Pb	2	0.0304	0.5534

		Pseudo-second-order kinetic model		
		q_e (mg/g)	k_2	R^2
Clinoptilolite	Cu	1.9643	0.0521	1
	Zn	1.9354	0.0268	0.9999
	Mn	1.8369	0.0358	0.9998
	Pb	1.9865	0.2889	1
Stilbite	Cu	2.0012	0.1786	1
	Zn	1.9497	0.0579	1
	Mn	1.6108	0.0540	0.9999
	Pb	2.0012	0.3065	1

From the plot between $\ln(q_e - q_t)$ versus time t (Figure 9) and the plot of t/q_t versus time t (Figure 10), the rate constant of first and second order of adsorption, also R^2 were determined.

Table 2 shows the kinetic parameters of adsorption of Cu, Zn, Mn and Pb onto clinoptilolite and stilbite. The kinetic model with a higher correlation coefficient R^2 was selected as the most suitable one. The results are shown that adsorption of Cu, Zn, Mn and Pb onto clinoptilolite and stilbite is followed by pseudo-second order kinetic model.

IV. CONCLUSION

The adsorption of Cu, Zn, Mn and Pb from aqueous solution using clinoptilolite and stilbite is effective, because, approximately 80-100% from metal ions are removed at equilibrium.

According to the each metal separately, can be concluded that copper and zinc ions are better adsorbed using stilbite, but manganese ion is better adsorbed using clinoptilolite as adsorbent.

About lead ion could not be choose better adsorbent, because a both of used adsorbent gave a similar results.

According to the measured pH value at equilibrium can be concluded that clinoptilolite and stilbite have a buffering effect.

According to the obtained results about maximum adsorption capacity (q_e) of clinoptilolite and stilbite were determine the selectivity series for the respective heavy metals ions. The unique selectivity series on investigated clinoptilolite and stilbite was the same ($Pb^{2+} > Cu^{2+} > Zn^{2+} > Mn^{2+}$). This selectivity series corresponding to the series obtained according to the hydration radii.

The results from the fitting with the kinetic models shown that adsorption of Cu, Zn, Mn and Pb onto clinoptilolite and stilbite is followed by pseudo-second order kinetic model.

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