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Removal of copper from copper-contaminated river water and aqueous solutions using *Methylobacterium extorquens* modified Erzurum clayey soil

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Abstract: The objective of this study was to investigate the possibility of using natural and bacteria-modified Erzurum clayey soil with *Methylobacterium extorquens* as an alternative to high cost commercial adsorbent materials for the removal of copper from aqueous solution. The copper concentrations in the samples of the polluted river water and $CuCl_2$ solutions treated by the natural and bacteria-modified Erzurum clayey soil (ECS) have been determined by spectrophotometric method. Firstly, the surface of ECS was modified with *M. extorquens* and surface functionality was increased. Then, the adsorption of Cu (II) from solution phases was studied with respect to varying metal concentration, pH, and temperature and agitation time. The maximum adsorption of Cu (II) for natural and bacteria-modified Erzurum clayey soil was observed at pH: 5.0. At different copper concentrations, copper adsorption analysis was performed on 1 g using clay soil or modified clay soil. Maximum adsorption of Cu (II) was obtained as 45.7 and 48.1 mg g^{-1} at initial concentration (50 mg/50 mL) and optimal conditions by natural and bacteria-modified clay soil, respectively. The copper concentration was decreased in the substantial amount of the leachates solutions of natural and bacteria-modified clay soil. Langmuir and Freundlich isotherms were used to describe the adsorption behavior of Cu (II) ions. The results showed that modified clay soil had a high level of adsorption capacity for copper ion. The various thermodynamic parameters such as $\Delta G°$, $\Delta H°$ and $\Delta S°$ were analyzed to observe the nature of adsorption. The structural properties of the natural and bacteria-modified-ECS have been characterized by SEM, FTIR and XRD techniques. Consequently, it was concluded that the bacteria--modified clay soil could be successfully used for the removal of the copper ions from the aqueous solutions.

Introduction

Nowadays industrialization and urbanization in the world have led to an increase in ecological problems. Heavy metal pollution has become a serious threat for environment and it is non-biodegradable (Benaissa and Elouchdi 2007). Various toxic heavy metal ions discharged through different industrial activities constitute one of the major causes of water pollution. Heavy metal residues in contaminated habitats may accumulate in microorganisms, aquatic flora and fauna, which in turn, may enter the human food chain and result in health problems (Bhatnagara, et al. 2010)

Copper is known to be one of heavy metals and is widely used in many industries including metal cleaning and plating baths, paints and pigments, fertilizer, paper board, wood pulp, printed board circuit production, etc. (Aksu and Isoglu 2005, Zhu et al. 2009). The higher concentration of copper will cause

severe mucosal irritation and corrosion, widespread capillary damage, hepatic and renal damage, and central nervous system irritation followed by depression (Ahmad et al. 2009).

Copper metal ions are especially discharged from the industrial waste streams of metal cleaning and plating baths, pulp, paper, paperboard and wood, preservative-employing mills, the fertilizer industry, etc. Although copper is an essential metal for human life and health, it is potentially toxic like all heavy metals (Sarioglu et al. 2009, Ibrahim et al. 2009, Jaman et al. 2009). Copper ions are limited for environmental pollution, but the waste produced by copper-based industries with various toxic elements can pollute the environment (Nohut, et al. 1999, Nadaroglu, et al. 2010, Kalkan et al. 2012, Nadaroglu and Kalkan 2012).

In the water treatment process, adsorption process method is chosen using the low-cost adsorbents in the removal of heavy metal. This process has more techno-economic

and environmental advantages such as cheapness, easy obtainability, efficiency of adsorption, and environmental friendliness associated with low-cost adsorbents than other water treatment techniques. Some low cost adsorbents have been investigated including modified clays (Bhattacharyya and Gupta 2008). But most of these investigated adsorbents did not support the expected efficiency of pollutant removal in terms of technicality, low stability, low mechanical strength, non-durability, and/or poor re-usability, thus limiting their potential for applications (Nadaroglu, et al. 2014, Wang et al. 2012, Kakitani et al. 2009, Sahan et al. 2010, Chen et al. 2011, Sarioglu et al. 2005). The aforementioned factors have led to the search for more efficient and lower cost adsorbents.

Among previously used removal techniques, adsorption process has been found as one of the most promising technologies in water pollution control in terms of cost, simplicity of design and operation. Activated carbon has undoubtedly been the most popular and widely used adsorbent in wastewater treatment applications throughout the world (Bansal and Goyal 2005) and has been successfully utilized for the removal of diverse types of pollutants including metal ions. However, the high capital and regeneration cost of the activated carbon limits its large-scale applications for the removal of metals and other aquatic pollutants, which have encouraged researchers to look for low-cost alternative adsorbents (Dias et al. 2007).

Clay geological materials are low cost and readily available materials functioning as excellent cation exchangers, and have often been used in adsorption and catalysis. They play an important role in the environment acting as natural scavengers of pollutants through ion exchange or adsorption. Erzurum clayey soil is a natural material which is abundant in nature. It can be obtained directly from nature, and it can be used without any processing. For this reason Erzurum clayey soil is cheaper than other adsorbents (Kalkan and Yarbası 2013).

Synergistic combinations of clays and microorganisms (both of them are low cost adsorbents) have attracted much attention because of their growing properties. These synergistic combinations may gain better sorbent properties such as high cation exchange capacity, bleeding reduction, enhanced mechanical strength, increased pore size, and consequently higher adsorption efficiency, better stability and durability, re-usability, sometimes larger surface area, and even comparatively lower cost for water treatment.

The aim of this study was to examine the efficiency of natural and modified-ECS as adsorbent for the removal of copper ions from aqueous solutions. We wanted to determine whether this material might be cost-effective and be an alternative adsorbent that could replace the expensive resins now used for wastewater treatment. Erzurum clay soil was modified with *M. extorquens* and bacteria-modified ECS was carried out in this study in order to ascertain the above. The bacteria-modified sorbent obtained was tested for the removal of Cu (II), ions from aqueous solutions.

Materials and method

Bacterial strains, culture conditions, media and treatments

M. extorquens bacteria have the ability to produce bioplastics using different carbon sources. The general structure of bioplastics is polyhydroxyalkanoates (PHA). Thus, Erzurum

clayey soil surface which is used as a sorbent was made rougher for adsorption. For this reason, *M. extorquens* bacteria were selected and the sorbent surface was modified by Erzurum clayey *M. extorquens* bacteria (Jan et al.1996). *M. extorquens* was grown on Nutrient Agar (NA) for routine use, and maintained in Nutrient Broth (NB) with 15% glycerol at – 80°C for long-term storage. For each experiment, a single colony was transferred to 500 mL flasks containing NB, and grown aerobically in flasks on a rotating shaker (150 rpm) for 48 h at 27°C (Merck KGaA, Germany). *M. extorquens* suspension was then diluted in sterile distilled water to a final concentration of 10^8 CFU/mL, and the resulting suspensions were used to modify the Erzurum clayey soil.

Adsorbent

In this study, the ECS was used as adsorbent to remove copper ions from aqueous solutions. It was supplied from the clay deposits of Horasan Formation of Pasinler Basin. This basin lies at approximately 50 km East of Erzurum, NE Turkey.

Adsorbent characterization

The chemical and mineralogical compositions of ECS were determined by X-ray powder diffraction (XRD) using Philips PW 1010/80 diffractometer with graphite-filtered CuKα radiation. Furthermore, the pH values were determined with a pH meter (Thermo scientific Orion 5 star plus multifunction). The scanning electron microscope (SEM) was used to examine the surface of the adsorbent. Images of native adsorbent and metal loaded adsorbent were magnified 5000 times by SEM modeled JEOL JSM-6400 SEM. Before SEM examinations, the sample surfaces were coated with a thin layer (20 nm) of gold to obtain a conductive surface and to avoid electrostatic charging during examination. In addition, the Fourier Transform Infrared Spectroscopy (FTIR) analyses were carried out to identify functional groups and molecular structure in the adsorbent and copper loaded adsorbent. FTIR spectra were recorded using Perkin-a Perkin-Elmer GX 2000 FTIR spectrometer. The spectrum of the adsorbent was measured within the range of 4000–700 cm^{-1} wave number.

Adsorbent preparation

The ECS was thoroughly washed with distilled water until it became neutral. The suspension was wet sieved through a 200 mesh screen. A little amount of the suspension remained on the sieve and was discarded. The solid fraction was washed five times with distilled water following the sequence of mixing, settling, and decanting. The last suspension was filtered, and the residual solid was then dried at 105°C, ground in a mortar, and sieved through a 200 mesh sieve. 1 g of this ECS sample was shaken with 10^8 CFU/mL *M. extorquens* solution for approximately 1 h, and then the separated particles were stored. The ECS and bacteria-modified ECS were used in the study.

Adsorption of copper ion on the natural and modified ECS

For studying metal adsorption, 1 g of ECS as adsorbent was taken and it was then suspended in 50 mL $CuCl_2$ at 1 mg/mL concentration, at pH between 2.0 and 9.0 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. At each pH, it was waited on for a term of 1 h. Also, the same experiment was performed at varying temperatures in the 20–80 range. The suspensions of samples were centrifuged at 5000 rpm for 10 min, and the supernatant was filtered through a 0.45 µm pore, cellulosic membrane filter to make possible the measurement of the heavy metal concentration in the filtrate. After centrifuging, the amount of decreasing copper at the top level of liquid solution was measured. The copper ion concentration was determined by spectrophotometric method using 1-amino-2-hydroxy-4-naphthalenesulfonic acid (Seifullina and Skorokhod 1991). The amount of copper ions adsorbed was calculated as:

$$q_e = (C_o + C_e)V / m \qquad (1)$$

where q_e (mg/g) is the amount of adsorbed copper ions, C_o (mg/L) is the initial concentration of copper, C_e (mg/L) is the concentrations of copper at equilibrium, V (L) is the volume of solution, and m (g) is the weight of ECS adsorbent. The same procedure was done by using bacteria-modified ECS.

Results and discussion

Adsorbent properties

The X-ray diffraction (XRD) pattern of the ECS is shown in Fig. 1. The XRD results show that the dominant clay mineral is smectite and the other non-clay minerals are quartz, calsite and feldispare. Its chemical composition consists of Al_2O_3, Fe_2O_3, $CaCO_3$, CaO, MgO, SiO_2 and SO_3 (Table 1). The engineering properties of ECS have been determined by laboratory experiments and the results have been summarized in Table 1. It is over-consolidated and it has clayey-rock characteristics in natural conditions. It is defined as a high plasticity soil according to the Unified Soil Classification System. The ECS includes some fossils such as *Dreissensia sp., Gastropoda sp. and Congeria sp* (Kalkan and Bayraktutan 2008).

Effect of contact time

The effect of contact time on the adsorption process is illustrated in Fig. 2. It can be observed that the removal of copper increases with time in the first 180 and 30 min for natural and bacteria-modified ECS, respectively. It was
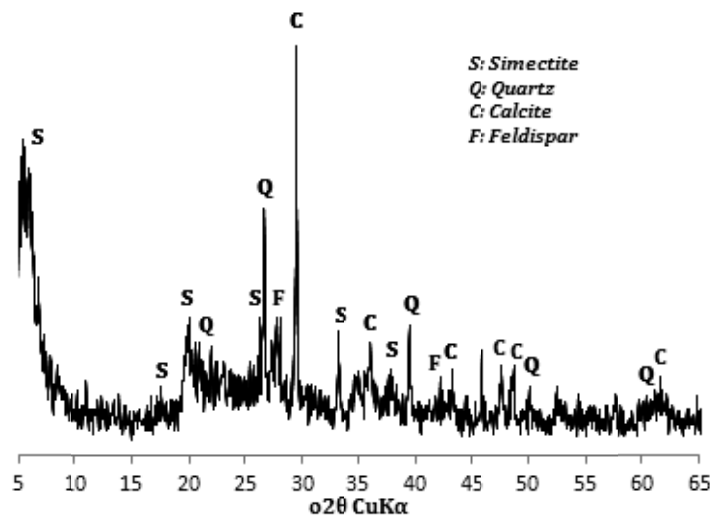

Fig. 1. XRD pattern for ECS sample used in this study

Table 1. Chemical and Engineering compositions and properties of ECS used in the study

Property Compound	ECS	Density	ESC
Al_2O_3, %	10.32	Density, (mg/m³)	2.57
Fe_2O_3, %	6.89	*Grain size*	
CaO_3, %	2.75	Sand (2000–75 mm), %	26.5
CaO, %	13.65	Silt (2–75 mm), %	8.2
MgO, %	2.54	Clay (<2 mm), %	65.3
SiO_2, %	48.71	*Atterberg limits*	
SO_3, %	0.07	Liquid limit, %	84.4
Heat loss, %	15.5	Plastic limit, %	35.5
		Plasticity index, %	48.9
		Adsorption	
		Water absorption, ml/100 g	34.28
		Specific surface area	
		Specific surface area, m²/g	36.2

observed from Fig. 2 that the copper removal increases during the contact time. After that point there was no considerable change in copper removal recovery. This indicates that clay modification by bacteria provides rapid removal of copper ions. It is clearly shown that the amount of copper removal is higher in the beginning. This is probably due to a larger surface area of the ECS being available in the beginning for the adsorption of copper ions. As the surface adsorption sites become exhausted, the uptake rate is controlled by the rate at which the adsorbate is transported from the exterior to the interior sites of the adsorbent particles (Kalkan and Bayraktutan 2008, Kumar et al. 2011). This result is important, as equilibrium time is one of the important parameters for selecting a wastewater treatment system, when the time consumed for wastewater disposal should be considered. The rapid removal of the adsorbate has significant practical importance as it will facilitate smaller reactor volumes ensuring efficiency and economy (Aksu 2001, Dhabab 2011).

Effect of pH

The pH of the aqueous solution is an important operational parameter in the adsorption process because it affects the solubility of the metal ions, concentration of the counter ions on the functional groups of the adsorbent and the degree of ionization of the 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 (Ghazy and Ragab 2007, Onundi et al. 2010). In order to establish the effect of pH on the adsorption of copper ions, the batch equilibrium studies at different pH values in the range of 3–6 have been carried out. The effect of initial pH on the adsorption process is presented in Fig. 3. It is shown that the absorption amount of copper increases with increasing pH and maximum adsorption of copper ions are obtained at pH 5 which is the initial pH of the solution for natural and bacteria-modified ECS. This is due to the surface complexation reactions, which are mostly influenced by the
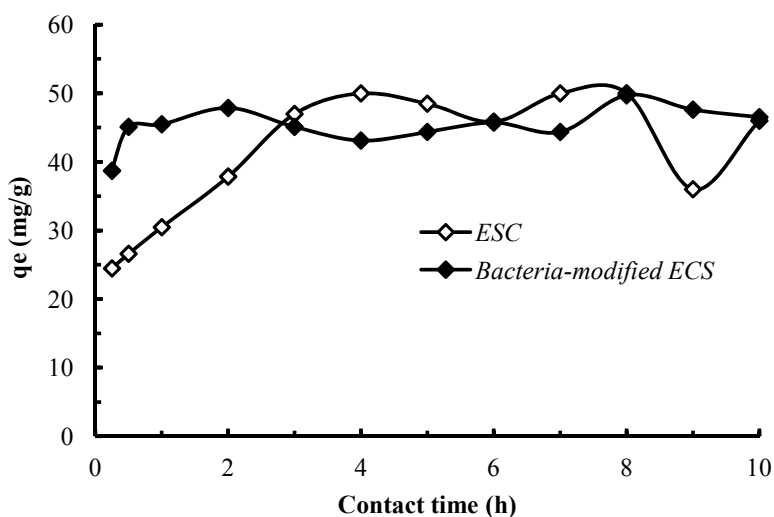
Fig. 2. Removal of copper as a function of equilibrium time (pH: 5.5, initial copper concentration: 1 mg/mL, adsorbent dose: 1 g/50 mL, agitation speed: 500 rpm and temperature: 30±1°C)
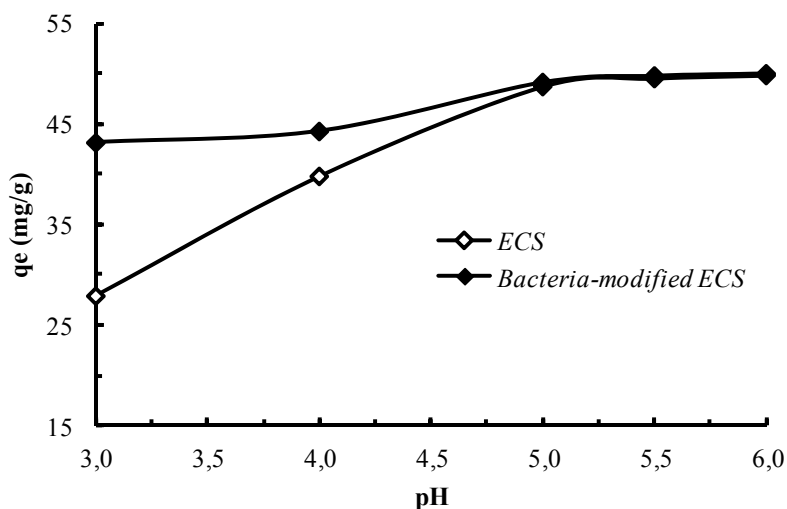
Fig. 3. Effect of copper as a function of pH (initial copper concentration: 1 mg/mL, adsorbent dose: 1 g/50 mL, agitation speed: 500 rpm and temperature: 30±1°C)

electrostatic force of attraction between copper and the surface of the adsorbent. The acidity of the medium can affect the metal ions uptake amount of the natural and bacteria-modified ECS adsorbent because hydrogen ions in the solution could compete with copper on the adsorbents surface (Rashad et al. 2011).

The removal of metal ions from aqueous solution by adsorption is highly dependent on the pH of the solution since this affects the surface charge of the adsorbent and the degree of ionization and speciation of the adsorbate (Bansal et al. 2009, Najua et al. 2008). From the results it was shown that the pH of the solution played a very important role in the metal uptake. The adsorbent surface metal binding sites as well as metal chemistry in solution were influenced by solution pH. It is to be expected that with increase in pH values, more and more ligands having negative charge would be exposed which results in the increase in attraction of positively charged metal ions (Sekher et al. 1998). In low pH value, binding sites are generally protonated or positively charged (by the hydronium ions). Thus, repulsion occurs between the metal cation and the adsorbent at a higher pH value, binding sites start deprotonating and make different function groups available for metal binding. In general, cation binding increases as pH increases (Dhabab 2011, Yang et al. 2016). *Burkholderia sp.* Z-90 has the ability to adsorb maximum Cu at pH 5 which is similar to our results and similar to the results of Quan et al., and adsorption occurs at pH ranges from 3–6. This pH range is widely accepted as being optimal for metal uptake of almost all types of adsorbent (Quan et al. 2013, Elouear et al. 2008).

Effect of temperature
Temperature is known to have a profound effect on various chemical processes. Temperature affects the adsorption rate by altering the molecular interactions and the solubility of the adsorbate (Quan et al. 2013). The effect of temperature influencing the adsorption has been studied in the range of 20–80°C. The effect of temperature on the adsorption capacity of natural and bacteria-modified ECS is shown in Fig. 4. It is observed that the degree of adsorption increases with increasing temperature and the maximum adsorption of copper

ions is obtained at 40 and 30°C, which is the temperature of the solution for the natural and bacteria-modified ECS. The results in Fig. 4 show that the temperature did not have a significant effect on the Cu(II) biosorptions. Therefore, the process responsible for biosorption in this case seems to be largely physico-chemical in nature (Wang et al. 2005).

Effect of initial metal ion concentration
The variation in the amount of metal ion bound to the natural and bacteria-modified ECS with increasing initial metal ion concentration is illustrated in Fig. 5. The plot showing the effect of initial concentration on the adsorption of copper ions indicates that the total copper ions adsorbed by ECS slightly increased up to the end of the run and the total copper ions adsorbed by bacteria-modified ECS increased sharply in the beginning and then slowly towards the end of the run. When the initial copper ion concentration was increased from 1 to 10, the amount of removed metal ions increased from 41.5 to 150.64 mg/g for the native ECS. Also, when copper ion concentration was increased from 1 to 7, the amount of removed metal ions increased from 61.5 to 226.5 mg/g for the bacteria-modified ECS. This indicates that bacteria-modified ECS increases the amount of copper removal from aqueous solutions. The initial faster rate of removal of the metal ion could be due to the availability of the uncovered surface area of the adsorbents, since adsorption kinetics depends on the surface area of the adsorbent (Qadeer and Akhtar 2005). This trend is that of the result of the progressive increase in the electrostatic interaction between the copper ions and the adsorbent active regions. Moreover, this can be explained by the fact that more adsorption sites were being covered as the copper ions concentration increased (Kumar et al. 2011, Gupta et al. 2003). These could also be explained in terms of the progressive increase in the electrostatic interaction between the metal ion and the absorbent active regions, moreover, more adsorption sites were being covered as the metal ions concentration increased (Laraous et al. 2005). Besides, higher initial concentrations led to an increase in the affinity of the metal ion towards the active sites (Al-Asheh and Banat 2001).
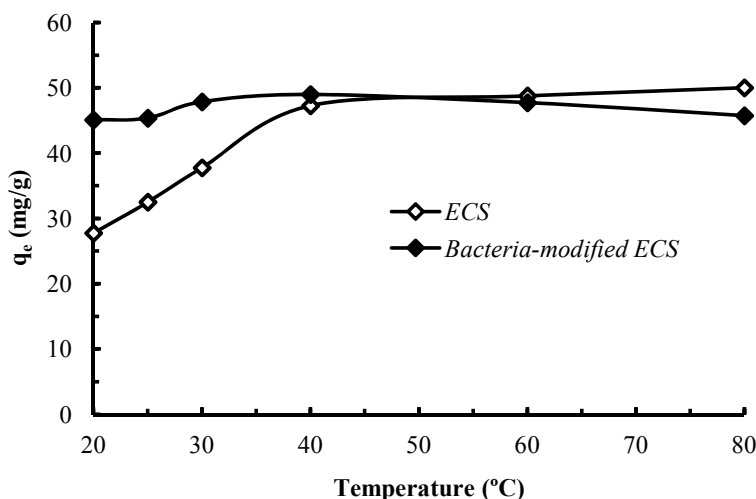

Fig. 4. Effect of temperature on the copper removal (pH: 5.0, initial copper concentration: 1 mg/mL, adsorbent dose: 1g/50 mL, agitation speed: 500 rpm, contact time 90 min)

Effect of adsorbent dosage

The dosage study is an important parameter in the adsorption studies because it determines the capacity of an adsorbent or a given initial concentration of metal in solution. A graph was plotted between the different dosages of adsorbent natural and bacteria-modified ECS, and the amount of copper removal. The effect of adsorbent dosages was studied by varying the sorbent amounts from 0.5 to 3 mg/mL (Fig. 6). The amount of metal ions removal increases from 14.2 to 43.6 and from 25.2 to 45.2 mg/g as the adsorbent dosage increases from 0.5 to 1, and from 0.5 to 1 mg/mL for the natural and bacteria-modified ECS, respectively. It is seen that more copper ions are removed by bacteria-modified ECS for the same dosage. This indicates that adsorption increased with increasing natural and bacteria--modified ECS up to a certain value and then became almost constant. The results showed that the removal of copper ions increased rapidly with increase in the amount of natural and bacteria-modified ECS due to greater availability of the surface area at higher concentration of the adsorbent (Kumar et al. 2011, Nadaroglu and Kalkan 2014). This is because an increase in biomass concentration generally results in an increase in the surface area of the biosorbent with bacteria immobilized. The increase in adsorption with increase in adsorbent dosage is attributed to the availability of larger surface area and more adsorption sites. At a very low adsorbent concentration, the adsorbent surface becomes highly saturated with the metal ions and the residual metal ion concentration in the solution. It is plausible to suggest that with higher dosage of adsorbent there would be greater availability of exchangeable sites for metal ions as noted by Najua et al. (Najua et al. 2008). Moreover, the high adsorbent dosage could impose a screening effect on the dense outer layer of the cells, thereby shielding the binding sites from metals (Pons and Fuste 1993).

The copper concentration in the aqueous solution taken from samples of polluted river water solution treated with ECS and bacteria-modified ECS indicates that these
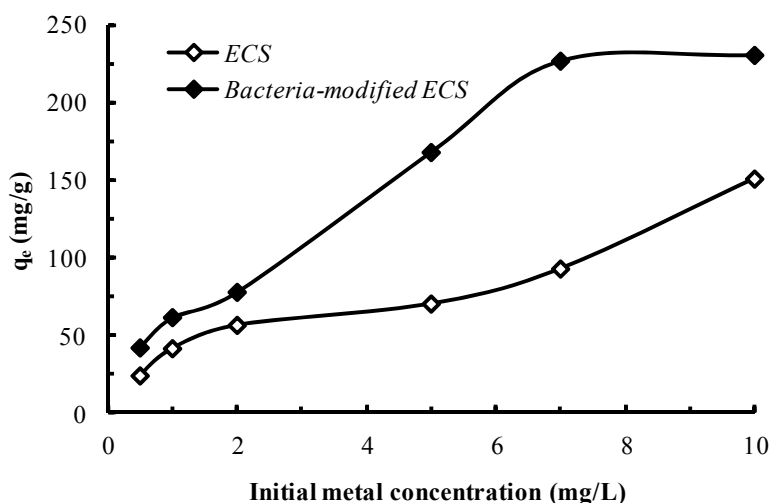

Fig. 5. Effect of initial metal ion concentration on the copper removal: 1 mg/ mL, adsorbent dose: 1g/50 mL, agitation speed: 500 rpm and temperature: 30±1°C)
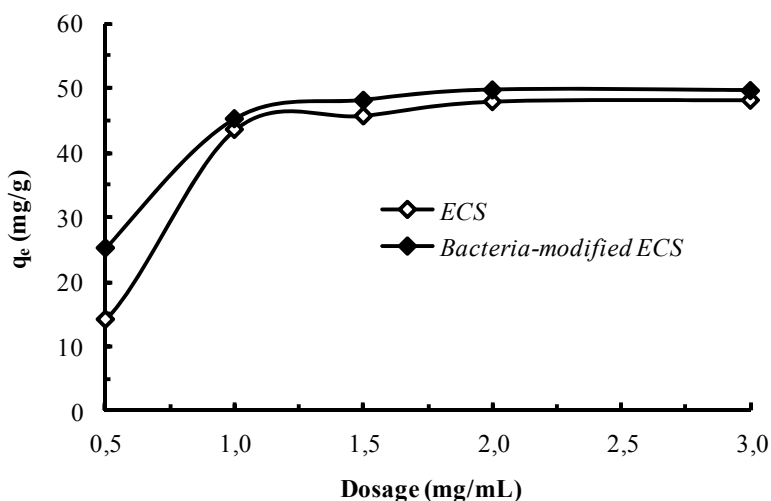

Fig. 6. Effect of adsorbent dosage on the copper removal (pH: 5.0, initial copper concentration: 1 mg/mL, agitation speed: 500 rpm, contact time 60 min)

absorbents enhanced adsorption capacity. Without the addition of the adsorbents, the leachate copper concentration had approximately 1.262 and 11.742 mg/mL for polluted river water and CuCl$_2$ solutions, respectively. The addition of ECS and bacteria-modified ECS strongly inhibited the leaching of copper in both solutions. When the ECS and bacteria-modified ECS are added to the aqueous solutions contaminated with copper, the concentration of copper in the leachate drastically decreases, whereas the adsorption capacity increases. It is seen from Fig. 7 that the copper concentration in the samples of ECS and bacteria-modified ECS treated leachates solution of polluted river water decreases from 1.262 to 0.456 and from 1.262 to 0.120, respectively. Similarly, the copper concentration in the samples of ECS and bacteria-modified ECS treated leachates solution of CuCl$_2$ solution decreases from 11.742 to 4.115 and from 11.742 to 0.860, respectively. It is seen that the bacteria-modified ECS adsorbent has a high level of adsorption capacity for copper ions more than the ECS (Fig. 7).

SEM study on adsorbed surface

The SEM enables the direct observation of the surface microstructures of different adsorbents (Onundi et al. 2010). Images of native adsorbent (Fig. 8A) and metal loaded adsorbent (Fig. 8B and 8C) were magnified 1000 times. SEM was used to examine the surface of the adsorbents. It was observed that there are some cavities on the ESC and bacteria-modified ESC surface, which become larger in size for large size of ESC and bacteria-modified ESC. The above observations showed that the cavities on the ESC and bacteria-modified ESC surface were the active centers, and these centers were attracted to the copper ions for adsorption. Thus the amount of adsorbed equilibrium increased as the particle surface size of ESC and bacteria-modified ESC got larger.

Equilibrium adsorption 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 have been developed to describe adsorption isotherm relationships.

The Langmuir (Langmuir 1918) and Freundlich (Freundlich 1926) equations are the world-widely used models because of their simplicity (Polowczyk et al. 2007). Langmuir adsorption isotherm is often used to describe the maximum adsorption capacity of an adsorbent and it is given as:

$$q_e = q_m K_L C_e / (1 + K_L C_e) \qquad (2)$$

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:

$$C_e/q_e = (1 / K_L q_m) + (C_e / q_m) \qquad (3)$$

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. The 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:

$$q_m = K_F C_e^{1/n} \qquad (4)$$

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:
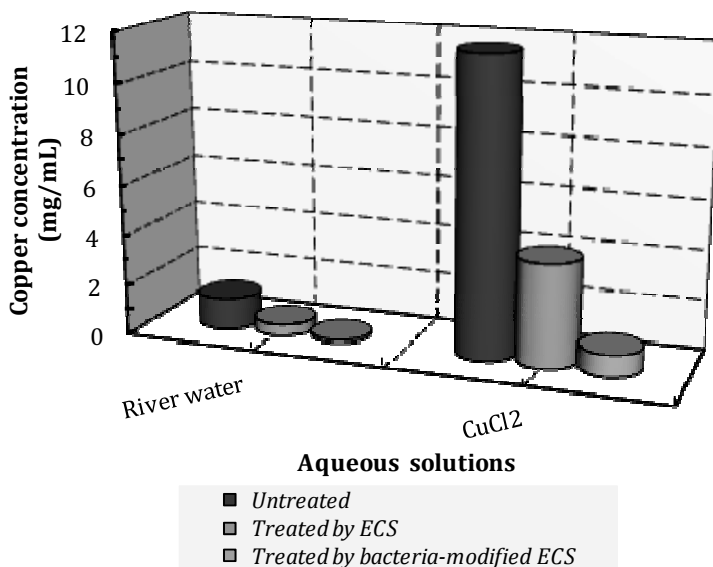

Fig. 7. Variation of copper concentration with natural and bacteria-modified ECS on the river water and CuCl$_2$
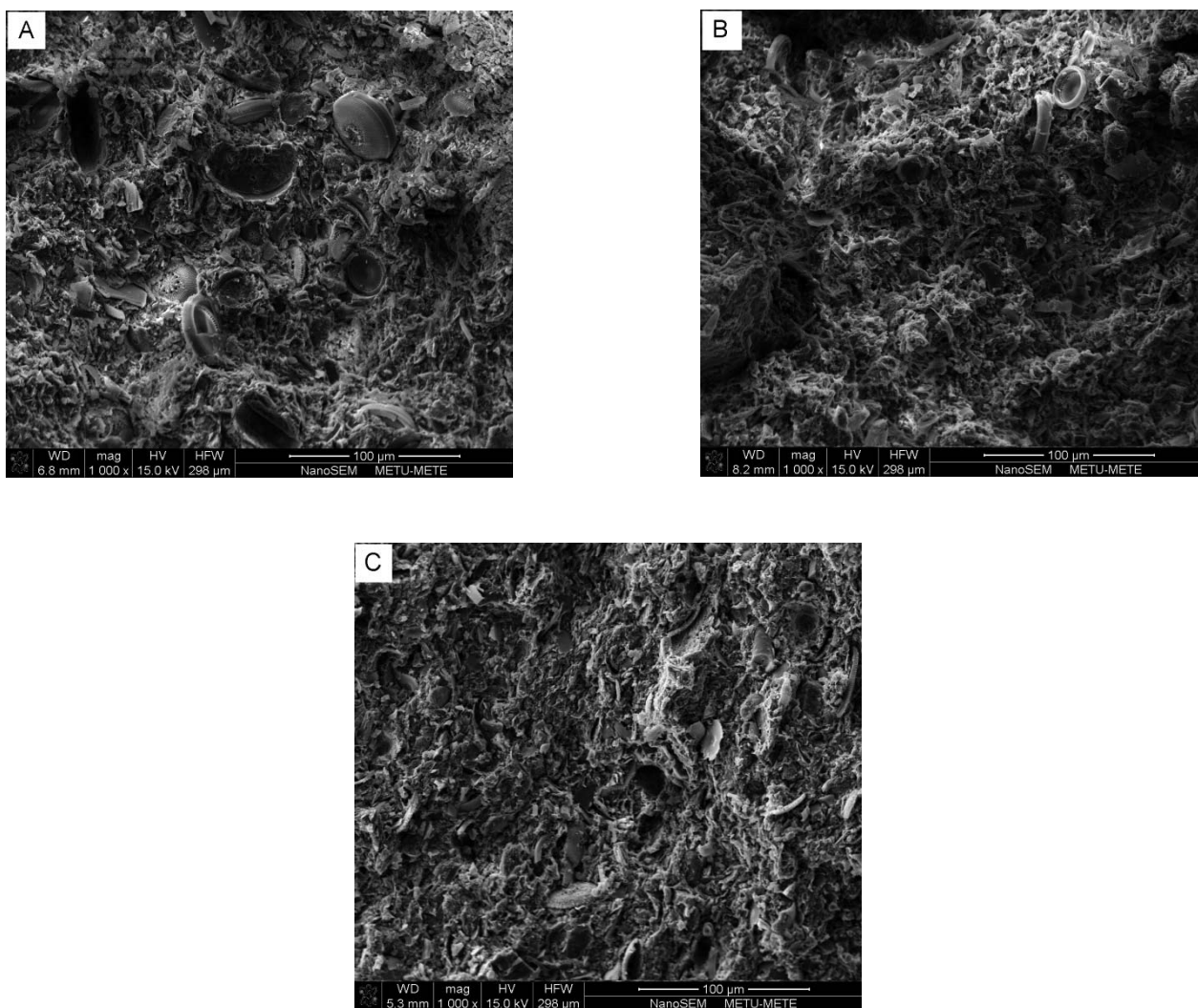
Fig. 8. SEM analysis of copper adsorbed ESC surface A: Before adsorption with copper; B: After adsorption with copper by using ESC; C: After adsorption with copper by using bacteria-modified ESC (pH: 5, temperature: 30±1°C)

$$logq_e = logK_F + 1/n \, logC_e \qquad (5)$$

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.

The Langmuir and Freundlich isotherms were obtained from the experiments. The graphical comparison of the experimental value with the calculated value from the Freundlich and Langmuir isotherms for copper adsorption by natural and bacteria-modified clay are shown in Figs 9 and 10. It is obvious that the adsorption capacities calculated from the Langmuir isotherms are much closer to the experimental values of adsorption capacity than that of Freundlich isotherms. The constants of Freundlich and Langmuir isotherms and correlation coefficients calculated from the adsorption data are given in Table 2. The high correlation coefficients show that both models are suitable for describing the adsorption equilibrium of copper ions. The adsorption capacity of natural and bacteria-modified ECS adsorbent for the uptakes of copper is 79.37 and 93.46 mg/g, respectively (Gangoli et al. 1975, Ramesh et al. 2005, Demirbas et al. 2008, Nadaroglu et al. 2015).

Thermodynamics studies

The sorption capacity of natural and bacteria-modified clay adsorbent increased together with increase in the temperature of the system from 293–313 K. Thermodynamic parameters such as change in free energy (ΔG°) kJ/mol, enthalpy (ΔH°) kJ/ mol, and entropy (ΔS°) J/Kmol were determined using the following equations:

$$KD = Cs / Ce \qquad (6)$$

$$DG° = -RT \, lnKL \qquad (7)$$

$$lnKL = (DS°/R) – (DH° / RT) \qquad (8)$$

where K_L is the equilibrium constant, Cs is the solid phase concentration at equilibrium (mg/L), Ce is the liquid phase concentration at equilibrium (mg/L), T is the temperature in Kelvin, and R is the gas constant.

From the temperature variation from 293 to 313 K on the sorption, ΔH° and ΔS° were obtained (Fig. 11). The $\Delta H_{ads}°$ and $\Delta S_{ads}°$ values obtained from the slope and intercept of Van't Hoff plots are presented in Table 3. Gibbs free energy (ΔG) was calculated as:
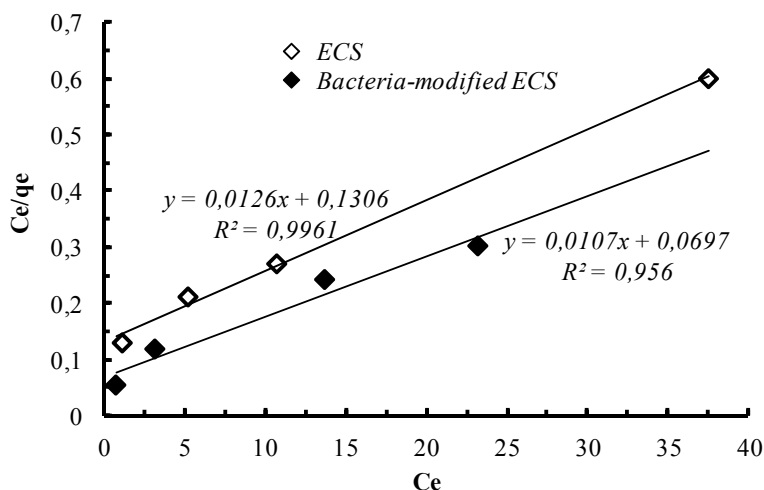
Fig. 9. The Langmuir isotherm for the adsorption of copper by natural and bacteria-modified ECS
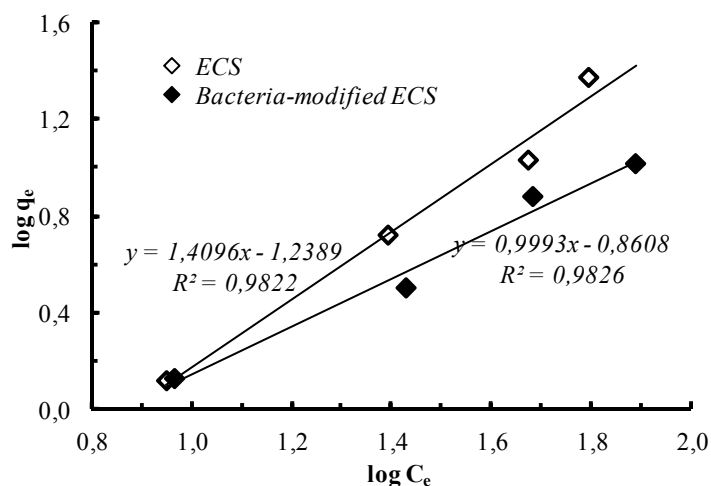

Fig. 10. The Freundlich isotherm for the adsorption of copper by natural and bacteria-modified ECS

Table 2. Values of adsorption isotherm parameters for adsorption of copper

	ECS	Bacteria-modified ECS
Langmuir constant		
Q_M (mg/g)	79.37	93.46
K_L (L/mg)	0.1306	0.00075
R^2	0.9961	0.9560
Freundlich constant		
KF	0.058	0.138
n	0.709	1.000
R^2	0.9822	0.9826

$$\Delta G° = \Delta H° - T\Delta S\text{-}TDS \qquad (9)$$

The values of the thermodynamic parameters for the sorption of Cu (II) on clay soil and modified clay soil adsorbents are given in Table 3.

The Gibbs free energy change (DG°) was calculated to be -0.68, -2.20, -3.72 and -6.76 kJmol^{-1} on ESC and -5.10, -6.36, -7.62 and -10.14 kJmol^{-1} on bacteria-modified ESC for Cu^{2+} adsorption at 293, 298, 303, 313 K, respectively. Negative DG° values which were obtained for Cu^{2+} at each of the temperatures studied indicated the feasibility of the process and spontaneous nature of the adsorption. The DG° values decreased with an increase in temperature, indicating an increased trend in the degree of spontaneity and feasibility
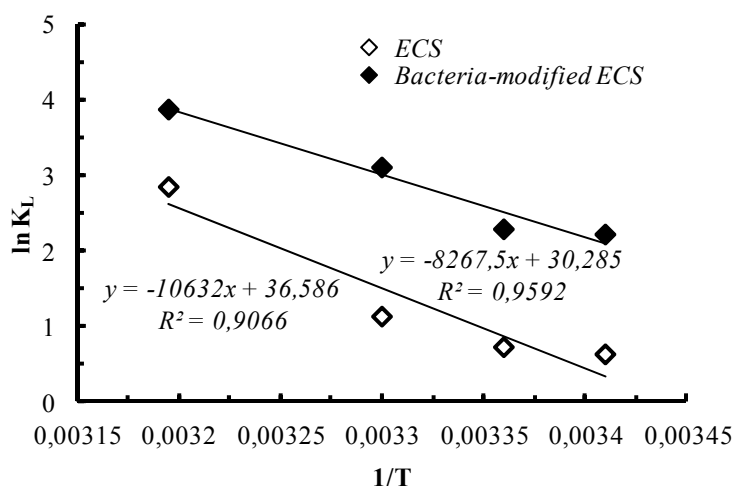
Fig. 11. Influence of temperature on the thermodynamic behavior of adsorption of copper onto natural and bacteria-modified ECS adsorbent

Table 3. Thermodynamic parameters for the adsorption of copper onto ECS and modified ECS adsorbents

	$\Delta H_{ads}°$ (kJmol^{-1})	$\Delta S_{ads}°$ (kJmol^{-1})	$\Delta G_{ads}°$ (kJmol^{-1})			
			293 K	298 K	303 K	313K
ECS	88.39	30.42	-88.25	-89.77	-91.29	94.33
Bacteria-modified ECS	68.74	25.18	-73.09	74.35	75.61	78.13

of Cu^{2+} adsorption. The DH° parameter was found to be 88.39, 68.74 kJ/mol for Cu^{2+} adsorption, on ESC and bacteria--modified ESC, respectively. The positive values of DH◦ further confirmed the endothermic nature of the adsorption process. The heat of adsorption value between 20 and 400 kJ/mol indicates the chemisorption process (Unlu and Ersoz 2007). Hence, the adsorption of Cu^{2+} on clay soil and modified clay soil was chemical in nature. The DS° parameter was found to be 304.2 and 251.8 (J/mol K) for Cu^{2+} adsorption on ESC and bacteria-modified ESC, respectively. The positive values of DS° suggested that the degrees of freedom increased at the solid-liquid interface during the adsorption. During the adsorption process, the coordinated water molecules were displaced by metal cations, resulting in increased randomness in the adsorbent-adsorbate system (Baraka et al. 2007, Li et al. 2011).

Conclusions

In this study, firstly, ECS was converted into an adsorbent, and the suitability of the bacteria-modified ECS with *M. extorquens* for adsorption of copper from the wastewater and standard CuCl$_2$ solutions was investigated. Secondly, optimal adsorption conditions were analyzed. It was observed that the maximum copper removal was at the pH 5.0 for both ECS and the bacteria--modified ECS. The adsorption is too fast at the first 30 min of contact time for the bacteria-modified ECS. The rapid removal of the adsorbate has significant practical importance as it will facilitate smaller reactor volumes ensuring efficiency and economy. It is observed that the degree of adsorption increases

with increasing temperature and maximum adsorption of copper ions are obtained at 30°C which is the temperature of the solution for the bacteria-modified ECS.

Thirdly, isotherm data of Cu^{2+} adsorption on ECS and M-ECS were calculated. Based on the correlation coefficient values, it has been deduced that the Langmuir and Freundlich isotherms are suitable for fitting the experimental findings. The high correlation coefficient showed that the Langmuir and Freundlich adsorption isotherm models are suitable for describing the adsorption equilibrium of copper ions. The adsorption of Cu (II) ions on to ESC and bacteria-modified ESC shows negative DG° values which indicates that sorption process is physisorption. The investigation showed that the ECS and the bacteria-modified ECS are very valuable material for the removal of copper ions from aqueous solutions. In addition, the use of the bacteria-modified ECS for the removal of copper ions from the aqueous solutions can potentially reduce the remediation costs.

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