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ADSORPTION KINETICS AT DIFFERENT CONCENTRATIONS OF Cu (II) ONTO LOCAL MARL

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ABSTRACT

Copper is known to be commonly used heavy metals. This metal, which find many useful applications in our life, are very harmful if they are discharged into natural water resources and many pose finally a serious health hazard .Therefore it is necessary to treat copper containing wastewater before discharging in to water streams.In this work ;kinetic investigations were carried out to evaluate the applicabiIity of used marl found in located in Oum-El-Bouaghi region (Algeria) as a low-cost adsorbent to the removal of copper ions from aqueous solutions.Marl was characterized with FTIR and SEM. The effects of initial concentration and temperature on adsorption of Cu(II) were investigated.,also Kinetic aspects of sorption of Cu(II)on marl has been studied through batch sorption experiments and test of experimental data with pseudo-first and -second order rate models.

Key Words: *Adsorption, Copper, Kinetic, Marl, Characterization.*

NOMENCLATURE

Symbols :

V	solution volume, L
m	marl mass, g
t	contact time, min
T	température absolue, K
k	rate constant
q	amount of Cu^{2+} adsorbed
Δq	relative error

Greek Letters:

λ	wavelength,nm

Indices / Exponents:

i	initial
1	pseudo-first-order
2	pseudo-second-order
e	equilibrium

1. INTRODUCTION

Environmental pollution and its abatement have drawn keen attention for a long time. The problem of removing pollutants from water and waste water has grown with rapid industrialization. Heavy metals, dyes, oil and other salts, which are toxic to many living life and organisms, are present in the waste water streams of many industrial processes, such as dyeing, printing, mining and metallurgical engineering, electroplating, nuclear power operations,aerospace,battery manufacturing processes, etc .The presence toxic heavy metals has been responsible for several health problems with animals, plants, and human beings. Numerous metals such as Sb, Cr, Cd, Zn, Ni, Cu, Pb, Hg, etc. have toxic effects on human and environment. Since copper is a widely used material, there are many actual or potential sources of copper pollution[1]. Copper may be found as a contaminant in food, especially shellfish, liver, mushrooms, nuts, chocolate, etc. Containers involving copper materials may contaminate the products such as food, water or drink. Copper is essential to human life and health however, like all heavy metals, it is also potentially toxic. As an example, continued inhalation of copper-containing spray is linked with an increase in lung cancer among exposed workers[2]. The permissible limit of Cu is 2.5mg/Lin water[3]. The adsorption technique has become one of the most preferred methods for the removal of heavy metals due to its high efficiency and low cost.The aim of the present work was therefore to study the removal of copper (II) using marl as an adsorbent . The kinetics of cu(II)adsorption on marl is discussed through batch experiments under the various conditions :the factors affecting the rate constant and the adsorption capacity were investigated with different kinetic models.

2. MATHEMATICAL MODEL/EXPERIMENTAL METHOD

2.1. Materials:

Marl was used as an adsorbent for the removal of copper (II) from aqueous solution. It was collected from Oum El Bouaghi mountain ,this adsorbent was washed with distilled water, and dried at temperature ambiant.After drying it was sieved under 180 mesh size and used as such without prior treatment The solution of copper (II) was prepared by dissolving a suitable amount of $CuSO_4,5H_2O$ (M=249,68g/L) in distilled water.

2.2. Sem images:

The microstructure of marl was examined by SEM (30-XL PHILIPS).

2.3. Characterization by infrared spectroscopy:

FTIR Analysis in the solid phase was performed using a Fourier transform infrared spectrometer (Jasco 460).Adsorbent powders was blended with IR-grade KBr in an agate mortar and pressed into tablet. Spectra of the marl before Cu(II) sorption was recorded and measured in the absorbance mode in the range of 400-4000 cm^{-1}.

2.4. Batch experiments:

Kinetic studies were carried out with a simple batch technique.Expirements were performed in a series of 500 mL conical, Each flask was filled with 25 mL solution of Cu(II) of desired concentration and adjusted to the desired temperature. A known amount of marl was added to each flask and kept in isothermal shaker , the solution was centrifuged to remove the marl particles and analyzed spectrophotometrically at λ =810nm_max for the concentration of Cu(II) remained in the solution. The effect of temperature on the adsorption of Cu(II) at different Heating (293K, 298K, 303 K), Cu(II) adsorption was also studied in concentration range of 1000–4000 mg/L. The amount of Cu(II) adsorbed was calculated by the above method (Eq. (1)).

$$q_t = \left(C_i - C_t\right)\frac{V}{m} \qquad (1)$$

3. RESULTS

3.1. Characterization by infrared spectroscopy:

Analysis FTIR is presented in fig 1. Data shows the peak of 3631cm^{-1} for the presence of free (AlOH) and SiOHgroup stretching vibrations while intermolecular hydrogen bonding seems to be present in the region of 3419 cm^{-1}. Band at 1637 cm^{-1} is due to the presence of H_2O bending vibration for interlayer water. Antisymmetric stretching vibration of CO_3^{2-} group in calcite is indicated by the peak at 1437 cm^{-1}. Region of 1027and 873 cm^{-1} indicates the presence of Si-O and deformation out of the plane of CO_3^{2-} group in calcite respectively .

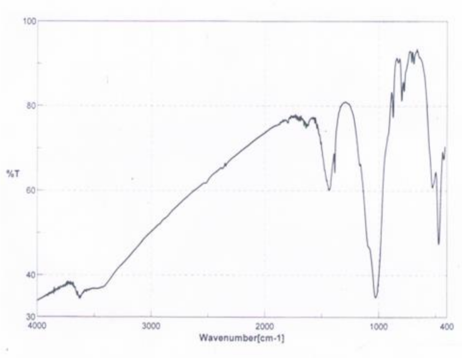

FIGURE 1.The Fourier-transformed infrared spectra of the marl

band observed at 530 cm^{-1} according to bending vibration of Si-O-M (M means the metals Al , Mg and Fe) the sharp peak of 472 cm^{-1} corresponding to bending vibration of Si-O-Si [4].

3.2.The effect of the initial Cu(II) ions concentration:

The adsorption of Cu(II) onto marl was studied at different Cu(II) ion concentrations in the range from 1000 to 4000mg/L.Results are presented in Fig 2.The initial concentration provides an important driving force to overcome all mass transfer resistance of Cu(II) ions between the aqueous and solid phases, hence a higher initial concentration of Cu(II) ions may increase the adsorption capacity showed that adsorption of Cu(II) ions increased as a function of increasing Cu(II) concentration [5]. We can indicated that at lower concentrations, all Cu(II) ions present in solution could interact with the binding sites.At higher concentrations, lower adsorption yield is due to the saturation of adsorption sites[6].

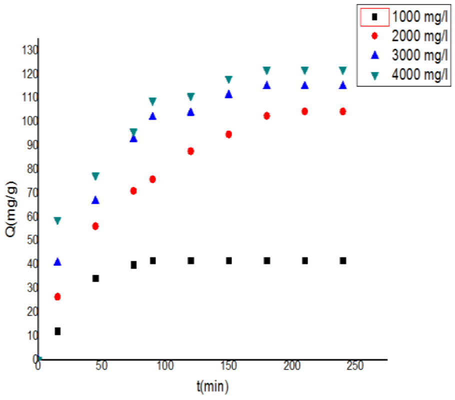

FIGURE 2. Effect of initial concentrations

3.3.The effect of the temperature

The effect of temperature on the Cu(II) ions removal was illustrated in Fig 3. The maximal adsorption efficiencies were found at 303K . While the increasing trend of adsorption was observed with increasing temperature from 298 to 303K. The increase in adsorption capacity of marl with temperature indicates an endothermic process, reported that the increase in adsorption with temperature may be attributed to either increase in the number of active surface sites available for adsorption on the adsorbent or the decrease in the thickness of the boundary layer surrounding the adsorbent with temperature [7].

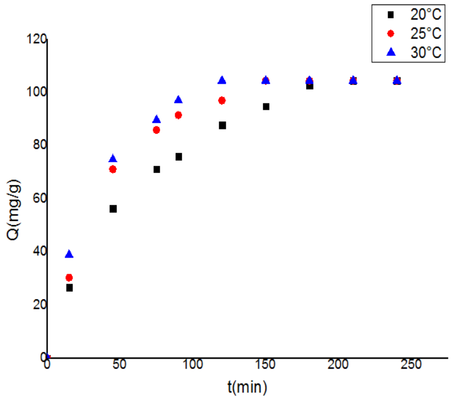

FIGURE 3. Effect of temperature

3.4. Adsorption dynamics:

The rate constant of adsorption is determined from the first order rate expression given by Lagergren :

$$q_t = q_e(1 - \exp(-k_1 t)) \qquad (2)$$

Values of k_1 were calculated from the curves of q_t vs t (figures not shown) for different temperature and different concentrations of adsorbate, it is more likely to predict the behaviour over whole range of adsorption .The non linear curve of q_t vs t show a good agreement of experimental data with the first-order kinetic model for different initial Cu(II) concentrations (Table 1). The calculated q_e values agree very well with the experimental data.The second-order kinetic model is expressed as

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \qquad (3)$$

the experimental qe values do not agree with the calculated ones, obtained from the non linear curves (Table 1). This shows that the adsorption of copper marl is not a second order reaction . These indicate that the adsorption system belongs to the firt order kinetic model . In this study, we based the calculation of $\Delta q_e(\%)$ and Vi, expressed as follows:

$$\Delta q(\%) = \frac{\left| q_{e,exp} - q_{e,cal} \right|}{q_{e,cal}} \mathrm{x}100 \qquad (4)$$

$$V_i = k_2 \left(q_e \right)^2 \qquad (5)$$

Parametres	1000 mg/L	2000 mg/L	3000 mg/L	4000 mg/L
		Pseudo-first order		
k_1	0.02496	0.01506	0.02201	0.0271553
q_e(exp)	41.96	104.45	115.06	122
q_e(cal)	47.68703	107.3243	115.37231	118.984
$\Delta q(\%)$	14.0227	2.67814	2.7069	2.5347
R^2	0.98773	0.99342	0.98985	0.9719
		Pseudo-second order		
k_2	2.66908E-4	1.03843E-4	1.7776E-4	2.5277E-4
q_e(cal)	69.20304	138.99859	139.96229	138.69219
V_i	1.2782	2.0063	3.4822	4.8811
$\Delta q(\%)$	39.3668	24.8558	17.7921	12.7564

R^2	0.95464	0.99812	0.99221	0.98848

TABLE 1.Kinetic parameters for adsorption of Cu^{2+} onto marl with different concentrations

4. CONCLUSIONS

The amount of copper (II) ions adsorbed onto new adsorbent increased with an increase in concentration and temperature. The results indicates an endothermic process and.the pseudo-first order rate expression provided the best fit kinetic model for all system studied therfore this adsorbent which have a very low economical value may be used effectively for the adsorption of copper (II) ions from aqueous solutions. The results indicates an endothermic process .

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