Experimental study of coupling complexation-adsorption of Cu(II) on activated carbon

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Abstract

The water consumed for the industrial or domestic needs is rejected to 80\% on average in the form of effluents in charge of harmful substances for the environment, the health of the men, and all the alive beings.

An experimental study relating to on the one hand the adsorption of Cu\textsuperscript{2+} on the activated carbon was undertaken to highlight the importance of certain experimental parameters, in particular the pH, the temperature, the agitation and the mass of carbon. In addition, our work concerned the Cu\textsuperscript{2+} complexation by the EDTA (Ethylene diamine tetra-acetate), then the adsorption of the complex formed on the activated carbon owing to the fact that this last has a great affinity of adsorption of the organic substances, therefore a comparative study was realised. The whole of our results makes it possible to confirm that the activated carbon absorbs preferentially the organic component, and that in the case of copper and the EDTA the adsorption of Cu\textsuperscript{2+} is more significant than the adsorption of the complex EDTA-Cu\textsuperscript{2+}, because this last was formed in small proportions with various values of the pH; the analysis of the free cation in solution is carried out by atomic absorption.

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1. Introduction

In front of the increasing requirements out of fresh water, and impossibility of being satisfied with the natural resources, humanity is led to study and develop various processes allowing to obtain it starting from sea waters, brackish water, and of the water used under acceptable conditions technically and economically. During many years, the industries located near river (for reasons of cooling of process, of transport) rejected their effluents in those. This phenomenon (limited more and more by the installation of purification station to the centre even of the factories site), it is necessary to add the erosion and the...
streaming of water on the grounds and roadways. Water constitutes a fundamental element as regards pollution, since in the case of metals, as for others made up, this one will support many chemical reactions. Water transports heavy metals, and the inserts in the food chains (algae, fish, etc.). Even if heavy metals are generally present at the state of traces, they do not remain about it less very dangerous, since their toxicity develops by bio-accumulation in the organizations. One calls heavy metals the natural metal elements whose density exceeds 5g/cm³. Those are generally present in the environment in the form of traces: mercury, lead, cadmium, copper, arsenic, nickel, zinc, cobalt, manganese. Most toxic of them are lead, cadmium and mercury. The objective of this study is to compare the elimination of a metal cation (Cu²⁺) by coupling complexation-adsorption with the traditional technique adsorption on activated carbon of the same cation Cu²⁺; owing to the fact that the activated carbon has a great affinity to adsorb the organic matter, knowing that the agent of complexation (ligand) is an organic molecule (ethylene diamine tetra-acetate:EDTA). In the first part, we were interested to adsorption of Cu²⁺ on the activated carbon to know the importance of certain experimental parameters, in particular pH, the temperature, the agitation and mass of adsorbant. In the second part, our work concerned the Cu²⁺ complexation by the EDTA, then the formed complex is adsorbed on the activated carbon.

2. Adsorption

Adsorption is a process of separation which consists of a solid fluid interaction, molecules of an aqueous solution in liquid phase (adsorbate) diffuse towards the porous solid phase (adsorbent) thus forming a new phase on solid, the surface known as: adsorbed phase. It is thus a phenomenon of transfer of matter; adsorption is a particularly effective treatment to remove organic matter.

Activated carbon, one of the most significant commercial adsorbent, is a carbonaceous material having a great porosity and a great specific surface. It is largely used in processes of purification, in the water treatment and catalysis [1,2]. The materials most used for the preparation of the activated carbon are wood, coal, lignin, bituminous coals and polymers [3,4,5].

3. Complexation of a metal cation by ligand

The complex is a soluble species (ion or molecule) resulting from association from ions or molecules (others that H⁺ and OH⁻) in water. That is to say a divalent cation M²⁺ (central ion), and is the ligand (particle) Y⁴⁻ (EDTA); in a solution which contains the mixture Y⁴⁻ et M²⁺ we will have the following reaction:

\[ Y^{4-} + M^{2+} \leftrightarrow MY^{2-} \quad (1) \]

With a dissociation constant of the complex \( K_c \), which is defined by:

\[ K_c = \frac{[Y^{4-}][M^{2+}]}{[MY^{2-}]} \quad (2) \]

\( K_c \) is the dissociation constant of the complex \( MY^{2-} \), 
[i] is the concentration of \( i \) species.

These complexes are formed by association of a central ion generally a metal M (very often a metal of transition), and of chemical species \( ^{''} \text{rich} ^{''} \) in electrons (anions, molecules having a doublet not divided) that one indicates under the name of co-ordinate.

It is said that the central metal ion is complexed by the co-ordinate which plays a role of complexant. The complexation causes to dissimulate the complex with its usual reagents. The complexation reaction can be used to prevent the precipitation of certain components. The complexation reactions are generally fast and can be regarded as instantaneous [6,7].
4. Materials and method

In a erlen Meyer, 1500 ml of a Cu$^{2+}$ solution are introduced with a given concentration, to which one adds a quantity of activated carbon, the solution obtained is provided with one agitation using a magnetic stirrer. After each 10 minutes, the solutions taken are filtered then the filtrate passes to the analysis. The method of analysis used is the atomic absorption.

For the whole of our handling, it was studied the influence: mass of the activated carbon, stirring velocity, temperature, pH and of the initial concentration of the EDTA on the elimination of copper according to time.

5. Results:

5.1. Case of the adsorption of Cu$^{2+}$ on activated carbon

5.1.1. Influence of stirring velocity

According to figure 1, it is shown that one increase stirring velocity involves a reduction in the quantity of Cu$^{2+}$, that wants to say that agitation supports the contact between Cu$^{2+}$ and the activated carbon.

5.1.2. Influence of temperature

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5.1.2. Influence of temperature

According to figure 2, it is shown that one increase temperature involves an increase in the quantity of Cu$^{2+}$, that wants to say that temperature supports the contact between Cu$^{2+}$ and the activated carbon.
Increase in the temperature leads to a considerable reduction in the quantity of Cu²⁺, which was adsorbed on the activated carbon, thus this last adsorbs well at high temperatures.

5.1.3. Influence of pH

Figure 3 shows that with pH equal to 1 the Cu²⁺ remain almost in solution in free form and it is not adsorbed on the activated carbon; an increase in pH until 5 support a very great adsorption. On the other hand with pH equal to 10 the Cu²⁺ is in majority in form Cu(OH)₂ who precipitates and it is may be adsorbed mainly by the activated carbon.

![Figure 3: Variation of the quantity of Cu²⁺ according to time at various pH values.](image)

5.1.4. Influence of the activated carbon mass

The results deferred on Figure 4 show that for an increase in quantity of adsorbent (activated carbon) and for the same initial quantity of Cu²⁺, there is an evolution of holding capacity in the course of time. This result can be explained by the increase in the active sites of adsorbant.

![Figure 4: Influence of the quantity of the activated carbon on the elimination of copper according to time.](image)
5.2. Case of the coupling of the complexation of Cu\(^{2+}\) by the EDTA and adsorption on activated carbon

The EDTA (Y\(^4-\)) can react on Cu\(^{2+}\) to give the complex CuY\(^2-\) which is a rather stable complex according to the reaction:

\[
Y^{4-} + Cu^{2+} \leftrightarrow CuY^{2-} \tag{3}
\]

This reaction (3) is favoured in basic medium, if the pH solution becomes lower than 10, the Y\(^4-\) reacts on the H\(^+\) ions according to the following reactions:

\[
\begin{align*}
Y^{4-} + H^+ &\leftrightarrow HY^{3-} \quad pK_a=10.3 \tag{4} \\
HY^{3-} + H^+ &\leftrightarrow H_2Y^{2-} \quad pK_a=6.2 \tag{5} \\
H_2Y^{2-} + H^+ &\leftrightarrow H_3Y^{-} \quad pK_a=2.7 \tag{6} \\
H_3Y^{-} + H^+ &\leftrightarrow H_4Y \quad pK_a=2.0 \tag{7}
\end{align*}
\]

Where pKa is the acidity constant.

This whole of reactions can be recapitulated by the distribution diagram of the EDTA species according to pH (figure 5).

![Distribution diagram of the EDTA(Y\(^4-\)) species according to pH.](image)

Thus by decreasing pH values of the solution, the complexation reaction becomes slower until very weak because Y\(^4-\) are disappeared from the solution.

In addition, the Cu\(^{2+}\) is in free form up to a value near to 7 where it starts to precipitate according to the distribution diagram of the Cu\(^{2+}\) species according to the pH (figure 6).
Figure 6: Distribution diagram of the copper (II) species according to pH
For: \([\text{Cu}^{2+}]_{\text{total}} = 3.94 \times 10^{-4} \text{ M in 0.1 M NaNO}_3 \) \([8]\)

Figure 6 shows the various \(\text{Cu}^{2+}\) species according to the pH.

5.2.1. Comparison between adsorption and complexation-adsorption at pH=10

According to results presented on figure 7, it is noted that when it is about adsorption alone, one returns to the same case of figure 3, on the other hand when it is about a combination complexation-adsorption the results are very different, that can be explained by the fact that with the pH equal to 10 majority of \(\text{Cu}^{2+}\) as one has says it already is in the form of a precipitate \(\text{Cu(OH)}_2\) and that the EDTA can react only on the small quantity of \(\text{Cu}^{2+}\) (according to the distribution diagram of the \(\text{Cu}^{2+}\) species) which remains free, and as the activated carbon adsorbs the organic components preferentially, thus the free and complexed EDTA occupies the whole of the sites of adsorption, for this reason it finds after analysis by atomic absorption that there is a great quantity of \(\text{Cu}^{2+}\) in free form and precipitate remains in solution.

Reduction in the quantity of \(\text{Cu}^{2+}\) according to time (always in the case of the combination complexation-adsorption) can may be explained by the fact that the precipitate \(\text{Cu(OH)}_2\) is not very soluble with this value of the pH, it releases a small quantity of \(\text{Cu}^{2+}\) according to the reaction:

\[
\text{Cu(OH)}_2 \leftrightarrow \text{Cu}^{2+} + 2\text{OH}^-
\]  

(8)
This dissociation is weak with pH equal to 10; the EDTA react on the small quantity dissociated of Cu\(^{2+}\) of the reaction (8) according to:

\[
\text{Y}^{4-} + \text{Cu}^{2+} \rightleftharpoons \text{CuY}^{2-}
\]  
(9)

Reactions (8) and (9) moves on the right according to the Lechatelier law.

5.2.2. Comparison between adsorption and complexation-adsorption of Cu\(^{2+}\) (at pH =7):

![Figure 8: Comparison between adsorption and coupling complexation-adsorption of Cu\(^{2+}\) (by the EDTA) (at pH =7).](image)

We can say that at pH equal to 7, the adsorption of Cu\(^{2+}\) only is better that coupling complexation-adsorption, it is, perhaps, because the complexation is favoured in alkaline medium.

5.2.3. Influence of initial concentration of the EDTA:

![Figure 9: Influence of initial concentration of EDTA on the Cu\(^{2+}\) elimination according to time (with pH = 7).](image)
Figure 9 shows that when the concentration of the EDTA increases the Cu\textsuperscript{2+} elimination becomes less significant, made that with this value of the pH the EDTA and the Cu\textsuperscript{2+} do not react in great quantity and that increase in the concentration of the ligand (EDTA) support the occupation of the adsorption sites of the activated carbon, thus the sites are occupied almost entirely by the EDTA.

6. Conclusion

An experimental study relating to on the one hand the adsorption of Cu\textsuperscript{2+} on the activated carbon was undertaken to highlight the importance of certain experimental parameters, in particular pH, the temperature, the agitation and mass of activated carbon. In addition, our work concerned the Cu\textsuperscript{2+} complexation by the EDTA (ethylene diamine tetra-acetate), then the adsorption of the complex formed on the activated carbon, fact that this last has a great affinity of adsorption of the organic substances, thus a comparative study was undertaken.

The whole of our results makes it possible to confirm that: An increase stirring velocity and temperature of the solution involve a considerable reduction in the quantity of Cu\textsuperscript{2+} according to time. The adsorption of Cu\textsuperscript{2+} is favoured in the basic medium; and that the increasing quantity of adsorbent (activated carbon) increase the holding capacity of Cu\textsuperscript{2+} according to time.

The activated carbon adsorbs preferentially the organic component, and that in the case of copper and the EDTA, the adsorption of Cu\textsuperscript{2+} is more significant that the adsorption of the complex EDTA-Cu\textsuperscript{2+}, because this last was formed in small proportions with various values of the pH. Analysis of Cu\textsuperscript{2+} in all its forms is realized by atomic absorption.

7. References