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Isotherm Studies of Adsorption of Cadmium (II) ion from Aqueous Solution onto Zeolite: Effects of Time, Temperature and pH

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ABSTRACT

Today, synthetic zeolites are used commercially additional frequently than natural zeolites due to the purity of crystalline products and the regularity of particle sizes. A synthesized $Na_3K_6(H_2O)_{21}[Si_{27}Al_9O_{72}]$ (Lind type L) LTL zeolite was characterized using X-Ray diffraction (XRD), Field Emission Scanning Electron Microscopy (FE-SEM) and Transmission Electron Microscopy (TEM). The work reports the utilization of synthesized zeolite as an adsorbent for the removal of cadmium (II) ion from aqueous solution. The effects of sorption time, temperature, heavy metal concentration and pH, on the adsorption process were investigated using a batch method. Langmuir, Freundlich, and Temkin isotherms over the entire concentration range from 20-50 $mg.L^{-1}$ were used to narrate the adsorption isotherms and their constants evaluated. The equilibrium data were found to be fitted the Langmuir and Freundlich models. Our study shows that the maximum adsorption of Cd is at pH 8.0 and 313K.

1. INTRODUCTION

Nowadays, removing the toxic heavy metal contaminants from aqueous waste streams is one of the greatest matters of interest in the literature and studies. The main concern of environmentalists about heavy metals is that these elements are highly toxic and their detrimental impact on human health and surroundings is grave (Aklil, *et al.*, 2004). Cadmium is one of the most toxic metals levels in a low concentration. It is naturally formed in the environment and is a vital polluting. Cadmium (Cd) toxicity sources confusions like heart disease, cancer and diabetes. Cadmium poisoning may also consequence in lung cancer, anemia, skin, pulmonary edema, bone diseases, brain damage and trachea-bronchitis (Voegelin, and Kretzschmar, 2003). Cadmium gathers in bone, liver and kidney and is even more poisonous than mercury. Taking in any considerable amount of Cd leads to instantaneous intoxication and damage to the liver and the kidney (Deng and Ting, 2005). Cadmium is mainly produced when waste streams are released from metallurgical alloying, ceramics, metal plating and sewage sludge. Conventional methods including, reverse osmosis electrodialysis (Mohammadi, *et al.,* 2005), ion-exchange, chemical precipitation, ultrafiltration (Ennigrou, *et al.,* 2009) generally, the adsorption methods are favorable methods for removing heavy metals from aqueous solutions because it is economically advantageous, highly efficient and easily applicable (Hamedreza, *et al.,* 2015). Some materials can be used as adsorbents, like activated carbon, aluminosilicate (clay materials), natural and synthetic zeolites (Dawodu, *et al.,* 2012). Zeolites are hydrated aluminosilicate produced under the hydrothermal states. It can be discovered naturally, or can be synthesized. Synthetic zeolites were first deploying commercially as molecular sieve adsorbent. They are ideally synthesized from a solution of sodium silicate and sodium aluminates. Zeolites can then be synthesized from a variety of raw materials; natural and synthetic glasses, aluminosilicate gels, and clay materials, example kaolin (Vimala and Das, 2009). It has been discovered that the starting material and shapes for the preparation have an influence on the resulting kinds and amount of zeolites to be obtained (Prasad, *et al.,* 2009). Based on an obtainable materials and publications, it could be concluded that due to their unique properties, zeolites have a considerable potentials as effective sorbent material for large number of water treatment applications like water softening ammonia removal (from municipal sewage, animal farms, fertilizer mill waste water, fish breeding pond, swimming pools), move of heavy metals (from natural water acid mines drainages, industrial wastewater), phosphates ejection of dissolved organic compounds and dyes, oil spillage surgery and many others. Ions of heavy metals such as copper, nickel, zinc, cadmium, lead, chromium and mercury have a notable impact on the environment, since they are often detected in industrial wastewater (Ali and El-Bishtawi, 2012). Removal of ions can be an expert by a variety of techniques, in which adsorption method is currently considered very acceptable for water treatment because of its simplicity and cost success and zeolites is one of the adsorbents for the adsorption of a heavy metal. The presence of heavy metals in industrial wastewater as a result of many construct process is known to cause malignant effects on human health and environment (Selvi, *et al.,* 2011). Removing these heavy metals, demand high energy or advanced operational requirements, some conventional technologies like coagulation, precipitation, extraction, biosorption and adsorption have been considered for treatment of contaminated wastewater. Between these methods, adsorption is found to be very suitable for wastewater treatment because of its simplicity and cost effectiveness (Lei, *et al.,* 2017). Commercial activated carbon is considered as the most effective material for guide the metal ions load. Nevertheless, due to its high cost and 10%-15% lost through regeneration, unconventional adsorbents such as zeolites have attracted the attention of various investigations and adsorption characteristics have been widely investigated for the removal of metal ions (Amer, *et al.,* 2010). The aim of this study was to synthesize LTL zeolite type, which can be used as adsorbent for adsorption of Cd from aqueous solution. Additionally the effects of temperature, pH, Concentration and time were also studied to find out the maximum removal percentage, and applying isotherm models such as: Langmuir, Freundlich, and temkin isotherm models.

2. MATERIALS AND METHODS

2.1. Materials

An analytical grade of cadmium nitrate $Cd(NO_3)_2$ salt (Merck) was used to prepare the standard solution of cadmium. Aluminum foil (Aldrich), pyrogenic silica (SiO_2) (Aldrich), KOH (Merck), teflon-lined stainless steel autoclave. Zeolite LTL was used as an adsorbent. The stock solution was diluted to the needed concentration and appropriate pH with drop wise addition of 0.13M NaOH and 0.13M of HNO_3 using a pH meter. Freshly diluted stock solutions were used for each experiment. The concentration of metal ions was ponderous using atomic absorption spectrometer (GBC 932 plus) at the wavelength of 326 nm.

2.2. Zeolite LTL synthesis

In a typical experiment 0.40g of aluminum foil was dissolved in 50ml KOH and NaOH (0.3M) solution under stirring to obtain a clear solution followed by addition of 6.0g of pyrogenic silica. This particulate suspension was stirred over night at room temperature (25°C). After sealing in a teflon-lined stainless steel autoclave the mixed suspension was hydrothermally treated at 150°C for 1, 2 and 3h. The resulting solid masses were then washed with distilled water several times until the pH of washed liquid become 7.0. At the end the solid samples were dried at 60°C for 8h. (Rituparna, et al., 2014).

2.3. Characterization

Characterization of LTL zeolite formed was carried out by X-Ray Diffractometer (Siemens D5000) with radiation sources Cu Kα that has λ=0.154 nm at 40kV and current of 10mA. The diffractogram was scanned in the degree of 2θ at the range of 5-50 with the step size of 0.05. The morphology of LTL zeolite was elucidated using, FESEM and TEM (JEOL).

2.4. Adsorption procedure

The aqueous solution used, was cadmium stock prepared at different concentrations, for different runs, 0.25g of LTL zeolite was mixed with 25ml of the prepared cadmium stock solution at a particular concentration (20mg.L^{-1} - 50mg.L^{-1}), of a pH (4-10). The mixture was placed on a water bath constant temperature vibrator set at a particular temperature (303K-323K), for a particular duration/time (10min-60min). After adsorption, the solution was filtered and the filtrate's concentration was tested using Atomic Adsorption Spectrophotometer (AAS). The amount of equilibrium adsorption, Q (mg.g^{-1}) was calculated by

$$Q = \frac{(Ci - Ce)V}{m} \quad (1)$$

Where Ci (mg.L^{-1}) is the Initial cadmium ion concentration in solution, Ce (mg.L^{-1}) is the equilibrium concentration of cadmium ion concentration in solution, V (liters) is volume of the solution manipulate, and m (g) is the mass of the adsorbent (Wang and Chen, 2006). The percentage adsorbed is given as;

$$Percentage\ adsorbed\ (\%) = \frac{Ci - Ce}{Ci} x\ 100 \quad (2)$$

3. RESULTS AND DISCUSSION

Figure 1 shows the XRD of the synthesized zeolite sample LTL phase is found to match with the zeolite LTL and confirmed by contrast the diffraction peaks at 2θ degree, 5.55, 11.77, 14.71, 19.30, 20.47, 22.66, 23.35, 24.35, 26.21, 27.12, 27.97, 29.12, 29.66, 30.71, 34.21, 35.15 and 41.41. These peaks correspond to the planes [100], [001], [210], [220], [301], [221], [311] [320] [202] [321] [212] [330] [420] [222] [322] [412] and [313]. It can be seen from Figure 1 that all synthesized samples showed the formation of LTL zeolite phase (JCPDS File No. 43-560) was indicated. Figure 2 shows the FESEM image of the particles obtains hydrothermally at 150°C for 3h. It reveals the rod-shaped morphology of zeolite LTL of the length of 5-10µm with the diameter ranging from 110-200nm. Interval Figure 3 shows TEM image also obeys the rod shaped morphology of zeolite LTL. The presence of multiple nanodomains causes a random alignment among nanocrystallites in the zeolite LTL rods (Zhang, *et al.*, 2005).

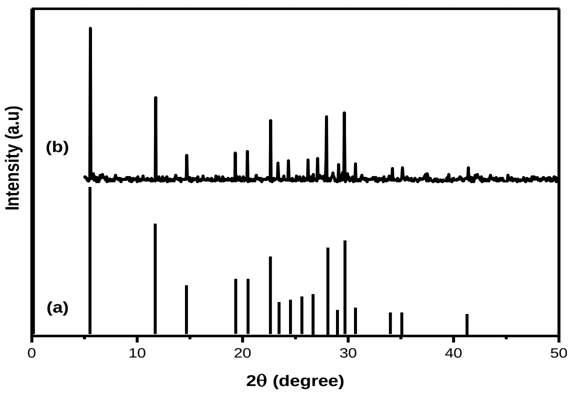

Figure (1): XRD patterns of (a) reference sample and (b) synthesized LTL zeolite.

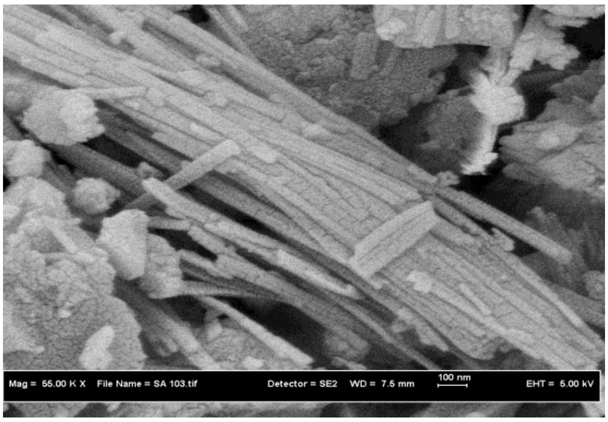

Figure (2): FESEM. Image of synthesized LTL zeolite.

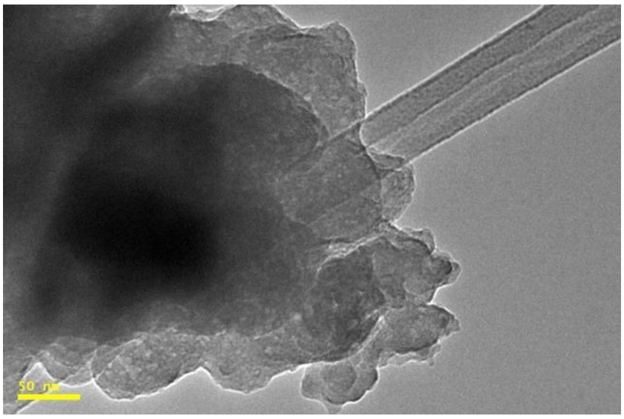

Figure (3): TEM. Image of synthesized LTL zeolite.

3.1. Effect of PH

The sequel of the pH of solution on adsorption was resolute because it is known to be one of the main factors affecting sorption. The result of the effect of pH on the adsorption of cadmium (II) ions is shown in Figure 4. The percentage of adsorption of cadmium was studied over a pH scope, and the result designated that maximum removal appeared at pH of 8.0. It has been reported that a relationship presence between the pH point of zero percentage removal of material, and proposed that cations adsorption on an adsorbent will be recommended at pH values above the pH point of zero, interval anions adsorption will be favored at lower pH worth. Although, metal precipitates at high pH values i.e. above pH of 8.0 impede the connect of a metal ion with the adsorbent. The decrease in sorption was noted with a further increase in pH and this may be attributed to the low solubility of cadmium at high pH. This result a good agreement with the literature reported in (Fan, et al., 2008).

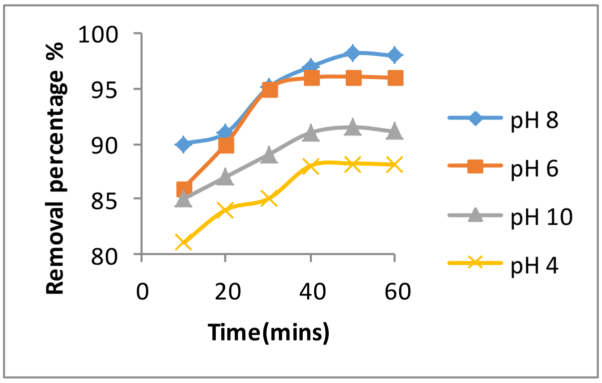

Figure (4): Effect of the pH on adsorption of cadmium on synthesized LTL zeolite.

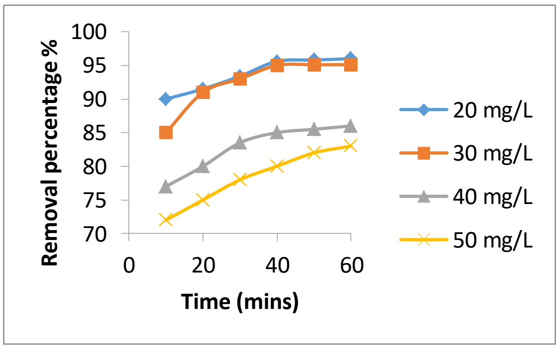

Figure (5): Effect of concentration on adsorption of cadmium on synthesized LTL zeolite.

3.2 Effect of Concentration

The sequel of initial ion concentration was studied for the initial ion concentration between 20 to 50 mg.L^{-1} and the results were presented in Figure 5. The result showed that a decrease in the percentage removal with an increase in the concentration of cadmium was perceived. This can be reported for that all adsorbents have a fixed number of substances during a reaction and at a certain metal ion concentration the active sites suits used up and saturated (Vimala and Das, 2009). This involves that further increase in the concentration of cadmium will decrease in the percentage transfer as the active sites have been before occupied. Hence more metal ions will be surviving in solution after adsorption, the increase in the concentration of metal ions to an increase in a clash between the ions and adsorbent hence increased the power to overcome resistance to mass transfer and thus an increase in uptake capacity (Ross, 1980).

3.3. Effect of Temperature

Temperature values varying from 303K to 323K were used to study the effect of temperature on adsorption. The consequence of the effect of temperature is shown in Figure 6. It was found out that, with an increase in temperature, the time to reach the parallel percentage removal was abundant less. This is due to as the temperature increases, the rate of dispersal of adsorbate molecules across the external frontier layer and internal pores of the adsorbent particles increased. This consequence indicated that as the temperature of the solution was increased from 303K to 323K, There was also a corresponding increase in the amount of cadmium ions adsorbed by the synthesized LTL zeolite. This increase in adsorption capacity escorted by an increase in temperature designated that the adsorption process is endothermic in nature, it also recommends chemisorptions process i.e. adsorption accompanied by a chemical reaction. It is cramped to just on a layer of molecules on the surface but may be followed by a supplementary layer of physically adsorbed metal ions (Olin, *et al.*, 1998). A similar result has been reported (Amer, *et al.*, 2010; Akpomie, *et al.*, 2002). A good literature search has divulged different types of consequences on the upshot of temperature on the adsorption of heavy metals. A decrease in adsorption potential accompanied by an increase in temperature has been perceived, the sight decrease at high temperature is probably due to the inhibiting effect of removal percentage which can be strongly adsorbed on the zeolite (Stumm, *et al.*, 1996).

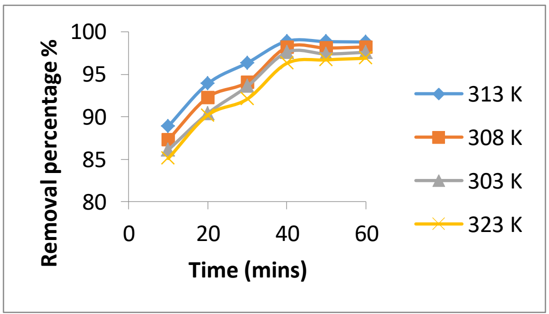

Figure (6): Effect of temperature on adsorption of cadmium on synthesized LTL zeolite.

3.4 Effect of Time

All the batch studies were carried out on time. The study shows that as the time increases, the percentage adsorbed increases till equilibrium was reached at regarding 60mins. The initial adsorption was caused by the availability of the positively charged surface of the adsorbent. The influence of time is also the main factor to be contemplated on the adsorption of metal ions by an adsorbent. It has been described that the contact time plays a main role in the adsorption process. The fast rate of adsorption discovered at the initial stage may be explained by an availability of plentiful active sites on the adsorbent surface which gradually became occupied with time. As these sites are progressively filled the more difficult the sorption becomes as the process tends to become unfavorable (Kapica, *et al.*, 2002).

3.5 Isotherm Studies

Adsorption isotherm is usually described through isotherms, that is, the purpose which connects the amount of adsorbate on the adsorbent. Dispersal of metal ions between the liquid phase and the solid phase can be delineated by several models of isotherm such as Langmuir, Freundlich and Temkin isotherm, etc. assumes monolayer adsorption onto a surface containing a limit number of adsorption sites of uniform schemes with no transmigration of adsorbate in the plane surface (Hameed, *et al.*, 2007). Once a site is packed, no further sorption can happen at that site. This indicates that the surface capacities a saturation point where the maximum adsorption of the surface will be achieved.

3.5.1 Langmuir isotherm model

The Langmuir isotherm is built on the theoretical principle that only a single adsorption layer exists on an adsorbent. It accepts that all active sites on the adsorbent are homogenous and there is no influence between active sites (Langmuir, 1916).

The linear shape of Langmuir equation is given as:

$$\frac{Ce}{qe} = \frac{1}{Q^{\circ}\,KL} + \frac{Ce}{Q^{\circ}} \qquad (3)$$

Hence a plot of Ce/ qe against Ce will give

$$Slope = \frac{1}{Q^{\circ}} \quad \text{and} \quad Intercept = \frac{1}{Q^{\circ}KL}$$

The Langmuir constants KL and Q° is the amount of adsorption was determined from the intercept and slope.

Langmuir model assumes that uptake of cadmium molecules occurs on a homogeneous surface by monolayer adsorption. For Langmuir isotherm, the values of specific adsorption (Ce/qe) were plotted against equilibrium concentration (Ce) and is shown figure 7 below. The Langmuir constant KL and Q° relate to the energy of adsorption and maximum adsorption capacity was founded from the intercept and slope of the linear plot, and showed in Table 1. The crucial features of Langmuir adsorption isotherm parameter can be used to forecast the affinity between the sorbate and sorbent manipulating a dimensionless constant called separation factor (RL), which is expressed by the following relationship (Malik, et al., 2004):

$$RL = \frac{1}{(1+KL\ Ci)} \quad (4)$$

Where KL is the Langmuir constant and Ci is the initial concentration of Cd (II). The value of RL indicated the type of Langmuir isotherm to be irreversible (RL =0), linear (RL = 1), unfavorable (RL > 1), or favorable (0 < RL < 1) (McKay and Gardner, 1982). The RL values between 0 and 1 show favorable adsorption. The RL value in the present investigation was found to be 0.0983-0.1980, indicating that the adsorption of the cadmium ion onto synthesized LTL zeolite is favorable.

3.5.2 Freundlich isotherm model

The Freundlich isotherm describes the range of heterogeneity of the adsorbent surface demanding a multilayer adsorption (McKay and Gardner,1982). Freudlich equation is given as:

qe= Kf Ce 1/n (5)

The linear form is

$$\log qe = \log Kf + \frac{1}{n}\log Ce \quad (6)$$

Where Kf = Freundlich constants which correspond to adsorption capacity, n= adsorption intensity.

Freundlich isotherm involves an empirical model, where qe represents the amount adsorbed per amount of adsorbent at the equilibrium (mg.g^{-1}), Ce represents the equilibrium concentration (mg.L^{-1}), Freundlich equilibrium constants were determined from the plot of logqe against logCe shown in figure 8. The values of the freundlich constants Kf and n are parameters that depend on the adsorbate and adsorbent. Were indicated from the intercept and the slope individually then shown in Table 1. The constant Kf is a measure of the adsorption capacity while constant n is a measure of the intensity or favorability of adsorption (Abdel-Fattah and Isaacs, 2003). For advantageous adsorption, the value of n will be between 1 and 10 represent good adsorption (Ozer and Pirinc¸ 2006). The n value designates the degree of nonlinearity between solution concentration and adsorption as follows: if the value of n=1, afterward adsorption is a straight line; if n<1, afterward adsorption is a chemical process; if n>1, afterward adsorption is the physical process. In this work, all the values scope from 3.5498 to 3.5549 showing beneficial adsorption of cadmium on the adsorbent. The circumstances n>1 is most habitual and may be due to a distribution of surface sites or any factor that sources a decrease in adsorbent adsorbate interaction with increasing surface density (Reed and Matsumoto, 1993). The correlation factor R^2 ranges from 0.9869 to 0.9937, indicating that the adsorption followed Freundlich isotherm model and n lies between 1 and 10 it indicates the physical adsorption of cadmium ions onto synthesized LTL zeolite so the process is favorable physical adsorption (Calace, *et al.*, 2002).

3.5.3 Temkin isotherm

The Temkin equation is given as:

$$qe = B \ln(ACe) \quad (7)$$

The linear form is

$$qe = B\ln A + B\ln Ce \quad (8)$$

qe = Amount adsorbed at the equilibrium, Ce = Equilibrium concentration.The constants A and

B were calculated; hence temkin isotherm was analyzed by plotting qe against lnCe as shown in figure 9. The values of constants A and B were calculated from intercept and slope respectively then the data was presented in Table 1. The correlation coefficient R^2 of about 0.8335 to 0.8743 indicates that cadmium adsorption did not follow the temkin isotherm. Thus R^2>0.91 indicates adsorption follows temkin isotherm (Tempkin and Pyzhev, 1940).

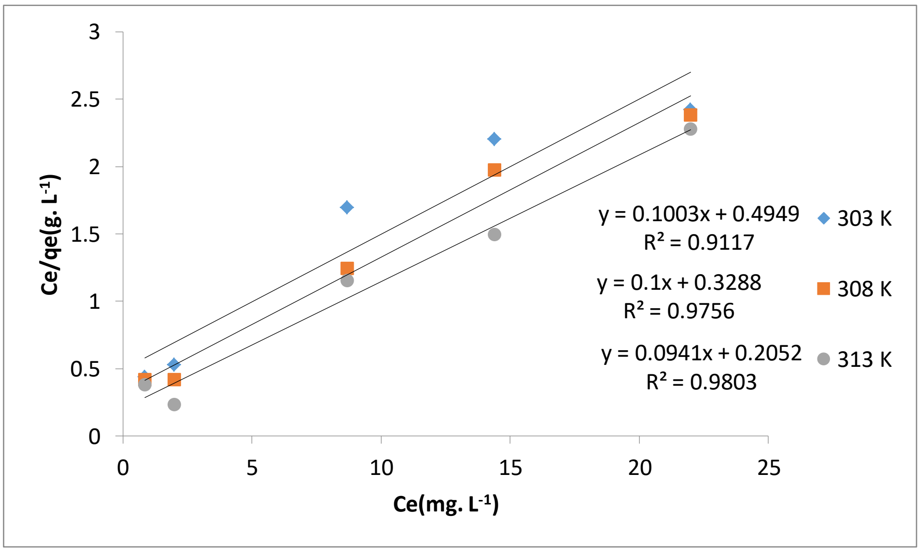

Figure (7): Langmuir isotherm for adsorption of cadmium on synthesized LTL zeolite.

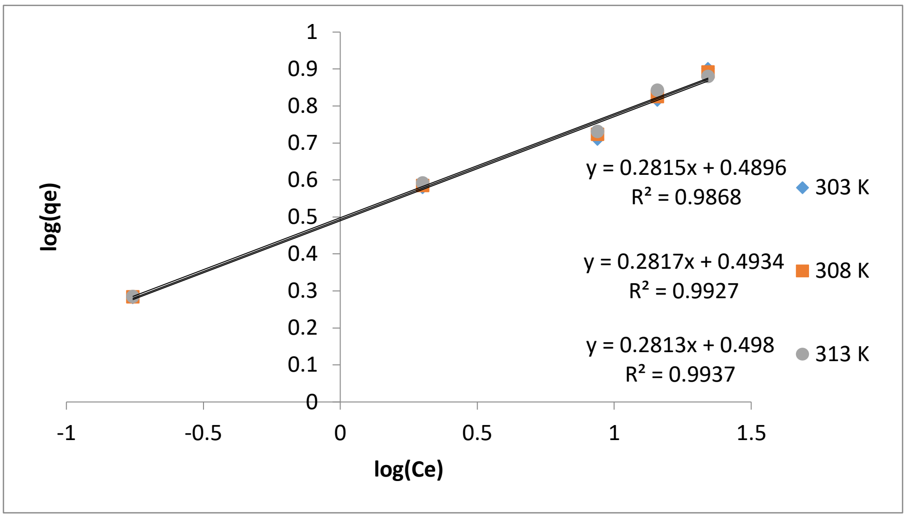

Figure (8): Freundlich isotherm for adsorption of cadmium on synthesized LTL zeolite.

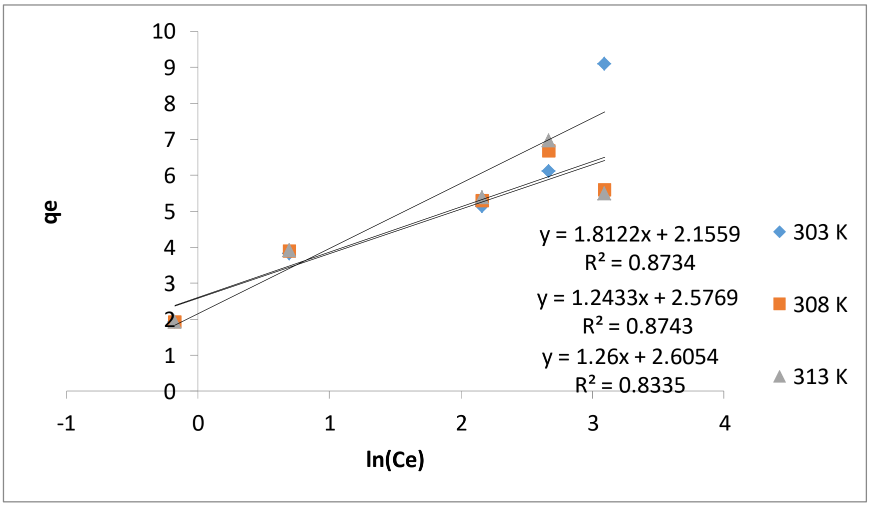

Figure (9): Temkin isotherm for adsorption of cadmium on synthesized LTL zeolite.

Table 1: Isotherm parameters for adsorption of cadmium ions onto synthesized LTL zeolite.

Isotherm models	**Temperature (K)**		
	303	308	313
Langmuir			
Q°($mg.g^{-1}$)	9.9700	10.0000	10.6269
KL($L.mg^{-1}$)	0.2026	0.3041	0.4585
RL	0.1980	0.1412	0.0983
R^2	0.9117	0.9756	0.9803
Freundlich			
n	3.5523	3.5498	3.5549
K*f* ($L.mg^{-1}$)	3.0874	3.1145	3.1477
R^2	0.9869	0.9927	0.9937
Temkin			
A($L.g^{-1}$)	3.2857	7.9454	7.9066
B	1.8122	1.2433	1.2600
R^2	0.8734	0.8743	0.8335

4. CONCLUSIONS

Our study for synthesizing zeolite LTL that can be used for removal of cadmium ion from aqueous solution showed that the best time for synthesizing LTL zeolite is 3h. Adsorption is a strong choice for removal of heavy metals from aqueous solution and the equilibrium data was found to fit the Langmuir and Freundlich models better than the Temkin model. From the Langmuir model the *RL* value in the existing investigation was less than one, indicating that the adsorption of the metal ion onto synthesized LTL zeolite is favorable, and according the obtained (n) value from Freundlich model the process is favorable physical adsorption. The maximum adsorption of cadmium occurred at a pH 8 and 313K. On the other hand increase in temperature improved adsorption performance for the zeolite; high metal uptake can be achieved with careful selection of slurry concentration to avoid masking of sorption by chemical precipitation. According to the results of our study the synthesized zeolite LTL showed promise as a highly efficient adsorbent for cadmium removal.

Conflict of Interest

The Author acknowledges to Ibnu sina institute for fundamental science studies University of UTM/Malaysia.

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