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Removal of Cu(II) from aqueous solutions using dried activated sludge and dried activated nano-sludge: Adsorption isotherm and kinetics

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Abstract

The aim of this study was to investigate the effectiveness of dried activated sludge (DAS) and dried activated nano-sludge (DANS) for removal of Cu(II). Dried activated sludge and dried activated nano-sludge prepared as a powder, were tested as sorbents for the removal of Cu(II) from aqueous solutions. The effects of various experimental parameters including pH, initial Cu(II) concentration, and mass of sorbent and contact time were examined and optimal experimental conditions were obtained. Bisorption tests confirmed maximum exchange between metal ions and protons at pH about 3.0. Langmuir, Freundlich and Dubinin-Radushkevich were used for the mathematical description of the adsorption equilibrium of the copper onto the both dried activated sludge and dried activated nano-sludge. The results show that Langmuir isotherm represented a better correlation compared to other isotherms.The maximum adsorption capacities were 65.2and 76.92 mg/g for dried activated sludge and dried activated nano-sludge, respectively. It was concluded that dried activated nano-sludge had great potential to remove Cu(II) ions from the aqueous solutions.

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Introduction

The presence of heavy metals in waste and surface waters is an environmental and public health problem. Strict environmental regulations on the discharge of heavy metal ions and rising demand for clean water with extremely low level of heavy metal ions make it greatly important to develop different efficient technologies for heavy metal removal (Roy and Bhattacharya,2012). Cu(II), in particular, is among the most common pollutants found in industrial effluents (Ren *et al.*,2012). Cu is widely used in various industrial activities such as metal plating, mining, tannering and vehicle industry. These applications have introduced Cu into aquatic ecosystems, which cause serious environmental pollution problems and bring harmful effect to living organisms (Khan *et al.*,2008). Long term exposure of copper can cause irritation of the nose, mouth and eyes as well as headache, stomach aches, dizziness, vomiting and diarrhea. Therefore, it is necessary to reduce Cu (II) from surface waters.

Conventional technologies for the removal of heavy metals from wastewater include chemical precipitation, ion exchange, electrochemical removal, membrane and microbe separation and adsorption (El Ashtoukhy *et al.*,2008; Gupta *et al.*,2003; Gupta *et al.*,2012; Olyaie *et al.*,2012).Some of these technologies produce chemical or biological sludge and can't be recovered or regenerated (Sud and Kumar,2008).

Among these methods, adsorption is an attractive approach in groundwater and drinking water treatment, due to high removal efficiency and without yielding harmful by-products (Eren,2008). However, adsorption of heavy metal with high adsorption capacity, fast adsorption-desorption kinetics, easy fixation and separation from water are in great demand. For example, activated carbon has been widely employed as the most popular adsorbent for the effluents treatment. Due to the high cost of adsorbents, there is an increasing interest in the use of low-cost adsorbents, which are able to remove metallic ions from liquid effluents (Babel and Kurniawan,2003).

The adsorption of metals onto various types of biomass has been introduced as a cost-effective method in multiple studies. In this method, in addition to direct use of microbial biomass, their by-products including biosorbent may be applied as a low-cost method of metal removal process. In addition to fermentation processes, production of biosorbent can be considered by employing simple and inexpensive culture propagation techniques (Kazemian and Mallah,2008; Mata *et al.*,2008; Pejic *et al.*,2008; Quintelas *et al.*,2009). Activated sludge is a biomass used for the purification of some industrial effluents and domestic wastes. Excess sludge from such wastewater systems can be separated and utilized for removal of heavy metal ions as an abundant and cheaper biosorbent (Kadirvelu *et al.*,2001). Due to the adsorptive capacity of the microorganisms for heavy metal ions, the biomass can be also be successfully used as a sorbing (Tsczos and Bell,1989; Brandt *et al,*.1997).

Capability of microorganisms to bind heavy metals in aqueous solutions has long been of scientific interest (Aksus and Gulen,2002; Sen and Dastiar,2007). Mapolelo *et al* .(2005) showed that yeast is a viable trace metal enrichment agent that can be used freely by suspending in solution to enrich metal ions at a relatively low concentration. Bisorption of uranium by filamentous fungus Mucor has been documented in study (Guibal *et al.*,1999). Homaidan *et al.*(2014) studied the removal of copper ions from aqueous solutions by Spirulina platensis biomass. Abdel Aty *et al*(2013) evaluated the potential of removing cadmium and lead from aqueous solution using fresh water alga Anabaena sphaerica biomas. Ong *et al.*(2013)analyzed the adsorption behavior of Cu(II), Cd(II) and Ni(II) ions from aqueous solution onto the activated sludge and dried sludge.

The main goal of this study was to investigate the removal efficiency of Cu(II) using two bioadsorbent

materials, namely dried activated sludge and dried activated nano-sludge. The influence of pH, initial copper concentration, adsorbent dosage and contact time on the adsorption capacity of DAS and DANS were investigated. The biosorption mechanisms involved of Cu(II) onto DAS and DANS biomass were also appraise in models of isotherms and kinetics.

Materials and methods

Preparation of biosorbent and copper solution

Activated sludge was obtained from Shazand Petrological Co. (Arak, Iran). The activated sludge was refluxed for 60 min with HNO_3 1 M and sieved through a Watman paper, and it was washed with distilled water. Then, the activated sludge was refluxed for 60 min with NaOH 1 M. The product was washed with the distilled water and then dried at room temperature to yield a powder. The activated sludge was characterized with scanning electron microscopy (model EM 3200 made KYKY). Fig.1(a,b) shows SEM pictures of the adsorbents before adsorption that showed rather rough surface of pure adsorbent. Solution of 1000 (mg/L) of Cu(II) was prepared by dissolving of $Cu(NO_3)_2{\cdot}3H_2O$ in double distilled water. All chemicals used in this study, were of analytical reagent grade and were used without further purification.

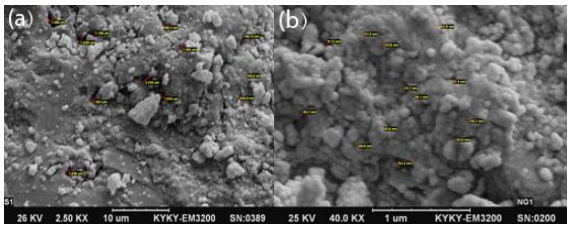

Fig.1. SEM image (a) activated sludge (b) activated nano-sludge before adsorption.

Batch adsorption experiments

Batch system was performed using 250-ml flask and on the shaker at 150 rpm at room temperature (25°C) to achieve sorption equilibrium time for experiments. Erlenmeyer flasks were filled with 10-100 mg/L of copper solution and different amount of biomass (0.5-7g/L). The flasks were charged with different concentrations of dried activated sludge and allowed to shake. Upon completion of shaking, the samples were withdrawn and their copper concentration was analyzed. The effect of different retention times of 5-90 min for nano-sludge and 5-140 min for dried activated sludge with variation of initial concentration (10-100 mg/L) of copper ion at constant pH and temperature on removal of copper by dried mass was considered in batch system. For separation of activate sludge from the solution, samples were centrifuged **(**model 2-6 Sigma made in Germany) at 3800 rpm for 15 min. Copper (II) concentration was measured by using atomic absorption spectrometer (model AA 680 made of SHIMADZU). Hollow cathode lamp of Cu(II) of the same manufacturer, was used as radiation source (324.7 nm).

The amount of copper adsorbed by biomasses was calculated using the following equation:

$$q_e = \frac{(C_0 - C_e)V}{M} \qquad (1)$$

where q_e (mg/g) is the amount of copper adsorbed by biomass and C_o and C_e (mg/l) are the initial and equilibrium liquid-phase concentrations of copper, respectively,V(l) represent the initial volume of copper solution, and M (g) the mass of the biomass. The performance of dried activated sludge and dried activated nano-sludge adsorption was evaluated in terms of its removal efficiency as *Re (%)*, estimated by the following equation:

$$\mathrm{Re}(\%) = \frac{(C_0 - C_t)}{C_0} \times 100 \qquad (2)$$

where C_t is the copper concentration at time t.

Adsorption isotherm

Adsorption isotherm is the basic requirement for designing any adsorption system. Isotherm express the relation between the amounts of adsorbate removed from liquid phase by unit mass of adsorbent at constant temperature. Since adsorption is one of the fundamental surface phenomena, it is important to have a satisfactory description of an equilibrium state in order to successfully represent the kinetic

adsorption behavior of any species from the fluid to the solid phase (Passos *et al.*,2008). Langmuir, Freundlich and Dubinin-Radushkevich models isotherm were used to analyze the biosorption isotherms of copper.

Adsorption kinetic

In order to determine the potential rate-controlling steps involved in the adsorption process, kinetic models should be established (Zhi Yan *et al.*,2008). Therefore, the first order and pseudo-second-order kinetics were used to analyze the biosorption kinetics of copper.

Results and discussion

Effect of pH

The influence of initial pH on the removal efficiency of the activated sludge is shown in Fig.2. All tests were carried out at room temperature, by 1g/Lof biomass and 25mg/L of copper ion concentration. Initial pH was adjusted at values below the metal precipitation and was controlled in experimental time. The perfect pH is equal about 3.0. Activated sludge present a negative net charge at surface level which facilitate its binding with positive metal cations. At very low pH, metal ions uptake was less and this is due to the facts that surface of adsorbents are closely associated to H^+ and access of metal ions to adsorbent surfaces would be restricted as a result of repulsive forces. Metal uptake increased with pH from 2-3 which is due to more adsorbent with negative charge being exposed with the subsequent increase in attraction sites to positively charged metal ions. Beyond pH 3 there is not much further increase the efficiency removal.

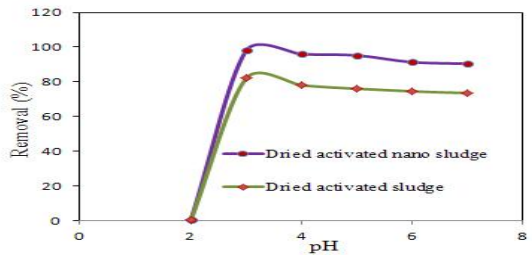

Fig.2. The influence of initial pH on the removal efficiency of Cu(II) by (DAS) and (DANS) (C_o 25mg/ L, temperature 25 °C and biomass dosage 1g/L).

Influence of initial copper concentration

The influence of initial copper concentration on the biosorption of copper is shown in Fig. 3. Considering steady values of other parameters, the initial copper concentration was increased from 10 to 100 (mg/L) which caused a removal efficiency decline from 91.5 and 73.5% to 58 and 40% for dried activated nano-sludge and dried activated sludge, respectively. Adsorption capacity of both dried activated sludge and dried activated nano-sludge, increased with increasing the initial copper concentration. This was due to an increase in the driving force of the concentration gradient, as an increase in the initial copper concentration.

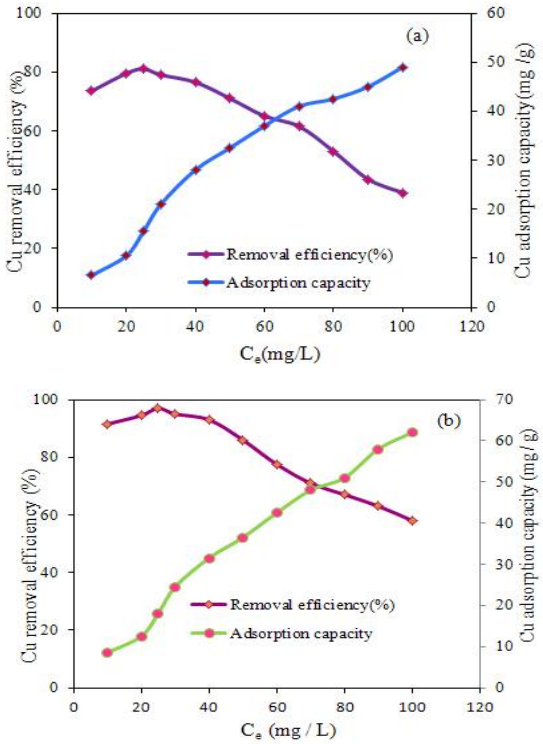

Fig. 3. Effect of initial Cu (II) concentration on copper removal efficiency by (a) DAS and (b) DANS (C_o 25mg/L, temperature 25 °C, biomass dosage 1g/L and pH 3).

Influence of contact time

Fig.4 shows the influence of contact time on the biosorption of copper by activated sludge and activated nano-sludge. Increasing contact time from 5 min to 90 min for activated nano sludge and 140 min for activated sludge caused a removal efficiency

improvement from 61.68 and 22.5% to 96.2 and 95% for activated nano-sludge and activated sludge, respectively. The Cu(II) removal onto the activated sludge and activated nano-sludge drastically increase during the initial adsorption stage and then continue to increase at a relatively slow speed with contact time until a state of equilibrium is attained after the optimized time. This phenomenon is attributed to the fact that a large number of vacant surface sites are available for adsorption at the initial stage, and after a lapse of time, the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the solute ions on the solid and bulk phases.

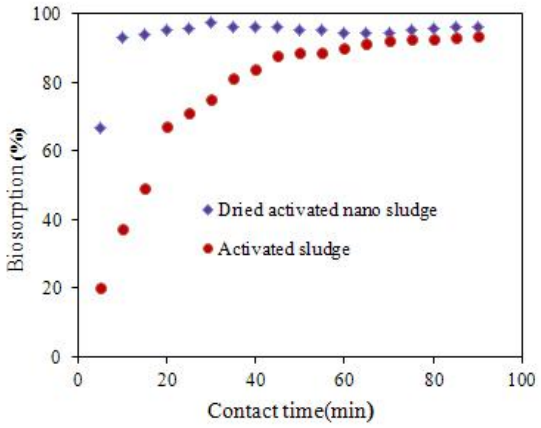

Fig. 4. Effect of contact time on copper removal efficiency by DAS and DANS (C_o 25 mg/L, temperature 25 °C, biomass dosage 1 g/L and pH 3).

Influence of the mass of biomass

The influence of mass of the biomass on the copper biosorption is shown in Fig. 5. When the weight of the biomass was increased from 0.5 to 7 g/L, the copper removal efficiency decreased from 94.8 and 98.48% to 82.2 and 92.5% for dried acativated sludge and nano-sludge, respectively.This observation can be explained by increase in the surface area and availability of more active sites for adsorption. Afterwards (from1g/ L), becomes fairly constant for any further increase in the dried activated sludge and nano-sludge dose because of the limitation copper ion as compared to the dried activated sludge and nano-sludge sites available for the reaction.

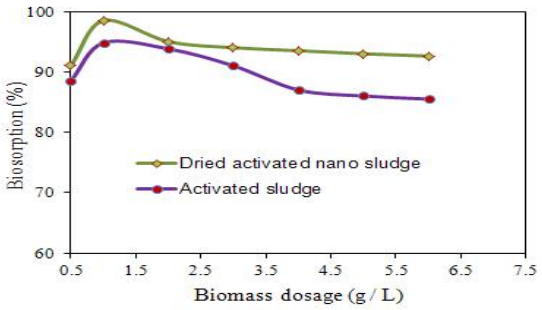

Fig. 5. Effect of biomass amount (g) on copper removal efficiency by DAS and DANS (C_o 25 mg /L, temperature 25°C, biomass dosage 1 g/L and pH 3).

Adsorption isotherm

Adsorption isotherms are introduced for the design of adsorption systems. Correlation of equilibrium data by either theoretical or empirical equation is important to practical operation. Langmuir and Freundlich equations were employed for further interpretation of the obtained adsorption data. The Langmuir isotherm is expressed as:

$$\frac{C_e}{q_e} = \left(\frac{C_e}{q_m}\right) + \left(\frac{1}{K_L q_m}\right) \qquad (3)$$

where K_L is the Langmuir adsorption equilibrium constant (l /mg) and C_e is the equilibrium metal concentration (mg/ L), q_e is the amount of metal ions adsorbed per unit of adsorbent (mg/g) at equilibrium concentration C_e, and q_m is the maximum. Adsorption capacity(mg/g), which depends on the number of adsorption sites. The Langmuir isotherm assumes that adsorption will increase with increasing metal concentration, but as soon as all of the sites are occupied, no further adsorption can take place at that site. As long as there is no interaction between the day molecules and that the adsorption is localized in a monolayer (Langmuir,1916).

Freundlich adsorption model takes the following form:

$$\ln\ q_e = \ln k_f + \frac{1}{n} \ln C_e \qquad (4)$$

where K_f is the Freundlich isotherm constant (mg/g), and n(g/L) are Freundlich constants depending on the intensity of adsorption. When $1/n$ are in the range

0.1< $1/n$<1 the adsorption process is favorable(Vazquez *et al.*,2007; Freundlich,1926). The Freundlich isotherm shows monolayer adsorption but not a saturation-type isotherm and suitable for adsorption over heterogeneous surfaces.

The Dubinin-Redushkevich (D-R) model is represented as:

$$Lnq_e = lnq_m - B\varepsilon^2 \quad (5)$$

where ε is the polanyi potential

$$\varepsilon = RTln\ (1 + \frac{1}{C_e}) \quad (6)$$

where R is the gas constant, T is temperature and the constant B(mol²/ J²) is activity coefficient. The parameters B and q_m possible to obtain from a plot of ln q_e versus ε^2.

The equilibrium established between adsorbed metal ions on the biosorbent and unadsorbed metal ions in solution can be described by adsorption isotherm models. In general, the adsorption isotherm describes how adsorbates interact with adsorbents, and thus is critical in optimizing the use of adsorbents. The analysis of the isotherm data, by fitting them to different isotherm models is an important step in finding a suitable model that can be used for design purposes.

Langmuir, Freundlich and Dubinin-Radushkevich adsorption isotherms were employed to determine the preference of one to another. Plot for the Langmuir equation is shown in Fig.6. The results show that Langmuir isotherm represented a better correlation compared to other isotherms (for dried activated sludge R^2 = 0.989 and for dried activated nano sludge R^2= 0.998). Table 1 gives the values of the isotherm constants.

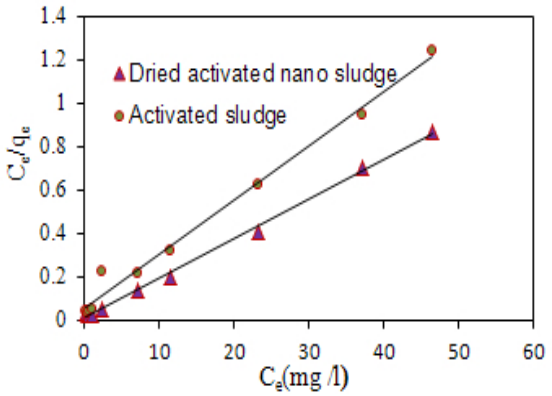

Fig. 6. Langmuir isotherms for the adsorption of copper by DAS and DANS (C_o 25 mg /L, temperature 25°C, biomass dosage 1g/L and pH: 3).

Table 1. Langmuir, Freundlich and D-R isotherm parameters for Cu (II) ions on dried activated sludge and dried activated nano sludge.

Adsorbent	Langmuir model			Freundlich model			D-R model		
	q_m (mg/g)	b (l /mg)	R^2	k_f (mg/g)	n (g/ l)	R^2	q_m (mg/g)	B (mol²/ J²)	R^2
DAS	65.2	0.909	0.987	21.57	4.1	0.710.68	47.65	0.188	0.767
DANS	76.92	0.644	0.998	27.2	3.9		55.14	0.114	0.984

Adsorption kinetics

In order to investigate the mechanism of adsorption, the pseudo first-order and pseudo-second order kinetics models (Ho and Mckay,1999). Were applied to fit the experimental data.Which can be expressed as the following equations:

$$\ln(q_e - q_t) = -k_1 t + \ln q_e \quad (7)$$

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e} \quad (8)$$

Where q_e and q_t are the sorption capacity (mg/g)at equilibrium and at time t(min), k is the rate constant, $h=k_2q_e^2$is the initial sorption rate in pseudo-second order kinetics model. To find the potential rate-controlling steps involved in the process of biosorption of copper onto activated sludge and activated nano sludge, first order and pseudo second-order kinetic models were tested to fit the experimental data at various adsorbents. Adsorption kinetic of copper pseudo second-order model shown

in Fig.7. Table 2 shows the comparison of first-order and pseudo second-order kinetics constants.

Table 2. Comparison first –order and pseudo second –order kinetic parameters for the biosorption of Cu (II) onto DAS and DANS.

Adsorbent	Pseudo-first-order			Pseudo-second-order		
	q_e(mg /g)	k_1(min^{-1})	R^2	q_e(mg /g)	k_2(g/ mg min)	R^2
DAS	23.02	0.0299	0.720	2.23	3.48×10^{-3}	0.990
DANS	24.10	0.0529	0.938	2.24	2.25×10^{-2}	0.999

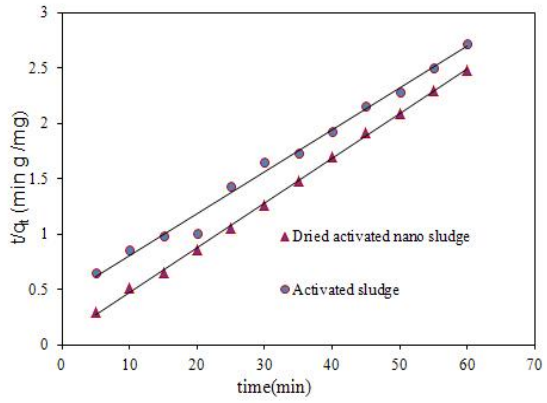

Fig. 7. kinetic experimental data and pseudo-second -order model for Cu (II) biosorption by DAS and DANS.

Conclusions

In this study, the capability of the use of dried activated sludge and dried activated nano sludge were collected from the system of wastewater refining of Shazand Petrological Co. for removing Cu(II) was examined. The removal of copper ions by adsorption on dried activated sludge and dried activated nano sludge were found to be rapid at the initial period of contact time and then slows down with increasing contact time. The isotherm experiments conducted at constant temperature showed that the biosorptive capacity of dried activated sludge and dried activated nano sludge was highly dependent on temperature, initial pH, initial copper ion concentration and adsorbent mass. The removal efficiency of the dried activated sludge and dried activated nano sludge for the same initial copper concentration was found to increase as the temperature increased. Initial pH plays a major role in the adsorption process. The optimum pH for the removal of copper ion from the aqueous solution under the experimental conditions used in this work was 3.0. Increasing the initial copper ion concentration decreased the removal efficiency. The removal efficiency of the dried activated sludge and dried activatednano sludge increases as the biomass mass increases. The Langmuir and Freundlich Eq. were used to model biosorbed metal ions on the biosorbent in solution. The data show that for both dried activated sludge and dried activated nano- sludge, the Langmuir equation provides a suitable description of the experimental data because of higher values of the correlation coefficients. Furthermore, the corresponding parameters indicate favourable and good adsorption in all cases.

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