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Araştırma Makalesi/Research Article

Cu (II) Removal from Industrial Waste Leachate by Adsorption Using Expanded Perlite

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Abstract: The aim of the present study is to investigate the feasibility of using expanded perlite for the adsorptive removal of Cu (II) from industrial leachate. The adsorption capacities and sorption efficiencies were determined. The pseudo-second order, Elovich and the intra particle diffusion kinetic models were used to describe the kinetic data to estimate the rate constants. The results indicated that expanded perlite showed excellent adsorptive characteristics for the removal of Cu (II) from industrial leachate.

Key words: Industrial waste; Leachate; Adsorption; Copper; Expanded perlite.

Genleştirilmiş Perlit Kullanılarak Adsorpsiyonla Endüstriyel Atık Sızıntı Suyundan Cu (II) Giderimi

Özet: Çalışmanın amacı endüstriyel atık sızıntı suyundan genleştirilmiş perlit kullanarak adsorpsiyonla Cu (II) gideriminin incelenmesidir. Çalışmada, adsorpsiyon kapasitesi ve giderim verimleri araştırılmıştır. Adsorpsiyon kinetiğini belirleyebilmek için ikinci derece, Elovich ve partiküller arası difüzyon kinetik modelleri kullanılmıştır. Sonuçlar, genleştirilmiş perlitin, endüstriyel atık sızıntı suyundan Cu(II) gideriminde oldukça yüksek adsorplama karakteristiklerine sahip olduğunu göstermiştir.

Anahtar kelimeler: Endüstriyel atık; Sızıntı suyu; Adsorpsiyon; Bakır; Genleştirilmiş perlit.

Introduction

Landfills are still one of the most common ways to manage municipal and industrial waste disposal. However, landfill generates large quantity of heavily polluted leachate (Jones et al., 2006). Landfill leachate is generated by the infiltration and percolation of rainfall, groundwater, runoff or flood water into and through the waste layers of an existing or abandoned landfill site (Müller et al., 2015). The composition of leachate can vary throughout a landfill and among landfills depending mainly on the degradation stage of the waste (Justin and Zupančič, 2009). Other factors that affect leachate composition are the type of waste and landfill technology (Kjeldsen et al., 2002).

Heavy metals are common pollutants of leachate. Heavy metals is a potential problem to water and soil quality due to their high toxicity to plant, animal, and human life (Pamukoğlu and Kargı, 2009). Moreover, heavy metals cannot be destroyed chemically as organic pollutants (Fonseca et al., 2006). Among the heavy metals, copper is usually considered to be non-toxic for human at lower concentration ranges, but its presence at higher concentrations (>5 mg dm^{-3}) in the body has been linked many of health problems such as kidney damage, high fever, hemolysis, vomiting, etc. (WHO, 2004; Ajmal et al., 2005; Bhattacharyya and Gupta, 2006; Gök et al., 2008). WHO recommended a maximum acceptable concentration of Cu (II) in drinking water of 1.5 mg dm^{-3} (Aman et al., 2008).

Several treatment technologies have been used for the removal of heavy metals such as chemical precipitation, ion exchange, reverse osmosis, ultrafiltration and adsorption (Viera et al., 2010). Among them, adsorption has been successfully applied for heavy metal removal. Activated carbons are widely used as adsorbent materials because of their extended surface area, microporous structure, high adsorption capacity and high degree of surface reactivity (Kula et al., 2008). However, it is restricted due to its relatively high price, high operation costs, and problems with generation for the industrial scale applications. Recently, cost effective sorbent materials in order to minimize their processing cost and solve their disposal problems in an environmentally sustainable way are investigated.

The perlite and expandable forms have been very significant natural materials in recent years. Expanded perlite finds diverse utilization in various applications such as as a lightweight aggregate in the construction industry; as a rooting medium and soil conditioner in horticulture; as a bleaching agent in the textile industry; as an adsorbent in the chemical industry; and as filter aid and as filler in miscellaneous processes (Zorpas et al., 1999).

The aim of this study is to investigate Cu (II) removal from aqueous leachate of industrial waste by expanded perlite. The effects of pH, adsorbent dosage and contact time on adsorption efficiency were analyzed, and the optimum values were determined from the experimental studies. Adsorption kinetics were applied in order to determine adsorption mechanism and adsorption characteristic constants.

Materials and methods

The industrial waste used for this study was obtained from the Kızılırmak Casting Industry & Trade Co. Ltd. in Çorum, Turkey. In order to prepare leaching solution of the industrial waste, the toxicity characteristic leaching procedure (TCLP), as given in EPA's SW846, was used. In the TCLP test, a 100-g size-reduced sample of waste is mixed with an appropriate extraction fluid at the rate of 20:1 (L/S) and the mixture is rotated for 18 ± 2 hr at 30 rpm. Then, the final pH is measured, and the mixture is filtered using a glass fiber filter. The filtrate is used as a leaching solution in the experiments (Townsend et al., 2003). The characteristics of leaching solution are presented in Table 1.

Table 1. The characteristics of industrial waste leachate

Parameters	Values
pH	4.98±0.11
E.Conductivity, mS/cm	5.45±0.41
Zn, mg L^{-1}	367.25±23.4
Cu, mg L^{-1}	45.51±4.01
Pb, mg L^{-1}	24.43±3.43
Fe, mg L^{-1}	15.81±2.21
Cd, mg L^{-1}	9.41±2.13

The value following "±" is the standard deviation.

The expanded perlite was obtained from Izmir-Bergama region of Turkey. The results of its chemical composition are given in Table 2. Moisture content is about 0.11% as dry basis. The pH value of the expanded perlite samples is 6.9. The expanded perlite samples were passed through a sieve and the particulate size of 1 mm was used in experiments.

Table 2. Chemical analysis of expanded perlite

Components	**%w/w**
Na_2O	3.29
MgO	0.18
Al_2O_5	11.9
SiO_2	72.9
P_2O_5	0.02
CaO	0.79
TiO_2	-
MnO	0.05
K_2O	4.47
Fe_2O_3	0.53

The batch studies were performed as one-factor-at-a-time experiment. Firstly, 1 g of adsorbent was added to the leaching solution of 100 mL, and was mixed by stirring at 200 rpm in a shaking incubator keeping constant working temperature. An aliquot of the solution was withdrawn at the pre-determined time intervals, and was filtered. The Cu (II) concentration in the filtrate was subsequently determined by using the atomic absorption spectrophotometer (UNICAM model 929). Final concentration of Cu (II) was measured for the calculation of heavy metal removal percentage as shown in the following equation:

$$\%R_{em} = ((C_i - C_e)/C_i) \times 100 \qquad (1)$$

where C_i is the initial concentration of Cu (II) ions in solution (mg L^{-1}), and C_e is the final concentration of Cu (II) ions in solution (mg L^{-1}), V is the volume of the solution (L) and W is mass of adsorbate (g). The adsorption capacity qt (mg g^{-1}) at any time was calculated using a mass balance equation as shown in the following equation:

$$q_e = \frac{C_i - C_e}{W} V \qquad (2)$$

The adsorption tests were continued until the equilibrium concentration was reached. The effects of initial pH, adsorbent dosage and contact time on the amount of Cu (II) adsorbed were investigated.

Results and discussion

Effect of leachate pH

In order to investigate the effect of pH on Cu (II) adsorption with expanded perlite, aqueous solutions of industrial leachate of 100 mL and expanded perlite content of 1.0 g were used at pH ranging from 2 to 8. Contact time was used to be 2 h at 200 rpm.

Fig. 1. shows the effect of pH on the removal of Cu (II) onto expanded perlite from aqueous solutions of industrial leachate. The maximum percent removal of Cu (II) were observed at pH 6. The adsorption of Cu(II) on expanded perlite increased slowly at the pH range of 2 to 5 due to the competition between H^+ and Cu^{2+} for the same sites on the expanded perlite surface. Then, pH was increased abruptly at pH 5 to 7, and finally reached the maximum and remained constant at pH>6. In this study, optimum pH value for Cu (II) removal was found as 7. At higher pH, Cu (II) precipitated as their hydroxides which decreased the rate of adsorption and subsequently the percent removal of metal ions.

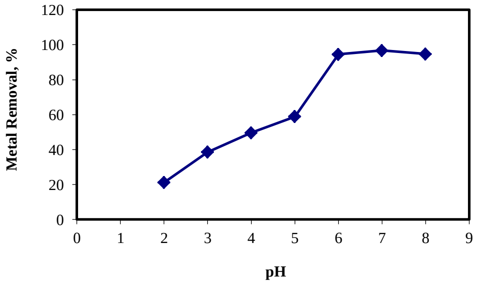

Fig. 1. Effect of pH for the removal of Cu (II) on expanded perlite

Effect of expanded perlite dose

Adsorbent dose is a significant parameter due to it determines the capacity of an adsorbent for a given initial concentration of the adsorbate. In order to determine the optimum expanded perlite dose, batch equilibrium tests were conducted adding various amount of expanded perlite to each flask containing industrial leachate of 100 mL. Contact time was used to be 2 h at 200 rpm.

Fig. 4. shows the effect of expanded perlite dose on the removal of Cu (II) ions. As seen in Fig. 4, increasing the adsorbent dose resulted in an increase in the Cu(II) % removal due to the greater availability of active sites on the surface of the adsorbent. In addition, it could also be noticed that the majority of the tested materials, steady state was reached for an adsorbent dose value between 15 and 25 g/L. Therefore, the optimum adsorbent dose of 15 g/L was selected in all the subsequent experiments.

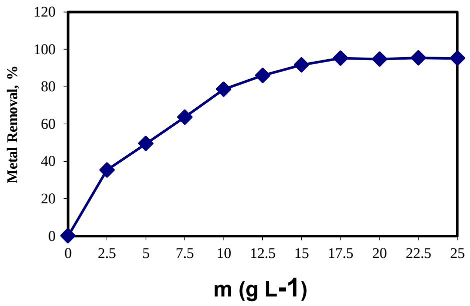

Fig. 4. Effect of dosage for the removal of Cu (II) on expanded perlite

Effect of contact time

The effect of contact time on Cu (II) adsorption with expanded perlite was also evaluated. In the experiments, optimum values of pH and expanded perlite dose were used for the experiments. The effect of contact time is shown in Fig. 5. By increasing contact time, an increase in the Cu(II) removal was obtained. In the study, the quick initial rate of adsorption during the first few minutes of contact was followed by a slower one, until equilibrium state was reached. This was due to the existence of abundant vacant active sites, whereas as adsorption continued a progressive saturation of these active sites with time occurred (Pellera et al., 2012). In addition, the required time to reach equilibrium was about 30 min, since an increase of contact time to 30 min did not have any significant effects. Therefore, the rest of the experiments maintained at 30 min contact time.

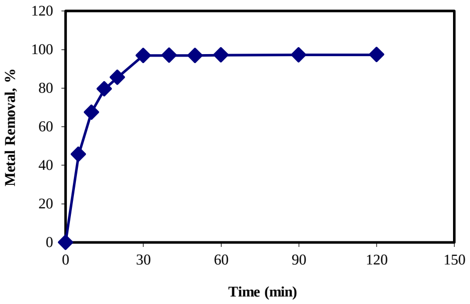

Fig. 5. Effect of contact time for the removal of Cu (II) on expanded perlite

Kinetic studies

Kinetic models can be helpful to understand the mechanism of metal adsorption and evaluate performance of the adsorbents for metal removal. A number of kinetic models have been developed to describe the kinetics of heavy metal removal. In this study, pseudo-second-order kinetic, Elovich kinetic and intraparticle diffusion kinetic models was used for the batch sorption of Cu (II) ions with the expanded perlite.

Adsorption data was evaluated according to the pseudo second order kinetic proposed by Ho (2004):

$$\frac{\mathrm{d}q_\mathrm{t}}{\mathrm{d}t} = k_2 (q_\mathrm{e} - q_\mathrm{t})^2 \qquad (3)$$

where q_e and q_t are the amount of heavy metal (mg g^{-1}) adsorbed at equilibrium time and time t (d) and k_2 is the second order reaction constant (g $mg^{-1}min^{-1}$), respectively. If Eq. (3) is integrated, the following expression is obtained:

$$\frac{1}{q_e - q_t} = k_2\, t + C_2 \qquad (4)$$

In Eq (4), C_2 is the integration constant of the second order reaction kinetic. With on algorithmic arrangement, the following statement is formed:

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

A straight line of t/q_t versus t indicates the application of the second order kinetic model (Fig. 4). The values of k_2 were determined from the slope of the plots.

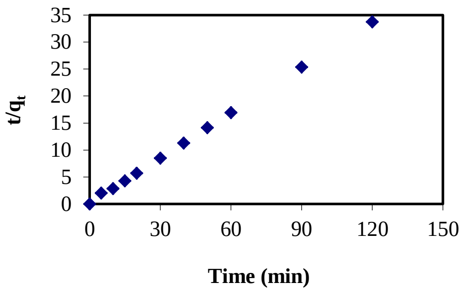

Fig. 4. Pseudo-second order reaction kinetics for the adsorption of Cu (II)

The Elovich equation is expressed as follows (Low, 1960):

$$\frac{\mathrm{d}q_t}{\mathrm{d}t} = \alpha \exp\,(\text{-}\beta\, q_t) \qquad (6)$$

where α is the initial adsorption rate (mg g^{-1} min^{-1}) and β is the desorption constant (g mg^{-1}). To simplify the Elovich equation, Chien and Clayton (1980) assumed $\alpha\ \beta_t >>1$ and by applying the boundary conditions q_t=0 at t=0 and q_t= q_t at t=t Eq (11) becomes (Sparks, 1999):

$$q_t = \frac{1}{\beta}\ln(\alpha\,\beta) + \frac{1}{\beta}\ln t \qquad (7)$$

A straight line plot of q_t versus ln t indicates the application of Elovich model (Fig. 5). The values of constants can be obtained from the slope and intercept of the plots.

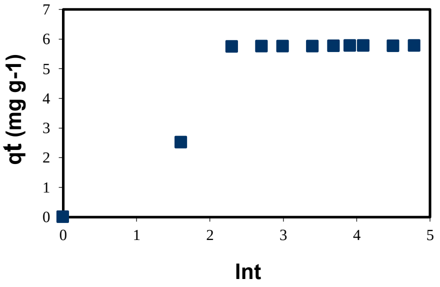

Fig. 8. Elovich kinetics for the adsorption of Cu (II)

The adsorbate transport from the solution phase to the surface of the adsorbent particles occurs in several steps. Generally, a process is diffusion controlled if its rate is dependent upon rate at which components diffuse towards one another. The possibility of intra-particle diffusion was explored by using the intra-particle diffusion model as (Allen et al., 1989; Srihari and Das, 2008):

$$q_t = K_{id}\, t^{1/2} + C \qquad (8)$$

where K_{id} is the intra-particle diffusion rate constant (mg g^{-1} $min^{-1/2}$) and C is the intercept. Values of C give an idea about thickness of the boundary layer, i.e., the larger intercept the greater is the boundary layer effect (El-Ashtoukhy et al., 2008; Kanan and Sundaram, 2001).

A plot of q_t versus $t^{1/2}$ indicates the application of the intra-particle diffusion model. The values of K_{id} were determined from the slope of the plots. If the plot of q_t versus $t^{1/2}$ gives a straight line, then the sorption process is controlled by intra-particle diffusion only. However, if the data exhibit multi-linear plots, then two or more steps influence the sorption process. The first sharper portion is external surface adsorption or instantaneous adsorption stage. The second portion is the gradual adsorption stage, where the intra-particle diffusion is rate-controlled. The third portion is the final equilibrium stage, where the intra-particle diffusion starts to slow down due to the extremely low solute concentration in solution (Wang and Ariyanto, 2007; Chiou and Chuang, 2006). Fig. 6 presents the plots of mass of Cu (II) ions adsorbed per unit mass of adsorbent versus $t^{1/2}$. In this study, the data points are related by two straight lines.

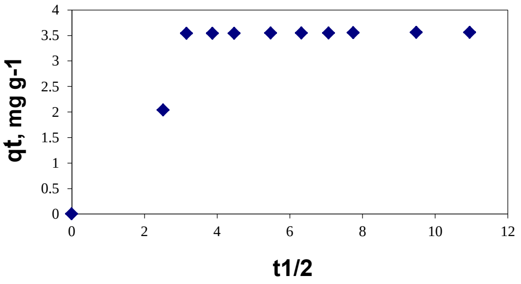

Fig. 6. Intra-particle diffusion kinetics for the adsorption of Cu (II)

The kinetic parameters of Cu (II) and Zn (II) ions onto natural zeolite were calculated from these plots and are given in Table 3. It can be seen in Table 3, the values of correlation factor R^2 obtained from the plots of pseudo-second order kinetics given in Figure 4 are greater than that of the Elovich and intra-particle diffusion kinetic models. Moreover, the calculated q_e values are agree with experimental q_e values for the pseudo-second order kinetic model. This is probable that it is fitted the pseudo second order kinetic model.

Table 3. Adsorption kinetic parameters of Cu (II) onto expanded perlite

Kinetic equation and parameter	
Second-order kinetic equation	
k_2 (g mg^{-1} min^{-1})	0.5838
q_2 (mg g^{-1})	3.5765
R^2	0.9998
Elovich equation	
α (mg g^{-1} min^{-1})	3.7199
β (g mg^{-1})	0.8603
R^2	0.7249
Intra-particle diffusion equation	
K_{id} (mg g^{-1} min$^{-1/2}$)	0.2394
R_2^2	0.4668

Conclusions

In this study, the removal of Cu (II) from industrial waste leachate by batch adsorption technique was investigated. It was found that expanded perlite can be used successfully as an adsorbent for the removal of Cu (II) from industrial leachate. The percentage of Cu (II) removal increased with an increase in the expanded perlite concentration. The pseudo second order kinetic model agrees very well with the dynamical behavior for the adsorption of Cu (II) from industrial waste leachate onto expanded perlite. The results showed that expanded perlite is a potential adsorbent for the removal of Cu (II) from the leachate.

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