Removal of Mercury from Aqueous Solutions by Waste Brick

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ABSTRACT: Mercury is one of the most toxic heavy metals present in aquatic systems, exhibiting a complex behaviour in the environment, where it may persist for decades after the source of pollution is stopped. Hence, it is important develop new techniques for its removal from the aquatic systems. In this context, a particularly promising line of research is the use of new materials capable of up taking mercury from aqueous systems. A new sorbent system for removing mercury (II) in presence of oleic acid, from aqueous solutions has been investigated. This new sorbent is waste crushed brick, obtained from local industries .Variables of the system include solution pH, sorbent dose and contact time. The adsorption isotherm data follow the Langmuir equation in which characteristic parameters was calculated. Waste crushed brick has a maximum mercury (II) removal capacity (87mg/g).

Key words: Adsorption, Hg (II), Crushed brick, Oleic acid, Langmuir isotherm

INTRODUCTION

Mercury is a highly toxic metal which is still used in various anthropogenic activities such as: the chlor alkaly industry (Davis, 2000; Chantawong, 2003), production of fluorescent lamps and in the recovery of gold by artisanal miners. It is naturally present in various concentrations in coal, natural gas and petroleum. Once delivered to the environment, the behaviour of Hg is very complex because it may be present in different oxidation states and species with different physicochemical properties (Andac *et al.,* 2003). Accordingly, improved and innovative methods of water and wastewater treatment are continuously being developed to treat water containing metals such as: Precipitation, cementation, ion exchange, solvent extraction and adsorption are the most widely used methods for cleaning water contaminated with metal pollutants (Bailey, 1999; Barron, 2002; Hunsom, 2005; Fischer, 2005). Limitations of these methods are: slow kinetics, low adsorption capacity and high cost Panayotova (2001). Thus, the use of industrial minerals with low cost and high sorption capacities has been tested for removal of heavy metals in general. However, data on the use of these minerals for mercury removal is scarce. In this work, cost-effective crushed brick was selected as adsorbents for the investigation of adsorption of Hg (II) species

from aqueous solution.The aim of this work is to study the removal of Hg (II) species from aqueous solution by adsorption onto waste crushed brick in the presence of oleic acid. The Influence of pH, contact time and the sorbent dose on adsorption process was also investigated. Isotherms was determined and modelled by the Langmuir model.

MATERIALS & METHODS

The adsorbent used in this study waste crushed brick was obtained from waste local industries. (East of Algeria). It was used directly for adsorption experiments without any treatment. It has received without any treatment. The chemical composition of the brick dried at 110 °C and crushed to sizes 01-1mm using ASTM Standard sieves. The sample was analyzed both by XRD using a BRUKER AXS, Cu-Kα_1 (λ= 1.5406 Å), and by chemical analyses. Detailed of the chemical composition of the sample is given in Table (1).Reagents grade (99%) oleic acid (HOL, $C_{18}H_{34}O_2$), purchased from (Aldrich) were used as received throughout the experiments, freshly prepared solutions was used in all the experiments. The diffractogram of crushed brick sample shown that The mineralogical composition of sample is made up of essentially of quartz (SiO_2) and dolomite $CaMg(CO_3)_2$ and calcite ($CaCO_3$) Fig.1.

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Table 1. Chemical analysis of crushed brick

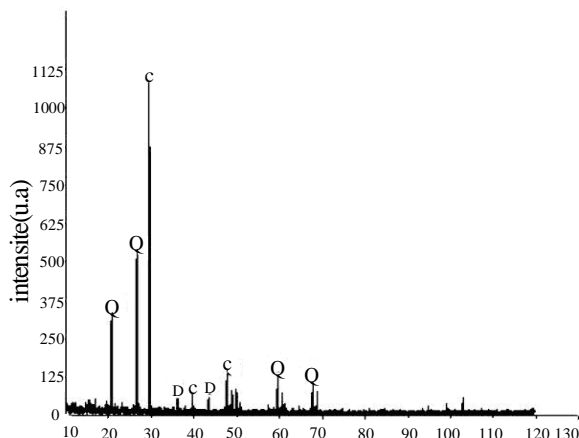| Compound	CaO	Fe₂O₃	SiO₂	Mn	Al₂O₃	MgO
Composition (%)	60.49	1.35	25.03	0.073	0.24	13.46

Fig. 1. Diffractogram of waste crushed brick

A stock solution of 1000 mg/L mercury Hg (II) was prepared from Hg $(NO_3)_2 \cdot 4H_2O$ (Fluka Chemika) in distilled water. This solution was diluted as required to obtain standard solutions containing 100-500 mg/L Hg (II). Batch adsorption studies were carried out with 50 mg of adsorbent and 50 mL of Hg (II) solution of a desired concentration with HOL 6.96×10^{-4} mol/L at pH 4.5 in 100 mL conical flasks. The flasks were agitated at 3500 rpm for 15 min using a temperature controlled shaking water bath for 15 min. The adsorbate was separated from adsorbent and analysed spectrophotometrically (Ramakrishna *et al.,* 1976). The amount of metal adsorbed per unit mass and the percent removal R (%) were calculated as follows was calculated as follows:

$$q_e = C_0 - C_e \ V/m \qquad (1)$$

$$R \ (\%) = (C_0 - C_e) \ .100/ \ C_i \qquad (2)$$

Where C_0 and C_e are the initial and equilibrium concentrations (mg/L), m is the mass of crushed brick (g), and V is the volume of the solution (l).The effect of pH on the adsorption capacity was investigated at the pH range 1.5–6. The ionic force of the electrolyte is 0.5M $(NaNO_3)$. The Hg (II) concentrations is C_0=100-500 mg/L. After determining the optimum time for Hg (II) adsorption, the kinetic study was performed at a room temperature of 25°C. The pH of the suspensions was maintained constant during the experiments at pH=4.5. Samples were collected at appropriate time intervals in order to analyze the mercury concentrations. The adsorption isotherm of Hg (II) on the crushed brick was investigated when the optimum pH and equilibrium time were evaluated. The equilibrium time selected was 200min.

RESULTS & DISCUSSIONS

In order to find out the proper concentration of oleic acid HOL required for the Hg (II) removal several experiments were conducted. The data in Fig. 2 shows the percent removal of 100 mg/L Hg (II) in neutral aqueous solution, using different concentrations of oleic acid. The results indicate that maximum removal takes place at 6.98×10^{-4} mol/L HOL. The figure shows a horizontal step removal exceeding 24% for a wide range of HOL concentration, starting from 6.98×10^{-4} mol/L. The concentration of oleic acid was therefore kept constant at 6.98×10^{-4} mol/L throughout the present study. The study of pH on the sorption of Hg (II) is important in determining the optimum sorption of metal ions. The results of the pH influence on the adsorption capacity of crushed brick for Hg (II) are given in Fig. 3. It was found that the amount adsorbed of Hg (II) increases with increasing pH from 1.5 to 4. At pH values above 4, the Hg (II) adsorption was not significantly affected by the solution pH. We can explain this interesting phenomenon by considering the interaction between the adsorption centers on the solid surface and various ions in the solution (Karabulut, 2000; Williams, 1998). The adsorbent surface may act as an ion exchanger and a special competition between protons and Hg (II) ions may take place at lower pH, at the higher pH this competition may occur between Hg (II) and sodium ions (Chairle, 2000; Schmuhl, 2000). To investigate the maximum adsorption capacity of the adsorbent for Hg (II), the dose of the adsorbent was varied from 0.1 to 1g stepwise, The
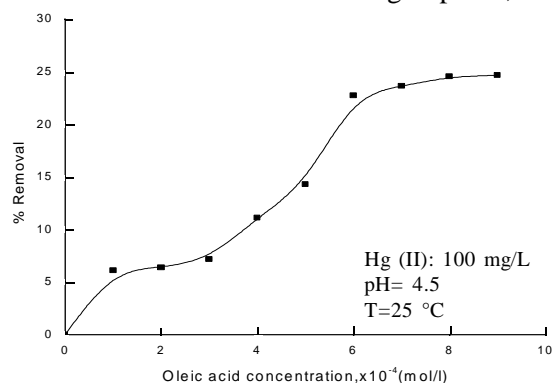

Fig. 2.Effect of oleic acid concentration on Hg (II) removal

maximum adsorption performance was achieved with 0.50g crushed brick and 87 % of Hg (II) could be removed, when Hg (II) initial concentration was 500 mg/L in aqueous solution. These findings are shown in Fig. 4 and their perusal indicates that the equilibrium state was affected by adsorbent dose. The experimental results of the adsorption kinetics for three concentrations of Hg (II) are illustrated in Fig. 5. The rate of adsorption of Hg (II) was followed by looking at the increase in the adsorption as a function of time until the adsorption remained constant, implying equilibrium was reached. As seen in Fig. 5, the adsorption of Hg (II) is rapid during the first 100 min and the equilibrium is then attained within 200 min contact time. Further treatment had no real effect on adsorption, and, consequently, 3 h was found to be optimal. The amount adsorbed increased exponentially with the increase in Hg (II)concentration . This indicates that there exists reduction in immediate solute adsorption, owing to the lack of available active sites required for the high initial Hg(II) concentration. Similar results have been reported on the extent of removal of dyes (Gücek, 2005; Ho, 2004), metal ions Bhatnagar (2007), and phenols (Khattri and Singh, 1999).The Hg (II) sorption isotherm on waste crushed brick Fig. 6 show that the maximal *Ce/qe* is 87 mg/g, this isotherm is in agreement with the Langmuir model expressed in its linear form by the following equation (3).

$$Ce/qe = 1/Q_o b + Ce/Q \qquad (3)$$

where C_e is the equilibrium concentration of Hg(II) (mg/L), q_e the amount of Hg(II) adsorbed at equilibrium (mg/g adsorbent), Q (mg/g) and b (mg/L) are the Langmuir constants related to adsorption capacity and energy, respectively. The plot of *Ce/qe* against *Ce* Fig. 7 give straight line with determination coefficient higher than 0.99. The adsorption process was found to follow the Langmuir adsorption isotherm showing the formation of monolayer coverage of adsorbate at adsorbent surface. According to (Khattri and Singh, 1999), the essential characteristics of Langmuir isotherm can be explained in terms of a dimensionless constant separation factor defined by:

$$R_L = 1 / (1 + bC_o) \qquad (4)$$

Where b is the Langmuir constant (mg/L) and Co is the initial concentration of metal ion (mg/L). The value of R_L indicated the type Langmuir isotherm

to be irreversible ($R_L = 0$), favourable ($0 < R_L < 1$), linear ($R_L = 1$), unfavourable ($R_L > 1$).The value of
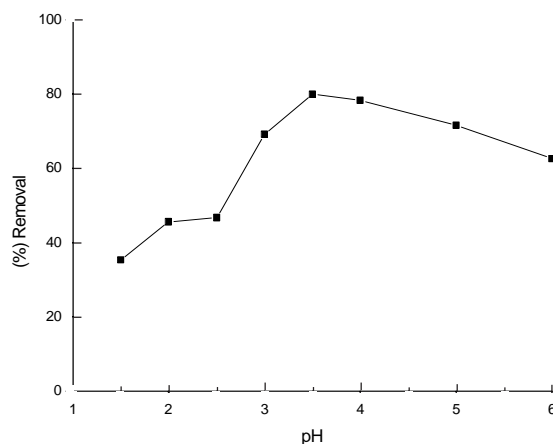

Fig. 3.The Effect of pH on Hg (II) removal. Hg (II) Concentration, 500 mg/L; Adsorbent dose. 50 mg/0 mL; Agitation time, 200 min; T 25°C.HOL 6.96x10⁻⁴ mol/L
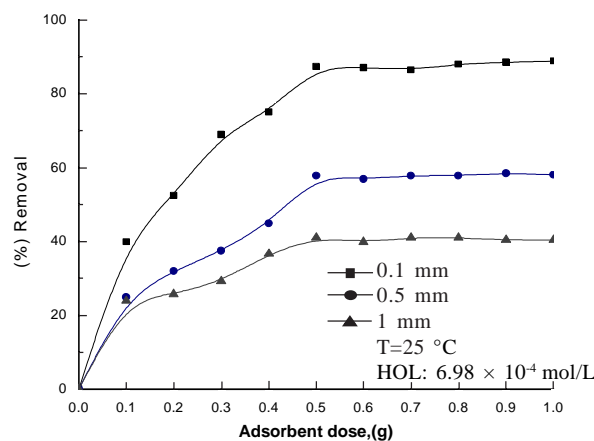

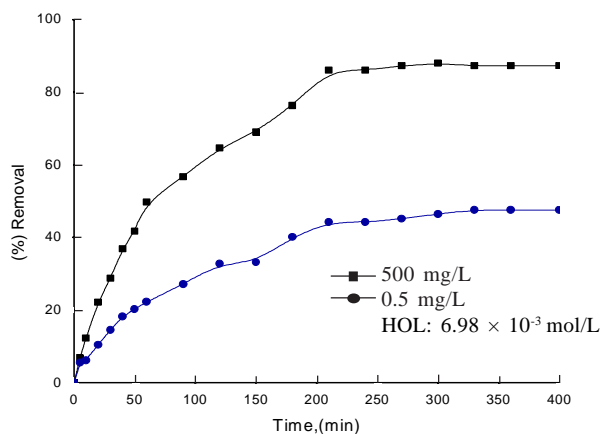**Fig. 4. Effect of adsorbent dose on adsorption efficiency**

Fig. 5. Effect of contact time and Hg(II) concentration on removal.pH=4.5; adsorbent dose 50 mg/ 50 mL; T=25°C
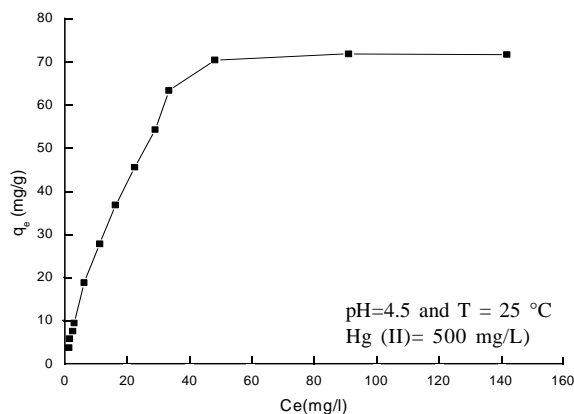
Fig. 6. Adsorption isotherm for Hg(II) onto waste crushed brick

the separation factor (R_L) calculated for this study is found to be between 0 and 1(R_L=0,198) and confirm that the ongoing adsorption process is favourable.

CONCLUSION

The effectiveness of waste crushed brick for removing Hg (II) in presence of oleic acid was examined. The experiments were performed as a function of initial pH and initial metal ions concentration. The Langmuir isotherms fitted very well with the concentration ranges studied, the dimensionless separation factor shows that the crushed brick can be used for the removal of Hg(II) from aqueous solution. Therefore, crushed brick may be used to eliminate Hg(II) species from wastewater. Crushed brick is a low cost industrial abundant adsorbent material and may be an alternative to more costly adsorbent materials.
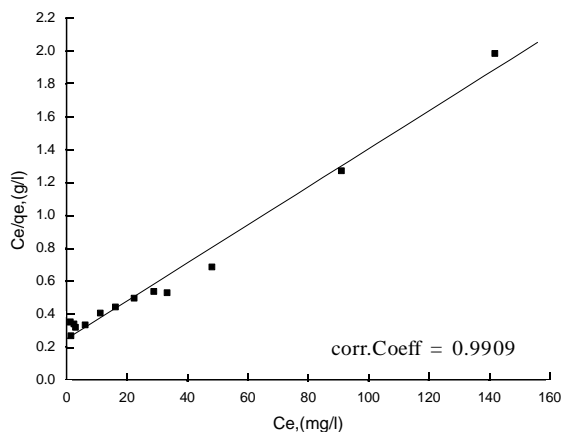
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Fig. 7. Langmuir plot for Hg (II) removal for waste crushed brick

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