Adsorption characteristics of Cu (II) onto CaCl₂ pretreated Algerian bentonite

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Abstract

Calcium treated bentonite clay (CTBC) was prepared by CaCl₂ impregnation of Algerian bentonite clay. The prepared adsorbent was characterized and successfully used to remove Cu (II) ions from aqueous solutions at different conditions (pH, stirring time and initial copper concentration). Results showed that the raw bentonite was changed completely into Ca-bentonite, which exhibits a high adsorption capacity (qt = 19.98 mg g⁻¹) at pH = 5.0. It appeared that the sorption mechanisms are simultaneous and strongly depend on pH value. In the pH range from 3–10, the removal of copper occurs mainly by ion exchange, surface metal complexation and precipitation of Cu(OH)₂. It was also found that the experimental data of kinetic adsorption are well fitted by the pseudo-first order model. Equilibrium data obeyed the Langmuir isotherm with maximum adsorption capacity of 55.48 mg g⁻¹. The mean adsorption energy predicted by Dubinin-Radushkevich model (E = 1.55 KJ/mol) shows the physical nature of the adsorption interactions. Results of this study suggest the potential of the prepared CTBC which can be used easily for fast decontamination of wastewater containing toxic metal ions.

1. Introduction

Heavy metals discharged in the environment form serious problems due to their toxic, accumulative, and non-degradable nature [1, 2]. Of these metals, copper is widely used in various industrial processes and present in fungicides and algicides [3]. At high levels, copper may be responsible for anemia, damage liver, respiratory problems or developed toxicity [4]. Hence, the recovery of excessive Cu (II) from wastewaters is necessary to avoid any damage of aquatic life related to this element.

To date, several techniques based on chemical precipitation, electrochemical processes, ion exchange, reverse osmosis [5], coagulation [6] and adsorption [7] have been investigated to remove Cu (II) ions from aqueous solutions. The latter is simple, available and recommended in the case of effluents with moderate and low Cu (II) concentrations [8]. In recent years, using clays such as sepiolite, zeolite, montmorillonite and smectite as low-cost adsorbent has attracted more attention among researchers [9]. Bentonite is available in nature that is a 2:1 clay mineral mainly consists of montmorillonite [10].

It contains an octahedral alumina sheet sandwiched between two tetrahedral silica sheets, forming a layered structure [11]. Bentonite has a cation-exchange capacity (CEC) ranging from 70 to 130 me q/100 g [12], chemical and mechanical stability, high specific surface area due to its textural characteristics [13]. The adsorption properties of bentonite can be improved by using pretreatment of calcination or doping with metal ions. In this regard, many researchers devoted to investigate the treatment of bentonite using metal salts such as Mg(OH)₂ [14], Mn(OH)₂ [1], CaCl₂ [15], Ca(OH)₂ [16], FeCl₃ [17], etc. But the use of CaCl₂ pretreated bentonite for heavy metals adsorption is very scarce in the existing literature. Hence, this work investigates the treatment of raw bentonite clay (RBC) by interacting with CaCl₂ to prepare calcium treated bentonite clay (CTBC) adsorbent. The adsorption mechanism of Cu (II) by using CTBC samples from aqueous solutions was
studied in batch mode. Clay samples were characterized by using XRD, FTIR, BET-N2, SEM-EDX and point of zero charge (pHpZC) analysis to gain insights on the adsorbents proprieties. Also, different kinetic and equilibrium models are used for analyzing experimental data and understanding the adsorption proprieties of Cu (II) onto CTBC samples.

2. Experimental

2.1. Materials and reagents

Calcium chloride (CaCl₂) and copper sulfate hydrated (CuSO₄·5H₂O) were of analytical grade (99%) and purchased from Aldrich. Samples of raw bentonite used in this study were obtained from Maghnia region in Algeria. Chemical composition of this clay is as follows: 55.00% SiO₂, 24.30% Al₂O₃, 3.58% MgO, 2.00% Fe₂O₃, 0.98% CaO, 0.70% Na₂O, 1.06% K₂O, 0.02% P₂O₅, 0.10% TiO₂, 0.10% SO₃, and 11% loss of ignition [18]. The cation exchange capacity (CEC) of the used clay is 0.97 meq g⁻¹ [19]. Others additives such as HCl (0.1 M) or NaOH (0.1 M) were used to control the pH of solutions.

2.2. Preparation of CaCl₂ treated bentonite

30 g of the starting clay was sieved to obtain particles size less than 80 μm and then ground. The purified material obtained was noted raw bentonite clay (RBC).

5 g of RBC was calcined at 500 °C for 4 h, crushed, and then dispersed in CaCl₂ solution at concentration equivalent to 100% CEC of bentonite as described by Meneguin et al (2017) [20]. The mixture was agitated for 24 h under vigorous stirring; the sorbent was separated and washed several times with deionized water until no more chloride ion was detected. Finally, the rinsed material was dried at 75 °C, and named CTBC.

2.3. Characterization of the clay adsorbents

The structural proprieties of clay samples were characterized by powder x-ray diffraction (XRD) using a PANalytical X’pert HighScore Plus’ diffractometer operating at 30 mA and 40 kV with CuKα radiation (λ = 1.5406 nm). The radial scans were recorded over the (2θ) range 3°–70° with scanning rate of 2° min⁻¹. The Fourier Transformed Infrared (FTIR) analysis was carried out using FTIR Affinity–1 Shimadzu apparatus. Measurements were obtained in the scan range of 400–4000 cm⁻¹ using the KBr disc technique (1/100 wt%).

The textural characteristics of adsorbents were investigated using the N₂ adsorption–desorption isotherms which measured on a Micrometrics ASAP 2420 instrument at 77.35 K. The BET surface area (S_{BET}) and total pore volume (V_{total}) were calculated using the Brunauer–Emmett–Teller adsorption method [21], and the micropores characteristics were determined according to the Barrett–Joyner–Hallender (BJH) method. The surface morphology and elemental analysis of adsorbents were studied by scanning electron microscopy (SEM) coupled by energy dispersive x-ray spectroscopy (EDX) analysis ‘Tescan Vega 3’. To investigate the surface properties of clay adsorbents, the pH_{PZC} (point of zero charge) was identified according to solid addition method [22]. 50 ml of 0.01 M NaCl was kept in flasks, for each the initial pH (pH₀) was adjusted at values ranging from 3 to 11. A 50 mg of clay was added to each solution, then, the dispersions were stirred for 24 h at room temperature. Finally, the final pH (pHₐ) of solutions was measured and the pH_{PZC} value is obtained from the plot of (pH₀–pHₐ) versus pH₀.

2.4. Batch adsorption experiments

All sorption experiments of Cu (II) onto clays were carried out in a batch manner. A known quantity of CTBC adsorbent was dispersed in copper solution at desired initial concentration (C₀). The mixture adsorbent–adsorbate was stirred at constant speed (200 rpm). After filtering the sample through a 0.45 μm membrane filter, the residual Cu (II) content was detected by atomic absorption spectrophotometer at the wavelength of 324.8 nm. All tests of adsorption were performed at pH = 5.0 (except for the pH influence study).

2.5. Data calculation and analysis

The quantity of Cu (II) adsorbed at time t (qt, mg/g) and the quantity adsorbed at equilibrium (qe, mg/g) were calculated by as follows:

\[ q_t = (C_0 - C_t) \times V / m \]
\[ q_e = (C_0 - C_e) \times V / m \]

where C₀, Cᵣ and Cₑ (mg/L) are the concentration of Cu (II) ions at initial, t time and equilibrium, respectively. V (L) is the volume of solution whereas m (g) represents the mass of clay.
**Table 1. Parameters of kinetic and isotherm equations.**

| Kinetic and isotherm models | Equation | Description parameters |
|-----------------------------|----------|------------------------|
| Pseudo-First-Order (PFO)    | \( q_t = q_e \left(1 - e^{-kt} \right) \) | \( q_e \) and \( q_i \) (in mg g\(^{-1}\)) are the adsorbed quantity of copper ions at equilibrium and at time \( t \), respectively. |
| Pseudo-Second-Order (PSO)   | \( q_t = \frac{q_e^{2}k_{t}}{1 + q_i^{2}k_{t}} \) | \( k_{t} \) (l/min), \( k_{i} \) (mg min\(^{-1}\) mg), \( K_p \) (mg g\(^{-1}\) min\(^{-1}\))\(^{1/2}\): rates constants. |
| Langmuir                    | \( q_t = \frac{q_{max}K_{c}C_{t}}{1 + K_{c}C_{t}} \) | \( C_{t} \): concentration of Cu (II) at equilibrium. |
| Factor of adsorption feasibility RL | \( R_L = 1/1 + K_{L}C_{i} \) | \( Q_{max} \) (mg g\(^{-1}\)): maximum monolayer adsorption capacity of the adsorbent. |
| Freundlich                  | \( q_L = K_{F}C_{t}^{n} \) | \( C_{i} \) (mg l\(^{-1}\)): initial copper ions concentration. |
| Dubinin-Radushkevich       | \( q_L = q_{c,cal}e^{-K_{D}c_{t}^{2}} \) | \( q_{c,cal} \) (mg g\(^{-1}\)): maximum sorption capacity. |
|                            | \( E = 1/\sqrt{2K_{D}n_{001}} \) | \( K_{D} \) (mol\(^{2}\)/l\(^{1}\)): constant related to the mean sorption energy. |

In order to investigate the Cu(II) adsorption mechanism onto tested clays, the experimental data were fitted to the pseudo-first-order [23], the pseudo-second-order [24] kinetic models. The adsorption isotherm was studied to describe the distribution of Cu (II) ions at the solid-liquid interface. The isotherm data were simulated by using Langmuir [25], Freundlich [26], and Dubinin-Radushkevich [27] isotherms to identify the appropriate model representing the sorption process. All equations of the aforementioned models are summarized in table 1.

The most suitable model for the kinetic and equilibrium data was identified by calculating the nonlinear \( R^2 \) [28], and residual root mean square error (RMSE) [29], which are given by:

\[
R^2 = 1 - \frac{\sum_{i=1}^{n}(q_{c,exp} - q_{c,cal})^2}{\sum_{i=1}^{n}(q_{c,exp} - q_{c,mean})^2}, \\
RMSE = \sqrt{\frac{1}{n-2} \sum_{i=1}^{n}(q_{c,cal} - q_{c,exp})^2}
\]

were \( q_{c,exp} \) (mg g\(^{-1}\)) is the adsorbed quantity at equilibrium, \( q_{c,cal} \) (mg g\(^{-1}\)) is the adsorbed quantity calculated from the equation, \( q_{c,mean} \) (mg g\(^{-1}\)) is the mean of \( q_{c,exp} \) values and \( n \) is the number of observations in the adsorption experiment.

### 3. Results and discussion

#### 3.1. Characterization of samples

Figure 1 illustrates the x-ray powder diffraction patterns of RBC and CTBC samples. In pattern of RBC, the peaks with distance of 12.45 Å, 4.48 and 1.49 Å correspond to montmorillonite phase. Distance of the (001) reflection corresponds to the interlamellar space [30], which was found to be 12.46 Å. This value corresponds to Na-montmorillonite clay with presence of a monolayer of water molecules [31]. XRD analysis also indicates that the studied bentonite contains quartz (Q), gypsum (G) and feldspar (F) as non-clay minerals. In CTBC sample, the value of \( d_{001} \) basal spacing shifted from 12.46 to 14.90 Å with displacement of its position (from 7.09° to 5.93°), which confirms that the raw bentonite has been changed completely into Ca-bentonite [15, 30].

The infrared spectrum (IR) of the RBC sample is presented in figure 2. The stretching band at 3632 cm\(^{-1}\) is due to the vibrations mode of OH groups bound to aluminium in the montmorillonite structure [30, 32]. The stretching of OH groups and angular deformation of H–O–H bands in the interlayer water molecules occur at 3468 and 1648 cm\(^{-1}\), respectively [33]. Bands at near 1031 and 795 cm\(^{-1}\) are assigned to the Si–O vibrations of tetrahedral layers [2, 34]. The pair of bands at 525 and 464 cm\(^{-1}\) result from Si–O–Al and Si–O–Si bending vibrations, respectively [2, 32]. The FTIR spectrum of CTBC shows a band at near 1645 cm\(^{-1}\) indicating the bending vibration of water. In addition, spectrum of CTBC-Cu(II) sample indicates that there was not structural change in clay sample after copper ion adsorption.

The morphology and elemental composition obtained from SEM-EDX analysis is provided in figure 3. Results show that the bentonite (RBC and CTBC) surface is dominantly composed of the silicon and aluminium oxide phases. A small amount of carbon contamination was detected and other elements such as Barium, Sodium, Magnesium, Calcium, etc. In CTBC sample, a decrease in Na\(^+\) an increase in Ca\(^{2+}\) content were
observed, indicating that the sodium interlayer cations were exchanged by Calcium. This finding was also confirmed by XRD analysis. Thus, the morphological properties of clays in figure 3 show an entirely amorphous material with presence of pores [33, 35].

Figure 1. X-ray diffraction patterns of RBC and CTBC samples (M: montmorillonite, Q: quartz, F: feldspar, D: dolomite).

Figure 2. FTIR spectra of RBC, CTBC, and CTBC after Cu (II) adsorption.

Figure 3. SEM images coupled by EDX analysis for RBC and CTBC samples.
Figure 4 shows the N2 adsorption/desorption isotherms of RBC and CTBC samples. According to IUPAC classification, the two plots are of type IV with hysteresis loops of H3 indicating the mesoporous structure of RBC and CTBC adsorbents [36]. It can be seen that the saturation of bentonite with calcium significantly reduces its uptake of N2. In similar study, Rutherford et al. (1997) [37] showed that the texture properties are related to the size of exchanged cation in the interlayer spacing of montmorillonite. The important textural characteristics of the RBC and CTBC adsorbents are listed in Table 2.

The point of zero charge (pHPZC) is defined as the pH value at which the total surface charge of adsorbent is zero [22]. The pH_{PZC} of RBC and CTBC samples was found at 7.38 and 7.04 respectively (figure 5), which is similar to other clays, such as Na-smectite (pH_{PZC} = 6.39) and Ca-smectite (pH_{PZC} = 6.24) [31]. When pH of solution > pH_{PZC}, the clay react as negative surface and as a positive surface when solution pH < pH_{PZC} [38]. In this study, the sorption experiments were performed at pH = 5.0 implying that the surface of CTBC was positively charged and the ion exchange mechanism can occurred [20].

Table 2. Textural parameters of RBC and CTBC samples.

| Samples | BET surface area (m² g⁻¹) | External surface (m² g⁻¹) | Total pore volume (cm³ g⁻¹) | Total volume in pores ≤185.8 nm |
|---------|---------------------------|---------------------------|-----------------------------|--------------------------------|
| RBC     | 52.82                     | 26.08                     | 0.0845                      | 0.0495                         |
| CTBC    | 28.47                     | 22.43                     | 0.0713                      | 0.0518                         |

Figure 5. Point of zero charge of RBC and CTBC samples.
3.2. Effect of pH and adsorption mechanism

The solution pH is a critical parameter in the mechanism study because it affects not only the dominant species of solute but also the surface charge of adsorbent. The effect of pH on Cu(II) adsorption using CTBC was studied at initial pH solution ranging from 3 to 10 (figure 6). Results show that the removal of Cu(II) increased with increasing pH values and reached its maximum at pH $\geq 7.0$.

According to the distribution of aqueous Cu(II) species as a function of pH, Cu(II) cation is the dominant copper species in the solution pH range of 3–6. These metal ions are weakly attached to the positive CTBC surface (figure 6) and compete with H$^+$ for available sites at acid pH $[39]$. The copper removal is mainly occurred by a cation exchange between Cu(II) and the interlayer Ca$^{2+}$ ions of montmorillonite. This spontaneous interaction is independent on pH value and can be given as follows $[10]$:

$$Ca^{2+} - \text{clay} + Cu^{2+} = Cu^{2+} - \text{clay} + Ca^{2+}$$

At pH above pH$_{PZC}$, the reduction of Cu(II) is improved by formation of surface metal complexes on the ionized silanol and aluminol groups (Si–O$^-$ and Al–O$^-$). The complex reaction of Cu$^{2+}$ and Cu(OH)$^+$ can be expressed as follows $[1, 10]$:

$$S - O^- + Cu^{2+} = S - OCu^+$$

$$S - O^- + Cu(OH)^+ = S - OCu(OH)$$

In addition, copper hydroxide (Cu(OH)$_2$) start to form precipitate and increase the removal of metal content at pH $> 7$ $[7]$.

3.3. Adsorption kinetic

The influence of stirring time on Cu(II) adsorption at initial concentration of 50 mg l$^{-1}$ is depicted in figure 7. As seen in this figure, the uptake of copper ions by CTBC adsorbent is a fast phenomenon and reaches its maximum in less than 60 min of stirring time ($q_t = 19.98$ mg g$^{-1}$). This rapidity of copper removal shows that CTBC has a good affinity toward metal cations. Moreover, an increase of final pH values was observed confirming the occurrence of exchange reaction of Cu(II) cations with H$^+$. Modeling of adsorption kinetic show that the PFO equation well describes the experimental data compared to PSO model (figure 7). This finding is confirmed by the higher correlation value ($R^2$) and the less difference between the experimental and calculated $q_e$ values in the case of PFO equation (table 3). The more suitability of the PFO model was also confirmed by the small value of RMSE.

3.4. Modeling of adsorption isotherm

To explore the interactions adsorbent-adsorbate involving adsorption, adsorption isotherm was obtained by varying the Cu(II) initial concentration at a fixed temperature and constant dose of adsorbent. In this study, the nonlinear forms of Langmuir, Freundlich and Dubinin-Radushkevich models were used to fit the equilibrium data. The curve of $q_e = f(Ce)$ shown in figure 8 corresponds to isotherm of type L according to Giles et al (1974) $[40]$, which indicate the high affinity of CTBC adsorbent toward Cu(II) in solution. As observed in table 4, the three models can describe the equilibrium data. But the Langmuir equation is more suitable than the Freundlich and D-R equations.
The best fit of Langmuir model is confirmed by the high correlation \( R^2 \approx 1 \) and the small error value \( \text{RMSE} = 1.098 \). According to this model, the maximum adsorption capacity is 55.48 mg g\(^{-1}\). Moreover, value of the dimensionless factor \( R_L \) (0 < \( R_L \) < 1) indicates the favorability of Cu(II) adsorption onto CTBC. The
mean adsorption energy calculated from D-R model was found to be 1.55 Kj mol⁻¹, which suggested the physical nature of the adsorption interactions [41].

4. Conclusion

In this study, bentonite was treated with calcium chloride to produce Ca-bentonite clay. This material was employed as efficient adsorbent to remove copper from aqueous solutions. Based on results of the batch adsorption experiments, some important conclusions can be noted below. First, adsorption kinetic of Cu(II) ions onto CTBC is fast and well described by the PFO model. Second, sorption process depends on pH value and occurs mainly by ion exchange, surface copper complexation and precipitation of copper hydroxide (Cu(OH)₂). Third, isotherm data follow the Langmuir model (Q max = 55.48 mg g⁻¹), and the adsorption energy (E = 1.55 Kj mol⁻¹) reflects the physical nature of adsorbent-adsorbate interactions according to theoretical assumptions. Finally, CTBC can be suggested as efficient adsorbent for the rapid removal of heavy metals from wastewater.

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