A new local adsorbent for the removal of toxic metals from industrial wastewater

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Abstract

The ability of light expanded clay aggregate from Shat al-Khora in the city of Basrah to remove heavy metal ions Cr(VI), Zn(II), Cu(II) and Fe(III) from industrial wastewater in the State Company of Petrochemical industries was studied in a batch mode adsorption process. The effects of process variables including: pH, adsorbent dose, contact time, adsorbent particle size and temperature were investigated. The results showed that the maximum removal percentage of Cr(VI), Zn(II), Cu(II) and Fe(III) ions was achieved at a pH values of 2 and 5 for Cr(VI) and Zn(II) respectively and at 4.5 for both Cu(II) and Fe(III). The experimental data were fitted using Langmuir and Freundlich adsorption isotherm models. The results indicated that the adsorption of Cr(VI), Zn(II) and Cu(II) matched with Langmuir model while for Fe(III) it fitted Freundlich model. Five kinetic reaction models were tested for fitting the experimental data, the results analysis showed successful fitting with the 1\textsuperscript{st} and the 2\textsuperscript{nd} pseudo models for all the heavy metal ions investigated.

Keywords: Heavy metals ions, light expanded clay aggregate, adsorption isotherms, adsorption kinetics.
1- Introduction

In recent years, water pollution with heavy metals has become an important environmental threat mainly because of the numerous industrial effluents containing these and other pollutants. Heavy metals are highly toxic non-biodegradable, and they tend to accumulate in human body and other living organisms causing several diseases and health disorders [1]. Heavy metals hazardous to humans include lead, mercury, cadmium, arsenic, copper, zinc, and chromium. Arsenic and cadmium, for instance, can cause cancer. Mercury can cause mutations and genetic damage, while copper, lead, and mercury can cause brain and bone damage [2]. The removal of Cr from contaminated wastewater is necessary because of its high toxicity to living organisms [3]. The maximum concentration limit for chromium (VI) for discharge into inland surface waters is 0.1 mg/L and in potable water is 0.05 mg/L [4]. High intake of copper (over 1.0 mg/l in drinking water) gets accumulated in the liver of human beings and animals resulting in ailments like hemochromatosis and gastrointestinal problems. It is highly toxic to fish even in small amounts and act as toxins to aquatic and terrestrial organisms [5]. The presence of iron at concentrations above 0.1 mg/l will damage the gills of the fish [2]. A wide range of methods are available for the removal of metal ions from aqueous solutions. These include ion exchange, solvent extraction, reverse osmosis, precipitation, chemical oxidation and reduction, filtration, electrochemical treatment and adsorption [1,3, and 5]. Adsorption systems is considered to be the simplest and most cost-effective technique in reducing heavy metal concentration. Natural materials that are available in large quantities, or certain waste products from industrial or agricultural operations, may have a potential as inexpensive sorbents. Due to their low cost, after these materials have been expended, they can be disposed of without expensive regeneration. The cost is an important parameter for the comparison of sorbent materials [6]. A number of workers have used different adsorbents such as Zeolite X [1 to 5], volcanic ash soil [3], Agricultural Waste Biomass [7], Leca [8], chitosan coated oil palm shell charcoal [9], Teawaste [10], Kaolinite Clay[11], sugarcane bagasse [12], wood ash [13], steel slag [14], coconut coir [15]. In this study light expanded clay aggregate from Shat al-Khora in Basrah city was selected as an adsorbent for the removal of metal ions from Basrah petrochemical company wastewater.
2- Materials and Methods

2.1 Preparation of the new adsorbent

Red clay was collected from the edge of Shatt al-Khora in Basrah. The clay was collected as small globes with 2 cm in diameter. It was fired in a muffle furnace at 900 °C for 3 hrs. to convert it to light expanded clay aggregate. The firing conditions were optimized after a set of preliminary experiments at different temperatures and times of ignition. The light expanded clay aggregate was then crashed and sieved to different particle size (0.15, 0.355, 1.00, 2.36 and 3.35) mm. The elemental analysis of the new adsorbent are shown in Table 1.

Table 1. The Elemental analysis of the light expanded clay

| Elements/compounds | Value (wt. %) |
|--------------------|--------------|
| CaO                | 21           |
| SiO$_2$            | 41.3         |
| Fe$_2$O$_3$        | 16.1         |
| MgO                | 5            |
| MnO$_2$            | 1.4          |
| Total Cu           | 6            |
| Total Al           | 4.3          |
| Total Ni           | 1.1          |
| Total Zn           | 0.8          |
| Total Co           | 0.3          |
| Total Cd           | 0.1          |
| Total Pb           | 0.1          |
| Contaminates       | 2.5          |

2.2 Preparation of the metal ions solutions

0.02 Molar stock solutions of Cr, Fe, Zn and Cu ions were prepared by dissolving predetermined amount of K$_2$CrO$_4$, FeCl$_3$ anhydrate ZnCl$_2$ and CuSO$_4$ respectively in deionized water.

2.3 Batch mode adsorption experiments

Batch adsorption experiments were conducted at lab scale to investigate the effects of pH, contact time, adsorbent dose, particle size and temperature on adsorption of the metal ions from its solutions by the new adsorbent. All the adsorption experiments were carried out in water bath maintained at 25 ±0.5 °C except when the effect of temperature was being investigated. The initial pH was adjusted with 1N HCl and/or 1N NaOH solutions. The solutions of the metal ions were mixed with the adsorbent and shaken manually for 35 minute except when the effect of
contact time was investigated. Then, the mixtures were filtered through filter paper, and the Chrome, Copper, Zinc and Ferric ions concentration were determined in the filtrate using multi parameter bench photometer. The removal % of Chrome, Copper, Zinc and Ferric ions adsorbed by the light expanded clay at time $t$ was computed by using the following equation:

$$\text{Heavy metals removal (\%) = } \left( \frac{C_0 - C_t}{C_0} \right) \times 100$$

Where $C_0$ is the metal ion solution, $C_t$ is the conc. of the effluent after time $t$.

3. Results and discussion

3.1 Effect of pH

The effect of pH on heavy ions removal from industrial wastewater have been studied by varying the pH value of the mixture from 2 to 11 at initial concentration of Cr(VI), Zn(II), Cu(II) and Fe(III). The expanded clay dose, particles size and contact time were kept constant. The optimum pH results found to be 2 for Cr(VI), 5 for Zn(II), and 4.5 for both Cu(II) and Fe(III)). The results are shown in Figure. 1.
3.2 Effect of particle size

The experiments were carried out for five different practical size 0.15, 0.355, 1.00, 2.36 and 3.35 mm. The amount of Cr(VI), Zn(II), Cu(II) and Fe(III) ions adsorbed increases with the decrease in particle size of the adsorbent. This is due to the increase in the availability surface area with the decrease in particle size[17] . The effect of particle size on the removal of metals ions by the light expanded clay aggregate is found to be significant for Cr(VI) and has little effect on the other ions as shown in Figure (2).

![Figure 1. Dependence of heavy metals ions removal % on the solution pH. Results obtained at: particle size = 0.15 mm, temperature = 25 °C, contact time = 35 min, adsorbent dose = 1.0 g, initial concentration for metal ions is 0.02M.](image-url)
3.3 Effect of temperature

The effect of temperature on metals ions adsorption is studied by conducting different sets of experiments at different temperatures 25, 35, 45 and 55 °C as shown in Figure 3. The decreasing of adsorption capacity with temperature increase indicated that the process is exothermic [19].

**Figure 2.** Dependence of heavy metals ions removal on the particle size. Results obtained at: temperature = 25 °C, contact time = 35 min, adsorbent dose = 1.0 g, pH = 2 for Cr(VI), 5 for Zn(II), and 4.5 for both Cu(II) and Fe(III), and initial concentration of metal ions 0.02 M.
3.4 Effect of contact time

The removal of metal ions increases with increasing contact time before equilibrium is reached. The saturation time are 90, 210, 80 and 75 min for Cr(VI), Zn(II), Cu(II) and Fe(III) respectively. Other parameters such as pH and adsorbent particle size were kept constant during studying the effect of temperature. Figure 4 shows the change in metal ions removal with respect to the contact time. The removal rate of metal ions after equilibrium showed gradual decrease with increasing the contact time. Initially, the rate of metal ion removal was higher because all sites on the expanded clay were vacant and concentration was high, but decrease of sorption sites reduced the uptake rate. Desorption may occur after saturation [8].
3.5 Effect of adsorbent dose

The effect of different amounts of light expanded clay aggregate 1, 2, 4 and 6 g on heavy metal ions removal were investigated. The results showed that the removal percentage increases by increasing the amount of sorbent. The situation may be attributed to increasing the adsorption sites of the adsorbent. Figure 5 shows the situation.
3.6 Adsorption isotherm studies

Analysis of the isotherm data is necessary in order to develop the adopted equation that can accurately represent the results and could be used for design purposes. The data obtained from the adsorption isotherm studies were fitted to the Langmuir and Freundlich isotherms (Equation 2 and 3 respectively). The Langmuir model representing by Equation 2, assumes that the uptake of metal ions occurs on a homogenous surface by monolayer adsorption without any interaction between the adsorbed ions and the energy of adsorption is the same for all surface sites. \( Q_0 \) and \( b \) are Langmuir constants which correspond to the maximum adsorption capacity (mg/g) of adsorbent and energy of adsorption respectively. The parameter \( C_e \) corresponds to the remaining metal ion concentration in the solution and \( Q_e \) refers to the amount of metal ions sorbed per unit weight of adsorbent. Freundlich isotherm, representing by Equation 3, assumes that the uptake of metal ions occur on a heterogeneous surface by multi-layer adsorption. Where, \( K_f \) and \( 1/n \) are the measures of adsorption capacity and intensity of adsorption, respectively.

![Figure 5. Influence of adsorbent dose on heavy metals ions removal. Results obtained at: temperature = 25 °C, particle size = 0.15 mm except for Zn(II) was 0.335 mm, contact time = 35 min, pH = 2 for Cr(VI) , 5 for Zn(II) , and 4.5 for both Cu(II) and Fe(III)).](image-url)
**Langmuir isotherm equation**

\[
\frac{C_e}{Q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \tag{2}
\]

Where \( Q_e \) is the amount of adsorbed at equilibrium (mg/g); \( Q_0 \) and \( b \) are Langmuir constant which correspond the capacity in (mg/g) and energy of adsorption respectively.

**Freundlich isotherm equation**

\[
\log Q_e = \log K_f + \frac{1}{n} \log C_e \tag{3}
\]

where \( K_f \) and \( (1/n) \) are the measures of capacity in (mg/g) and intensity of adsorption respectively.

Langmuir isotherm equation constants were calculated through the plot of \( (C_e/Q_e) \) vs \( C_e \), while Freundlich isotherm equation constant were calculated by plotting \( \log Q_e \) vs \( \log C_e \) [20]. The results are presented in Table 2. The high value of correlation coefficient \( R^2 \) for the adopted Langmuir isotherm for indicates that the experimental data are well fitted to Langmuir isotherm for Cr(VI), Zn(II) and Fe(III). On the other hand, it was found that there is a good fit of the experimental data to Freundlich isotherm for Cr(VI), Zn(II) and Cu(II).

| Metals ions | Freundlich Parameters | Langmuir Parameters |
|-------------|-----------------------|---------------------|
|             | \( K_f \)     | \( 1/n \)   | \( R^2 \) | \( Q_0 \)   | \( b \)   | \( R^2 \) |
| Cr(VI)      | 43.1519    | -0.069     | 0.031    | 62.5       | 5.862*10^{-3} | 0.938       |
| Zn(II)      | 16.3305    | 0.239      | 0.913    | 47.62      | 0.2658      | 0.998       |
| Cu(II)      | 22.2843    | 0.840      | 0.562    | 45.454     | 0.91667     | 0.999       |
| Fe(III)     | 22.3872    | 0.148      | 0.960    | 200        | 0.13157     | 0.572       |

**3.7 Adsorption kinetics**

The time-dependent experimental adsorption data are used for kinetic modeling of the experimental results. The kinetics model equations used for fitting the data are Zero order, 1st order, Second order, Pseudo first order (Lagergren equation) and Pseudo second order equations Table 3.
Table 3: Adsorption kinetics models and equivalent fitting linear equations

| Kinetics model       | Equation                                    | Plot   | (No.) |
|----------------------|---------------------------------------------|--------|-------|
| Zero order           | $C_t = C_0 + K_0 t$                         | $C_t$ vs $t$ | (4)[5] |
| First order          | $\ln C = \ln C_0 - K_1 t$                  | $\ln C$ vs $t$ | (5)[5] |
| Second order         | $\left(\frac{1}{C_t}\right) - \left(\frac{1}{C_0}\right) = -K_2 t$ | $\left(\frac{1}{C}\right)$ vs $t$ | (6)[5] |
| Pseudo first order   | $\log(Q_e - Q_t) = \log Q_e - \left(K/2.303\right) t$ | $\log(Q_e - Q_t)$ vs $t$ | (7)[16] |
| Pseudo second order  | $\left(\frac{t}{Q_t}\right) = \left(\frac{1}{KQ_e^2}\right) + \left(\frac{1}{Q_e}\right)$ | $\left(\frac{t}{Q_t}\right)$ vs $t$ | (8)[16] |

The adsorption capacities at time $t$ ($Q_t$) and equilibrium adsorption capacities ($Q_e$) at different concentrations were determined using equation 4 and 5 respectively:

$$Q_t = \left[\left(C_0 - C_t\right) V / W\right]$$

$$Q_e = \left[\left(C_0 - C_e\right) V / W\right]$$

where $C_0$, $C_t$, $C_e$ (mg/L) are the liquid-phase concentrations of metals ions at initial, at time $t$ and at equilibrium, respectively. $V$ is the volume of the solution, where $Q_e$ is the amount of light expanded clay aggregate adsorbed (mg/g) at equilibrium whereas $Q_t$ refer to the amount of light expanded clay aggregate adsorbed at any time $t$ (min). The estimated models and reaction rate constant are reported in Tables(4 to 7) for each ions. Table (3) for Cr(VI), Table (4) for Zn(II) , Table (5) for Cu(II) and Table (6) for Fe(III).

Table 4: Kinetic models of Cr(VI) ion at 25 °C, 45 °C and pH 2

| Temperatures | 25°C | 45°C |
|--------------|------|------|
| Kinetic model| $R^*$ | $K$  | $R^*$ | $K$  |
| Zero order   | 0.567 | 2.369 | 0.175 | 1.467 |
| 1st order    | 0.5   | 0.011 | 0.168 | 0.004 |
| 2nd order    | 0.417 | 6*10^{-3} | 0.16 | 2*10^{-3} |
| Pseudo first order | 0.905 | 0.0414 | 0.655 | 0.046 |
| Pseudo second order | 0.807 | 0.0334 | 0.116 | 0.3 |
Table 5: Kinetic models of Zn(II) ion at 25°C, 45°C and pH 5

| Temperatures | 25°C | 45°C |
|--------------|------|------|
| Kinetic model | R²  | K    | R²  | K    |
| Zero order   | 0.651 | 1.072 | 0.802 | 0.392 |
| 1st order    | 0.899 | 0.014 | 0.915 | 0.017 |
| 2nd order    | 0.977 | 0.001 | 0.808 | 0.0002 |
| Pseudo first order | 0.989 | 0.027 | 0.973 | 0.027 |
| Pseudo second order | 0.999 | 0.001 | 0.995 | 0.0334 |

Table 6: Kinetic models of Cu(II) ion at 25°C, 45°C and pH 4.5

| Temperatures | 25°C | 45°C |
|--------------|------|------|
| Kinetic model | R²  | K    | R²  | K    |
| Zero order   | 0.388 | 0.073 | 0.637 | 0.801 |
| 1st order    | 0.393 | 0.013 | 0.663 | 0.077 |
| 2nd order    | 0.242 | 0.003 | 0.717 | 0.012 |
| Pseudo first order | 0.947 | 0.0759 | 0.895 | 0.317 |
| Pseudo second order | 1 | 2.5*10⁻⁶ | 0.999 | 4*10⁻³ |

Table 7: Kinetic models of Fe(III) ion at 25°C, 45°C and pH 4.5

| Temperatures | 25°C | 45°C |
|--------------|------|------|
| Kinetic model | R²  | K    | R²  | K    |
| Zero order   | 0.75 | 0.205 | 0.612 | 0.054 |
| 1st order    | 0.782 | 0.031 | 0.455 | 0.029 |
| 2nd order    | 0.683 | 0.007 | 0.288 | 0.0180 |
| Pseudo first order | 0.917 | 0.089 | 0.901 | 0.096 |
| Pseudo second order | 1 | 3.333*10⁻⁸ | 1 | 1.333*10⁻¹ |

The results of the five kinetic reaction models tested for fitting the adsorption experimental data, showed successful fitting with the Pseudo 1st order for all the heavy metal ions while the experimental data of all the metal ions except Cr(VI) seemed to fit with the pseudo 2nd order model.
4. Conclusions

Light expanded clay aggregate has been prepared and tested in this research as an adsorbent for removal of Cr(VI), Zn(II), Cu(II) and Fe(III) from petrochemical industry wastewater. The equilibrium contact times are (90, 210, 60 and 75) min, respectively. The maximum adsorption took place at pH 2 for Cr(VI), 5 for Zn(II), 4.5 for both Cu(II) and Fe(III)). The optimum adsorption capacity at adsorbent practical size 0.15 mm for Cr(VI), Cu(II) and Fe(III) and 0.355 mm for Zn(II)). Increase in removal percentage of heavy metals ions with increase adsorbent dose was observed due to increase active sites in adsorbent. The adsorption data fitted well to the Freundlich isotherm model for Cr(VI), Zn(II), Cu(II) and Fe(III). The adsorption data of Zn(II), Cu(II) and Fe(III) fitted well to Pseudo second order reaction model while for Cr(VI) is fitted well to Pseudo first order. Decrease in percentage of adsorption Cr(VI), Zn(II) and Cu(II) with increase in temperature indicates that the process is exothermic in nature so low temperatures favor the adsorption process, except for Fe(III); the percentage of adsorption increases with increase in temperature indicates that the process is endothermic. Due to availability and high efficiency for removal of heavy metals ions the light expanded clay aggregate is an ideal adsorbent for removal of Cr(VI), Zn(II), Cu(II) and Fe(III) from aqueous solution.

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