Carpathian Journal of Earth and Environmental Sciences, February 2014, Vol. 9, No. 1, p. 69 - 80

REMOVAL OF COPPER FROM AQUEOUS SOLUTIONS BY USING MICRITIC LIMESTONE

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Abstract: The presence of heavy metals in wastewater is major concern of public health and environment. Industrial wastewaters usually contain high levels of heavy metals and treatment is needed before disposal, in order to avoid water pollution. Adsorption process is one of the most promising technologies in water pollution control in terms of low cost, simple design and operation. The most popular and widely used adsorbents in wastewater treatment applications have high cost; and unfortunately regeneration costs of these adsorbents limits their large-scale applications for the removal of metals. As a result, researchers started to look for alternative low-cost adsorbents utilizing natural material and industrial wastes. They were thought to use as a replacement for current costly methods of removing metals from aqueous solutions. In this study, the use of micritic limestone as low-cost adsorbent was investigated. From the results, the micritic limestone had the merits of high specific surface area, significant adsorption sites and functional groups. Copper-adsorption significantly depends on the pH, adsorbent dosage, temperature and contact time. The maximum adsorption capacity was 237.05 mg/g for 1 hour and 1 g dosage. The experimental investigation results show that powdered micritic limestone has a high level of copper ions adsorption capacity. Adsorption data was correlated with Langmuir and Freundlich isotherm models. It was found that Langmuir and Freundlich isotherms fitted well to the data. Consequently, it is determined that powdered micritic limestone can be successfully used for removing copper ions from aqueous solutions.

Keywords: Micritic limestone, Heavy metal, Copper removal, Aqueous solution, Adsorption isotherms

1. INTRODUCTION

Contamination of water by toxic heavy metals during the discharge of industrial wastewater is a worldwide environmental problem. According to the reports of World Health Organization (WHO), water contamination causes more than 3.5 million deaths per year worldwide; additionally, heavy metals pollution makes the situation worse due to their immense toxicity and non-biodegradability (Jayakumar et al., 2010; Pronczuk et al., 2011). High concentration of heavy metals in the environment can be harmful for a variety of living species. Heavy metal ions can be accumulated through the food chain even at lower concentrations, and can cause decrease in the functions of mental and central nervous system. In addition to these, the harmful ions lower the energy levels, damage blood composition, lungs, kidneys, liver and other vital organs (Lopez et al., 2003; Kalkan et al., 2012; Nadaroglu & Kalkan, 2012; Setshedi et al., 2012).

Population explosion, irregular and rapid urbanization, industrial and technological expansion, high-energy consumption and wastes from domestic and industrial sources has caused increasing heavy metal emission into the environment. Presence of these heavy metals in environment is important because of their toxicity and effects on human and living creatures' health (Gupta & Ali, 2004; Jiang et al., 2008; El-Said, 2010; Kiurski et al., 2012). Heavy metals and dyes are found in industrial wastewater, textiles, paper, paint manufacture, leather tanning, battery manufacture, dyeing etc... Recently, their removal has attracted much practical and academic interest because of increased knowledge about their significant impact on environment. As a result, the world industry is in an increasing need for decreasing heavy metal ions amount in waters; additionally

industrial waste should urgently be decreased under an admissible level. For the past several years, high levels of heavy metals in drinking water and foods have been associated with several acute and chronic illnesses in humans all around the world (Lee & Davis, 2001; Ramesh, et al., 2005; Gupta et al., 2006; Aman et al., 2008; Andras et al., 2009; Nadaroglu et al., 2010; Pop et al., 2012).

Increased concern of environmentalists and governments on the effects of heavy metals and their attempts to protect public health increased the number of researches about the development of advanced technologies to remove heavy metals from water and wastewater (Bong et al., 2004; Karbassi et al., 2007; Shetty & Rajkumar, 2009; Onundi et al., 2010). Removal of toxic metal ions can be made various techniques such as coagulation, flocculation, precipitation, filtration, ozonation and ion exchange. However, these methods have high costs (Sohail et al., 1999; Rao et al., 2002) while adsorption proved to be versatile and readily applicable (Gupta & Ali, 2000). While activated charcoal is more preferable, high cost is an important problem (Pollard et al., 1992; Gupta et al., 2003; Aravindhan et al., 2009; Sousa et al., 2010). Therefore, cheap natural materials of renewable sources are suitable alternatives. In recent years, in terms of environmental and economical aspects, special attention has been given to the use of natural adsorbents as an alternative to replace conventional adsorbents. Natural materials that are available in large quantities, or certain waste products from industrial or agricultural operations, have the potential to be inexpensive sorbents. Due to their low cost, when these materials can be disposed of without expensive regeneration at the end of their lifetime (Özpinar, Y., 2011; Gunel et al., 2012; El-Said et al., 2010).

Copper is known to be one of the most common toxic metals; it finds its way to the water stream of industries like electroplating, mining, electrical and electronics, iron and steel production besides nonferrous metal industry, printing and photographic industries and metalworking and finishing processes (Mukhopadhyay et al., 2007; Nemeth et al., 2010). Copper as a metal provides limited scope for environmental pollution, but the waste generated by copper-based industries with various toxic elements can pollute the environment. Copper mining, smelting, and refining activities are often associated with the generation of large quantity of wastes. Overburden, mine tailings, sediment from concentrator plants and scrap, slag, dross, slime, flue dust, mill scales, and sludge from the process are the major sources of pollution unless handled and treated suitably (Nadaroglu et al., 2010; Nohut et al., 1999; Agrawal et al., 2004).

Geological materials are generally used as adsorbent for removing heavy metal from wastewater. One type of geological materials, limestone, is comprised primarily of calcite, (CaCO3) and is derived from marine organisms and/or chemical precipitation. The use of limestone as a soil or surface water amendment to neutralise acidity is a common practice (Skousen, 1991; Skousen et al., 1996). Limestone produced in large quantities in many countries is a low-cost reactive medium that can be used for retaining heavy metals and the subsequent clean up of industrial effluents, leachates and contaminated ground water (Sharma & Srivastava, 2006; Ghazy & Ragab, 2007).

In this research, we studied the adsorption capacities of the micritic limestone material for removing copper ions from wastewater. We wanted to determine if this material might be economic and be an alternative adsorbent that could replace the expensive resins currently used for wastewater treatment. Copper ions were absorbed by micritic limestone from polluted river water and $CuCl_2$ solution; and adsorption data was analyzed with the help of adsorption models to determine the mechanistic parameters associated with the adsorption process.

2. MATERIALS AND METHODS

2.1. Adsorbate

Industrial wastewater sample was used as adsorbate in batch experiments. The wastewater was supplied from Erzurum Industrial Zone (NE Turkey). An aqueous solution of copper metal was prepared for batch experiments of adsorption study in laboratory conditions.

2.2. Adsorbent

Micritic limestone used as adsorbent in this study was taken from the limestone geological unit located in the southern Olur (Erzurum), NE Turkey. Adsorbent was grinded with a ring grinder to obtain granular absorbent material. It was washed with distilled water to remove fines and dirt according to the procedure of Goel et al., (2005). The suspension was wet sieved through a 200-mesh screen. A little amount of suspension remained on the sieve and was discarded. Solid fraction was washed five times with distilled water following the sequence of mixing, settling, and decanting. The last suspension was filtered, and residual solid was then dried at 65 ºC; was grounded in a mortar,

and sieved through a 200-mesh sieve. After these steps, the suspension was subjected to acid pretreatment as recommended in other resources (Nadaroglu et al., 2010; Shiao & Akashi, 1977). After micritic limestone adsorbent was washed with distilled water, acid pretreatment was carried out by boiled 100 g of adsorbent. Then, it was washed with distilled water, filtered, and dried. This adsorbent was used in our research.

2.3. Adsorbent characterization

Chemical and mineralogical compositions of clayey material samples were determined by X-ray powder diffraction (XRD) by using Philips PW 1010/80 diffractometer with graphite-filtered CuKα radiation. Furthermore, pH values were determined with a pH meter (Thermo scientific Orion 5 star plus multifunction). Scanning electron microscope (SEM) was used to examine the surface of adsorbent. Images of native adsorbent and metal loaded adsorbent were magnified 5000 times by SEM modeled JEOL JSM-6400 SEM. Before SEM examinations, sample surfaces were coated with a thin layer (20 nm) of gold to obtain a conductive surface and to avoid electrostatic charging during examination. The same machine was also used for the energy dispersive X-ray (EDX) spectra analysis in order to determine the elemental composition of the powdered micricit limestone. In addition, the Fourier Transform Infrared Spectroscopy (FTIR) analyses were carried out to identify functional groups and molecular structure in the raw limestone and copper loaded limestone. FTIR spectra were recorded on the Perkin-a Perkin-Elmer GX2000 FTIR spectrometer. The spectrum of the adsorbent was measured within the range of 4000-700 cm^{-1} wave numbers.

2.4. Adsorption study

1,5 g of powder of micritic limestone was taken as adsorbent for studying metal adsorption and it was then suspended in 50 mL of 1 mg/mL $CuCl_2$, at pH between 2 and 6, and contacted batchwise in a thermostatic (t=25°C±0.1°C) water-bath agitator for 1 h to enable equilibration of the sorbent and solution phases. It was waited for 1 h at each pH level. The suspension was centrifuged at 3000 rpm for 10 min, and the supernatant was filtered through a 0.45 μm pore, cellulosic membrane filter to ensure the measurement of heavy metal concentration in filtrate. After centrifuging, the amount of decreasing copper at the top level of liquid solution was measured. Copper ion concentration was determined by spectrophotometric method using 1-amino-2-hydroxy-4-naphthalenesulfonic acid (Seifullina & Skorokhod, 1991). The adsorption capacity of adsorbent (q_t) was calculated using Eq.1.

$$qe = \frac{(C_o - C_t) * V}{m} \quad (1)$$

where, q_t is the adsorption capacity of the adsorbent at time t (mg adsorbate/g adsorbent); C_o is the initial concentration of metal (mg/L); C_t is the residual concentration of metal after adsorption had taken place over a period of time t (mg/L); V is volume of metal solution in shake flask (L) and m is mass of adsorbent (g). Metal removal percentage ($R\%$) was calculated using Eq. 2.

$$R(\%) = \frac{(C_o - C_t) * 100}{C_o} \quad (2)$$

where (R %) is the ratio of difference in metal concentration before and after adsorption; C_o is the initial concentration of metal (mg/L); C_t is the residual concentration of metal after adsorption had taken place over a period of time t (mg/L).

2.5. Equilibrium studies

Equilibrium data, commonly known as adsorption isotherms, are basic requirements for the design of an adsorption system. In an adsorption isotherm study, several equilibrium models are developed to describe adsorption isotherm relationships (Seader & Henly, 2006; Imamoglu & Tekir, 2008). Freundlich (Freundlich & Hatfield, 1926) and Langmuir (Langmuir, 1918) equations are the models used all around the world because of their simplicity (Polowczyk et al., 2007; Nadaroglu & Kalkan, 2012).

Langmuir adsorption isotherm model represents one of the first theoretical treatments of non-linear sorption and suggests that the uptake occurs on a homogenous surface by monolayer sorption without interaction between adsorbed molecules (Bansal et al., 2009). Langmuir adsorption isotherm is often used to describe maximum adsorption capacity of an adsorbent and it is given as;

$$q_e = \frac{q_m * K_L * C_e}{1 + K_L * C_e} \quad (3)$$

where q_e (mg/g) is the adsorption amount of adsorbent at equilibrium; q_m (mg/g) is the maximum adsorption amount of metal ions, C_e (mg/L) is the equilibrium concentration of adsorbate in solution and K_L (L/mg) is the equilibrium adsorption constant which is related to the affinity of the binding sites. The Langmuir constants K_L and q_m are calculated with the following equation;

$$\frac{C_e}{q_e} = \frac{1}{K_L * q_m} + \frac{q_e}{q_m} \quad (4)$$

where C_e (mg/L) is the equilibrium concentration of adsorbate in solution; q_e (mg/g) is the adsorption amount of adsorbent at equilibrium, q_m (mg/g) is the maximum adsorption amount of metal ions and K_L (L/mg) is the equilibrium adsorption constant which is related to the affinity of the binding sites. Freundlich isotherm is based on the assumption that adsorption is on a heterogeneous surface and exponential distribution of sites and their energies (Polowczyk et al., 2007), which can be expressed by the following equation;

$$q_m = K_F + C_e^{1/n} \quad (5)$$

where q_m (mg/g) is the maximum adsorption amount of metal ions, C_e (mg/L) is the equilibrium concentration of adsorbate in solution. K_F (mg/g) and n are the Freundlich constants related to the sorption capacity of the adsorbent and the energy of adsorption, respectively. They can be calculated in the following linear form;

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (6)$$

where q_e (mg/g) is the adsorption amount of adsorbent at equilibrium; C_e (mg/L) is the equilibrium concentration of adsorbate in solution, K_F (mg/g) and n are the Freundlich constants related to the sorption capacity of the adsorbent and the energy of adsorption. Langmuir and Freundlich isotherms were obtained from the experiments.

3. RESULTS AND DISCUSSIONS

3.1. Characterization of adsorbent

This geological unit consists of micritic limestone and clayey micritic limestone and includes chert nodules and bands at upper levels. The formation densely consisted of micritic limestone, which was named as Yeşilbağlar Formation by Yılmaz (1985) and then Soğukçam Formation (Konak et al., 2001). This formation deposited in the open and peep carbonate slope at Berriasiyen-Aptian geological time. The lower part of this sedimentary sequence is composed of white micritic limestone levels with cherty nodules and pelecypod shells. Micritic limestone with interbedded mudstone and sandstone increase from the bottom upwards in the sequence. Towards the top, the composition of the limestone changes to semi-pelagic micrite, and its bedding changes from thick to thin layers. Micritic portions of the carbonate beds are composed of fine-grained calcite with dispersed quartz. In addition, accessory apatite, very fine-grained Fe-Mn-hydroxides and some clay minerals occur. Some unidentified foraminifera and thin shell fragments are common within the micrite and filled with relatively coarse grains of calcite (Konak & Hakyemez, 2008; Duman, 2009). The micritic limestone used as adsorbent material collected from Soğukçam Formation deposited in Berriasiyen-Aptian geological time.

XRD results of micritic limestone were illustrated in the figure 1. The absorbent material dominantly contains calcite mineral and its second mineral is quartz (Fig. 1).

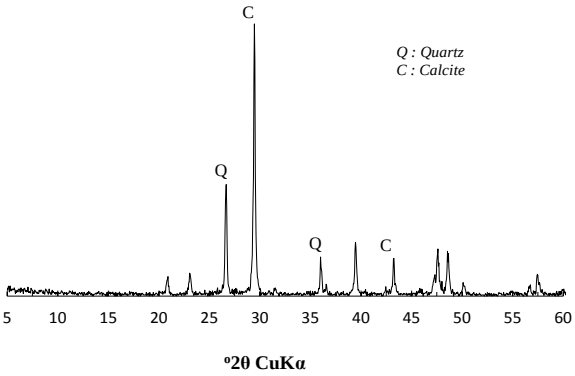

Figure 1. The XRD pattern of micritic limestone

Images of native adsorbent and metal loaded adsorbent were magnified 5000 times by SEM, which is used to examine the surface of adsorbent. SEM photographs showed that progressive changes occurred in the surface of native adsorbent (Fig. 2A) after its surface is loaded by copper ions (Fig. 2B). SEM of exhausted adsorbent clearly indicates the presence of new shiny bulky particles and layer over the surface of metal loaded adsorbent which weren't there in the native adsorbent before metal loading (Kalkan et al., 2012).

EDX is an electron beam induced X-ray spectrochemical technique that allows determination of local chemical composition of a sample by means of non-destructive analysis on a microscopic scale. It offers ability to gather information about particles finer than optical microscopes and can readily distinguish between clusters and agglomerates of particles besides the chemical analysis (Unabia & Zaide, 2002).

EDX measurements were recorded for qualitative analysis of the element constitution of adsorbents; EDX spectra of native adsorbent and copper ion loaded adsorbent were illustrated in the

Figs. 3A and 3B. From the EDX spectra, copper ions were sorbed onto the adsorbent. EDX analysis provided direct evidence for the adsorption of copper onto adsorbent (Bansal et al., 2009). It is shown from EDX spectra that after copper adsorption, copper concentration increased in the copper loaded adsorbent (Figs. 3A-B; Table 1).

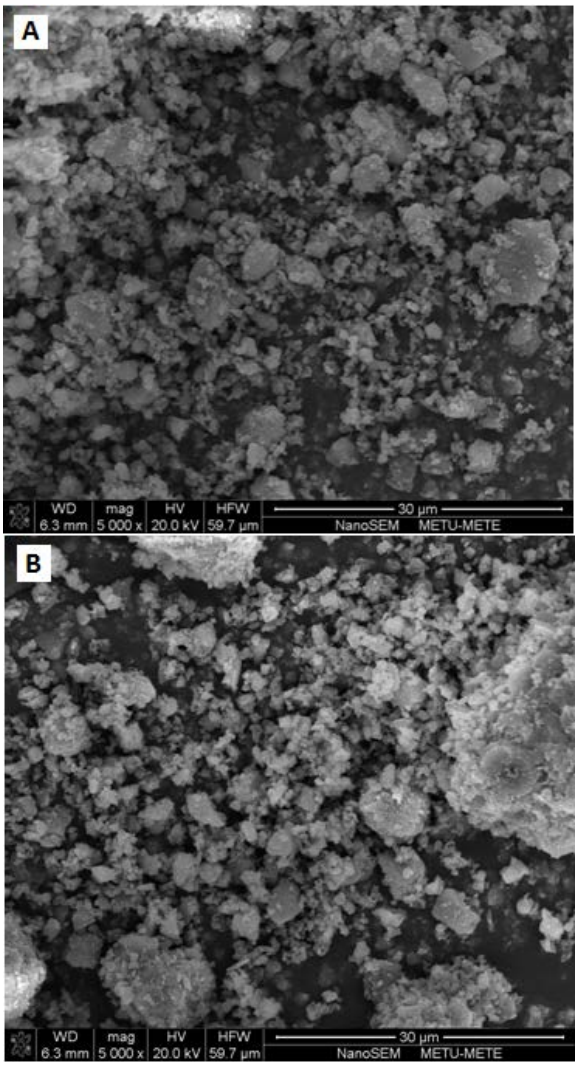

Figure 2. SEM images of native adsorbent (A) and copper loaded adsorbent (B)

3.2. Calibration curve

There is a limited linear range of most analytical instruments. Therefore, during method validation the linearity of calibration curve should be evaluated and the working range of the calibration curve should be determined (Massart et al., 1997; Loco et al., 2002). Calibration is fundamental for achieving measurement consistency. Calibration involves establishing a relationship between an instrument response and one or more reference values. Linear regression is one of the most frequently used analyses in calibration. Once the relationship between the input value and the response value assumed to be represented by a straight line is established, calibration curve is used in the evaluation of result's accuracy.

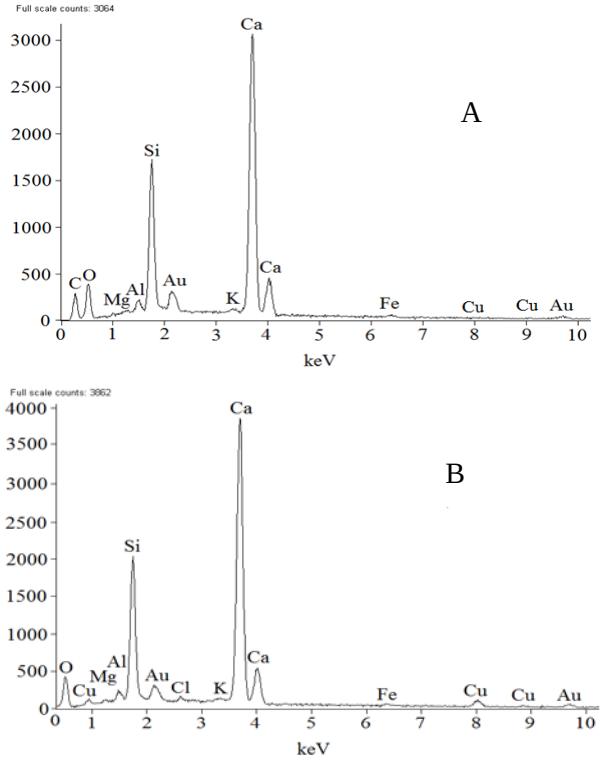

Figure 3. EDX spectra of native adsorbent (A) and copper loaded adsorbent (B)

Table 1. Results of EDX spectrum

Elements	Native adsorbent		Copper ion loaded adsorbent	
	Weight (%)	Atom (%)	Weight (%)	Atom (%)
Mg	0.84	1.25	0.68	1.05
Al	2.04	2.74	1.67	2.30
Si	21.92	28.28	20.76	27.46
K	0.79	0.73	0.55	0.52
Ca	73.45	66.38	68.86	63.82
Fe	0.96	0.62	0.81	0.54
Cu	0.39	0.23	5.78	3.38

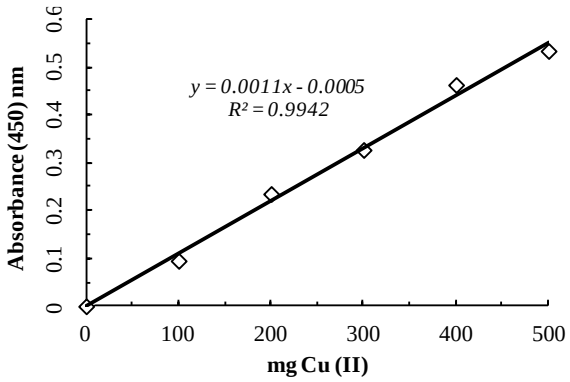

Figure 4. Calibration curve of copper adsorption

According to the calibration curve, there is an approximate linear relationship between absorbance and copper concentration in aqueous solutions (Fig. 4). It is observed that the regression coefficient (R^2) is quite high, and its value is 0.9942. The same results were obtained in our previous studies (Nadaroglu et al., 2010; Kalkan et al., 2012; Kalkan et al., 2013; Nadaroglu et al., 2013).

3.3. Effect of pH

pH level of the aqueous solution is an important operational parameter in the adsorption process as it affects solubility of the metal ions, concentration of counter ions on the functional groups of adsorbent and degree of ionization of adsorbate during reaction (Amuda et al., 2007). In other words, the uptake and percentage removal of metals from the aqueous solution are strongly affected by the pH of the solution (Benhammou et al., 2005; Ghazy & Ragab, 2007; Onundi et al., 2010). In order to find the optimal pH value for the sorption process, the removal of copper ions in the pH range 2-6 was researched and the data were illustrated in figure 5.

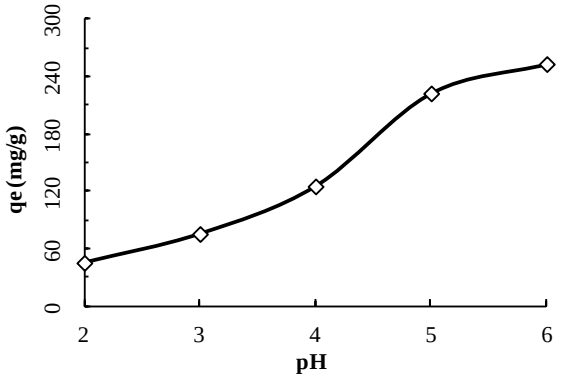

Figure 5. Effect of pH on the adsorption of copper

It shows the effect of pH variation of copper adsorption on micritic limestone particle surface. It was shown that the absorption amount of copper increased with increasing pH; and maximum adsorption of copper ions were seen at pH 6.0. The uptake of copper increased from 45.65 mg/g to 253.66 mg/g when the pH of solution increased from 2 to 5. This results from surface complexation reactions, which are mostly influenced by electrostatic force of attraction between copper and surface of the adsorbent. The acidity of the medium can affect metal ions' adsorbent uptake amount because hydrogen ions in the solution can compete with copper for active sites on the adsorbents surface (Imamoglu & Tekir, 2008, Nadaroglu et al., 2010).

Removal of metal ions from aqueous solutions by adsorption is highly dependent on the pH of the solution as it affects surface charge of the adsorbent, degree of ionization and speciation of the adsorbate (Bansal & Goyal, 2005; Benhammou et al., 2005; Najua et al., 2008). The results showed that the pH of the solution played a very important role in metal uptake. The adsorbent surface metal binding sites as well as metal chemistry in solution were influenced by pH solution.

3.4. Effect of adsorbent dosage

Dosage is important parameter in adsorption studies because it determines the capacity of adsorbent for given initial concentration of metal in solution (Bulut & Baysal, 2006; Memon et al., 2009). In this study, the effect of adsorbent dosage was studied by changing sorbent amounts from 0.5 to 10 mg/mL. Its effect on the process of copper removal is presented in figure 6. A significant increase in uptake was observed when the dosage was increased from 0.5 to 5 mg/mL. This indicates that the adsorption increased with increasing micritic limestone dosage up to a certain value and then became almost constant (Dakiky et al., 2002; Rao et al., 2008; Acharya et al., 2009; Kumar et al., 2010). The initial increment in adsorption capacity with increase in adsorbent dosage was expected because the numbers of adsorbent particles increases in parallel with the dosage, thus more surface areas were available for metals attachment; similar tendency was reported by Acharya et al., (2009).

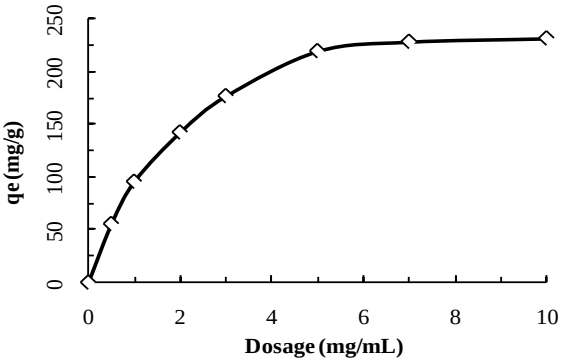

Figure 6. Effect of adsorbent dosage on the adsorption of copper

The increase in adsorption as parallel with the increase in adsorbent dosage was resulted from the availability of larger surface area and more adsorption sites (El-Said, 2010). It is reasonable to think that, there would be greater availability of exchangeable sites for metal ions with higher dosage of adsorbent (Najua et al., 2008). Moreover, higher

adsorbent dosage could impose a screening effect on dense outer layer of cells; thereby it would shield binding sites from metals (Pons & Fuste, 1993).

Copper concentration in the aqueous solution taken from samples of polluted river water and $CuCl_2$ solutions treated with micritic limestone indicates that micritic limestone enhanced the capacity of adsorption. Addition of micritic limestone strongly inhibited the leaching of copper in polluted river water and $CuCl_2$ solutions. The experimental results show that copper concentration of samples decreased from 1.325 to 0.324 mg/mL and from 3.236 to 0.365 mg/mL in the polluted river water and $CuCl_2$ solutions, respectively. It was also determined that micritic limestone decreased the copper concentration in polluted river water and $CuCl_2$ solutions (Fig. 7).

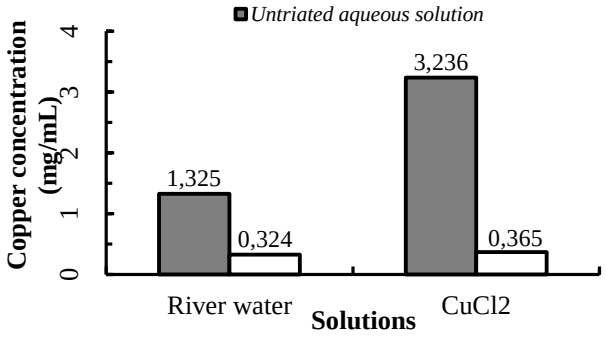

Figure 7. Variation of copper concentration after micritic limestone treating with river water and $CuCl_2$

3.5. Effect of temperature

Temperature is known to have a profound effect on various chemical processes. It affects the adsorption rate by altering molecular interactions and solubility of adsorbate (Ahmaruzzaman & Sharma, 2005; Setshedi et al., 2012). Figure 8 shows the effect of temperature on the adsorption of copper. The effect of temperature influencing adsorption has been studied in the range of 10-80 °C. It is observed that the degree of adsorption increases in parallel with the increase in temperature and maximum adsorption of copper ions are obtained at 25°C.

The results show that the adsorption capacity increased from 76.10 to 266.13 mg/g in parallel with the temperature increase from 10 to 80°C (Figure 8). This increase in adsorption capacity results from the chemical interaction between adsorbate and adsorbent, and creation of active surface centers; or the increase results from enhanced rate of intraparticle diffusion of copper ions into the pores of adsorbent at higher temperatures (McKay et al., 1980; Kalavathy & Miranda, 2010). An increase in temperature involves an increased mobility of metal ions and a decrease in the retarding forces acting on the diffusing ions. These results reflect the enhancement in sorption capacity of the adsorbent, which indicates that the temperature dependence of the adsorption process is associated with changes in several thermodynamic parameters (Larous et al., 2005; Das et al., 2006).

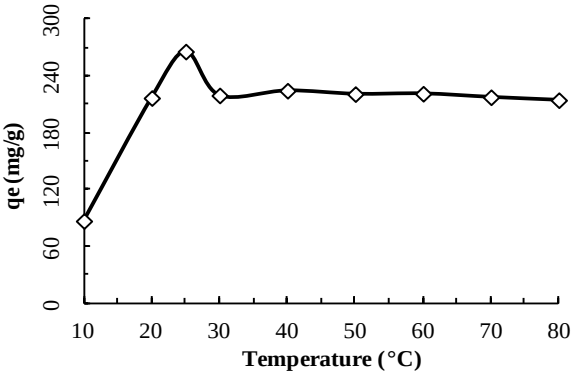

Figure 8. Effect of temperature on the adsorption of copper

3.6. Effect of contact time

The relationship between the amounts of metal removal and contact time was analyzed and presented in figure 9. It is observed that copper removal increases in the first 60 min of contact time. Basically, the removal of copper is fast at the beginning while it gradually decreases with time until it reaches equilibrium. This indicates that the concentration of copper in the solution decreased rapidly within 60 min and the removal was virtually completed within 120 min of contact time. The fast adsorption at the initial stage was probably due to the initial concentration gradient between adsorbate in solution and the number of empty sites available on the micritic limestone particle surface at the beginning. This is probably because of the larger surface area of the micritic limestone particle, which is available for the adsorption of copper ions at the beginning. As the surface adsorption sites are exhausted, uptake rate is controlled by the rate at which the adsorbate is transported from exterior to the interior sites of the adsorbent particles. Firstly, adsorption followed a linear rising in which instantaneous and extremely fast uptake takes place, and then stationary state observed a rapid decrease in copper ions' removal. The initial faster rate of metal transition can be explained by the large, uncovered available surface area of micritic limestone and its composites (Kalavathy & Miranda, 2010). The rapid removal of the adsorbate has significant practical importance as it facilitates smaller reactor volumes for ensuring efficiency and economy (Aksu, 2001).

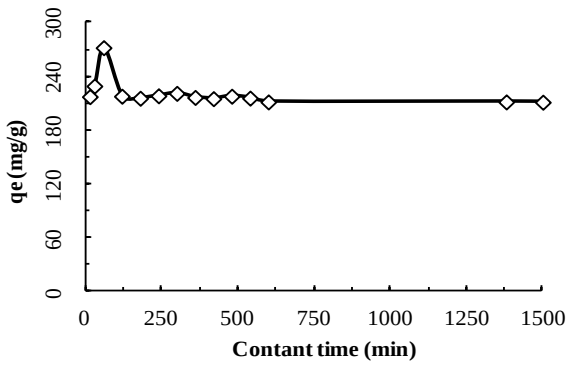

Figure 9. Effect of contact time on the adsorption of copper

3.7. Equilibrium adsorption isotherms

Langmuir and Freundlich isotherm models are the simplest and most commonly used isotherms that represent the adsorption of components from a liquid phase onto a solid phase. Langmuir adsorption isotherm model represents one of the first theoretical treatments of non-linear sorption and suggests that the uptake occurs on a homogenous surface by monolayer sorption without interaction between adsorbed molecules (Bansal et al., 2009). Langmuir model is based on the assumption that maximum adsorption occurs when a saturated monolayer of solute molecules is present on the adsorbent surface; and the energy of adsorbtion is constant and there is no migration of adsorbate molecules in the surface place (Acharya et al., 2009). Q_o (mg/g) and b (L/mg) parameters are Langmuir constants related to the adsorption capacity and rate of adsorption, respectively. Values of Q_o and b were calculated from the slope and intercept of Langmuir plot of C_e versus C_e/q_e. From Figure 10, the empirical constants Q_o and b were found to be 27.472 mg/g and 0.0796 (Table 2), respectively.

K_F and n are the constants incorporating all factors affecting the adsorption process (adsorption capacity and intensity) (Bansal et al., 2009). K_f and n values were calculated from the intercept and slope of the plot (Fig. 11).

It is pointed out in the literature that the parameters, K_F and n affect the adsorption isotherm. The larger K_F and n values indicate the higher the adsorption capacity. It is generally stated that the value of n in the range 1-10 represents good adsorption. The magnitude of the exponent n gives an indication of the favorability of adsorption. It is generally stated that values of n in the range 2-10 represent good, 1-2 moderately difficult and less than 1 poor adsorption characteristics (Treybal, 1980). The magnitude of exponent n indicates the favorability of the adsorption. The n value is 2.1413 L/mg (Table 2) and it is located at the range 2-10 represent good adsorption characteristic (Treybal, 1980; Bansal et al., 2009).

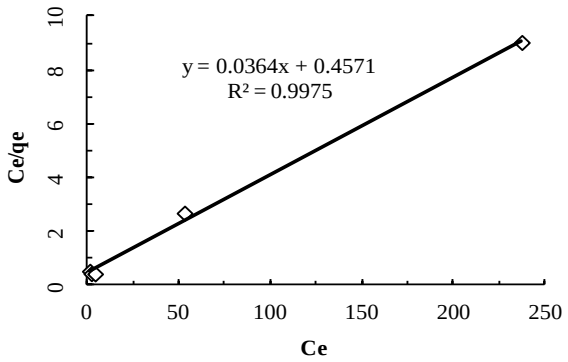

Figure 10. Langmuir adsorption isotherm

Table 2. Values of the Langmuir and Freundlich adsorption isotherms for adsorption of copper ions

Adsorption isotherms	Value
Langmuir constants	
Q_o (mg/g)	27.472
K_L (L/mg)	0.0796
R^2	0.9975
Freundlich constants	
K_F	0.4720
n	2.1413
R^2	0.8846

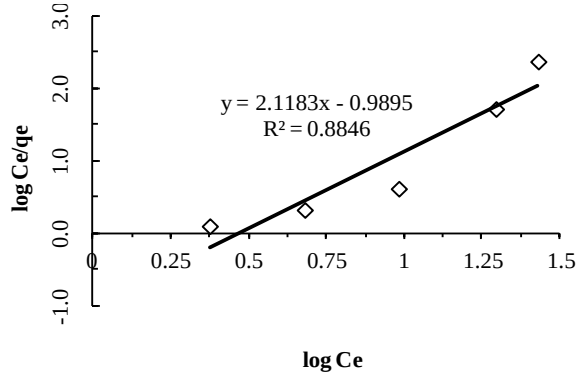

Figure 11. Freundlich adsorption isotherm

Based on the correlation coefficient values, it has been determined that Freundlich model fitted better to the experimental data (Table 2). High correlation coefficient shows that both adsorption isotherm models are suitable for describing the adsorption equilibrium of copper ions.

4. CONCLUSIONS

In this study, micritic limestone was converted into an adsorbent, and suitability of the powdered micritic limestone for adsorption of copper from $CuCl_2$ solutions was investigated by

adsorption experiments. Maximum copper removal by adsorbent was at pH 6.0. The amount of copper removal increases by time in the first 60 min; after that, removal is not significant. The rapid removal of the adsorbate has significant practical importance as it facilitates smaller reactor volumes ensuring efficiency and economy. It is observed that the degree of adsorption increases in parallel with the increase in temperature and maximum adsorption of copper ions are obtained at 25°C which is the temperature of the solution. The total amount of metal ions removed from solutions increases with the amount of adsorbent. The adsorbent concentration increases when the number of adsorbent particles surrounding the metal ions increases. Based on the correlation coefficient values, it has been deduced that Langmuir model fitted better to the experimental data. The high correlation coefficient showed that both adsorption isotherm models are suitable for describing the adsorption equilibrium of copper ions. The investigation showed that micritic limestone is a very valuable material for removing copper ions from aqueous solutions. Namely, it can favor chemical immobilization and reduce the solubility of wastewater. On the other hand, its use for the removal of copper ions from the aqueous solutions can potentially reduce the remediation costs.

ACKNOWLEDGEMENT

The laboratory study of this research was carried out in the Laboratories of Karadeniz Technical University and Ataturk University. So, the authors thank the authorities of these universities.

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Receieved at: 01. 04. 2013
Revised at: 02. 12. 2013
Accepted for publication at: 06. 12. 2013
Published online at: 12. 12. 2013