STUDY OF THE Cu(II) REMOVAL FROM AQUEOUS SOLUTIONS BY ADSORPTION ON TITANIA

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ABSTRACT

The removal of heavy metals from wastewaters is a matter of paramount importance due to the fact that their high toxicity causes major environmental pollution problems. One of the most efficient, applicable and low cost methods for the removal of toxic metals from aqueous solutions is that of their adsorption on an inorganic adsorbent. In order to achieve high efficiency, it is important to understand the influence of the solution parameters on the extent of the adsorption, as well as the kinetics of the adsorption. In the present work, the adsorption of Cu(II) species onto TiO_2 surface was studied. It was found that the adsorption is a rapid process and it is not affected by the value of ionic strength. In addition, it was found that by increasing the pH, the adsorbed amount of Cu^{2+} ions and the value of the adsorption constant increase, whereas the value of the lateral interaction energy decreases.

INTRODUCTION

The removal of toxic heavy metals from wastewaters is considered as one of the most important areas of water treatments, since the excessive industrial disposal of heavy metals creates major pollution problems (Li *et al.*, 2009). Species of toxic metals and metalloids, such as As, Sb, Cr, Cu, Pb, Zn, Co, Ni, Cd and Hg in the aquatic systems create serious health risks and problems to humans and other living organisms as well (Mckay, 1995). Copper containing wastewaters are waste products of various chemical industries, such as mining, smelting, extracting, and finishing processes. It is a highly toxic element and an excessive intake results in its accumulation in the liver and production of gastrointestinal problems, therefore its removal from wastewaters is of high importance (Spark *et al.,* 1995; Korngold *et al.*, 1996; Lee and Davis, 2001; Jung *et al.*, 2001; Vengris *et al.*, 2001; Alkan and Dogan, 2001; Goyal *et al.*, 2001).

Several methods have been widely applied for the removal of heavy metals from aqueous solutions, including precipitation, ion exchange, filtration, solvent extraction, membrane technology, etc. (Quintelas *et al.*, 2009), but most of these processes are not widely acceptable due to their high costs, low efficiency and inapplicability to a wide range of pollutants. On the other hand, adsorption process is well recognized as one of the most effective methods for removing heavy metals from their matrices. Adsorption is mainly based on the utilization of solid adsorbents (Camel, 2003; Jal *et al.*, 2004).

Inorganic solid adsorbents, as Al_2O_3, SiO_2, ZrO_2, and TiO_2 are characterized by their high mechanical properties and strong resistivity to thermal degradation, as compared to other biosorbents or organic adsorbents (Naiya *et al.*, 2009). In particular, TiO_2 presents several other advantages when applied as an adsorbent for heavy metal removal. It is an extensively studied oxide and it is used as model mineral because of its high chemical stability and negligible solubility over a wide pH range. In addition, it presents ideal point of zero charge [around 6

(Bourikas *et al.*, 2001)], which makes it possible to study adsorption on positively and negatively charged surfaces of TiO_2 over a broad pH range (Vandenborre *et al.*, 2007; Olsson *et al.*, 2003; Tel *et al.*, 2004). TiO_2 exists in two major polymorphic forms, anatase and rutile. Since the surface area of the anatase powder is typically greater than that of rutile, anatase is preferred in most applications (Henrich and Cox, 1994). Titanium dioxide has been studied as a photocatalyst and presenting many advantages in water purification in the presence of UV radiation (Legrini *et al.*, 1993). Anatase was extensively selected as a photocatalyst because it had been reported that it was more effective than rutile (Wold, 1993).

Concerning the sorption of the aquatic complex $[Cu(H_2O)_6]^{2+}$ on titania surface, there are rare relevant studies in the literature. Maybe in the most representative one, the study of the sorption of copper species on the titania's surface showed that it increases with increasing pH (2 to 5) and remains constant for greater pH values. Also it was found that it is an endothermic process, since the adsorption amount increases with increasing temperature (Kim *et al.*, 2003). On the other hand, a huge number of studies refer to the photocatalytic oxidation of organic substances, contained in TiO_2 suspensions, through solar or UV radiation. This photocatalytic effect increases by the presence of certain concentration of Cu^{2+} ions into the suspension (Fujihira *et al.*, 1981; Fujihira *et al.*, 1982; Okamoto *et al.*, 1985; Bideau *et al.*, 1990; Wei *et al.*, 1990; Butler and Davis, 1993). Besides the presence of Cu^{2+} ions, the adsorption of different Cu^{2+} species on the TiO_2 surface is determinant for the TiO_2 photocatalytic effectiveness, too. As an example, at the photocatalytic oxidation of the acetic acid, the species $Cu(CH_3COO)^+$ increases the effectiveness of the catalyst, whereas the species $Cu(CH_3COO)_2$ deactivates the catalyst (Bideau *et al.*, 1991). It is therefore obvious that the use of titania as an adsorbent, not only contributes to the removal of heavy metal ions from the wastewater, but also to the disintegration of the organic impurities of the wastewater, due to its photocatalytic activity (Matthews, 1986; Matthews, 1988; Nishimoto *et al.*, 1985; Tanguay *et al.*, 1989; Morooka *et al.*, 1989).

In order to design an adsorption column it is necessary to understand the mechanism and kinetics of the adsorption. A great number of studies, concerning heavy metal ion adsorption at the solid / liquid interface, showed that it depends on parameters such as the system pH, the initial metal concentration, the amount of the adsorbent and the temperature (Sen *et al.*, 2002; Salim *et al.*, 1992; Cheung *et al.*, 2000; Sen and Khilar, 2006; Gurses *et al.*, 2006). In the present work, the influence of the solution parameters on the extent of the adsorption was studied, in order to determine those that provide high efficiency for Cu^{2+} removal from wastewaters.

EXPERIMENTAL

Substances. Industrial titania (Degussa P25, with SSA 50 $m^2 g^{-1}$ and pore volume 0.15 $cm^3 g^{-1}$) rich in anatase (anatase 80% w/w) and rutile (20% w/w) was used as an adsorbent. Its composition was verified by XRD analysis. $Cu(NO_3)_2 \cdot 2.5H_2O$ reagent (98% ALDRICH) was used as copper source and KCl (MERCK), KNO_3 (RIEDEL – deHAEN) were used for the preparation of the indifferent electrolyte solutions. Standard solutions of KOH and HNO_3 were used for the pH adjustment and buffer solutions (NBS: pH_1 = 7.413 and pH_2 = 4.008) were used for the electrode's calibration.

Set up. All titrations took place in a thermostated at 25 ^{o}C, double walled Pyrex vessel equipped with a magnetic stirrer and a perspex lid with holes for the electrodes and nitrogen gas. The pH during the titration experiments was controlled by Metrohm 712SM Titrino and 714STAT Titrino, which were compiled with the suitable software. Nitrogen gas was passed into the vessel during the experiments in order to prevent the dilution of atmospheric CO_2, which would bring about a change in the pH.
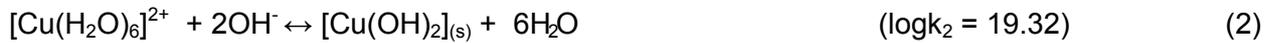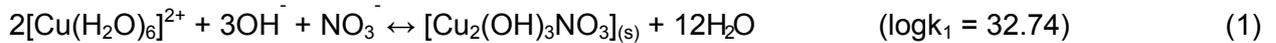
The first experiments were performed by using two different electrolytes, KCl and KNO_3, in order to choose the suitable one. The titrations took place by adding suitable volume of KOH every time the change of the pH was lower than 0.017 pH units per minute. Then, titration experiments of different Cu^{2+} concentration solutions were performed, both in the presence and in the absence of TiO_2, in order to obtain the pH range where no precipitation of copper occurred. These experiments were also performed for two different suspensions of TiO_2 as well

as for a blank solution, at ionic strength equal to 0.1M. Kinetics experiments were performed for five initial copper concentrations and three pH values, while each experiment held for 24 hours. Samples were collected at specific times and filtrated, in order to determine the adsorbed quantity of copper. Adsorption edges experiments were conducted at six different initial Cu(II) concentrations in the range $10^{-4} - 2\times10^{-2}$ M and in a pH range 3 – 7 with a step equal to 0.5, at ionic strength 0.1M KNO$_3$. The above procedure was repeated for two different values of ionic strength. Equilibrium adsorption experiments were performed for 4 initial pH values and in the range of Cu(II) concentrations 10^{-4} to 2×10^{-2} M. The change of the pH due to the sorption of Cu(II) species onto TiO$_2$ was corrected by the addition of KOH.

In all adsorption experiments, the filtrates of the aqueous suspensions were analyzed either spectrophotometrically (Lamda-35 UV-Vis, Perkin Elmer) or by atomic absorption analysis using air-acetylene flame (AAnalyst 700, Perkin Elmer, detection limit 0.077 ppm) and the corresponding solids were characterized by powder X-ray diffraction (XRD, Philips 1830/40).

RESULTS – DISCUSSION

The first step in our study was the selection of the suitable electrolyte (KNO$_3$ or KCl). Copper precipitates as Cu$_2$(OH)$_3$Cl$_{(s)}$ and/or Cu(OH)$_{2(s)}$ in the presence of KCl, according to equilibriums (2), (3) and as Cu$_2$(OH)$_3$NO$_{3(s)}$ and/or Cu(OH)$_{2(s)}$ according to equilibriums (1), (2).

$$2[Cu(H_2O)_6]^{2+} + 3OH^- + NO_3^- \leftrightarrow [Cu_2(OH)_3NO_3]_{(s)} + 12H_2O \qquad (\log k_1 = 32.74) \qquad (1)$$

$$[Cu(H_2O)_6]^{2+} + 2OH^- \leftrightarrow [Cu(OH)_2]_{(s)} + 6H_2O \qquad (\log k_2 = 19.32) \qquad (2)$$

$$2[Cu(H_2O)_6]^{2+} + 3OH^- + Cl^- \leftrightarrow [Cu_2(OH)_3Cl]_{(s)} + 12H_2O \qquad (\log k_3 = 34.60) \qquad (3)$$

As it is observed in Figure 1(a),(b), copper is precipitated at lower pH value in the presence of Cl$^-$ ions than in the presence of NO$_3^-$ ions. This observation is in agreement with the values of the respective formation constants (equilibria (1) to (3)). Thus, the most suitable electrolyte proved to be KNO$_3$.
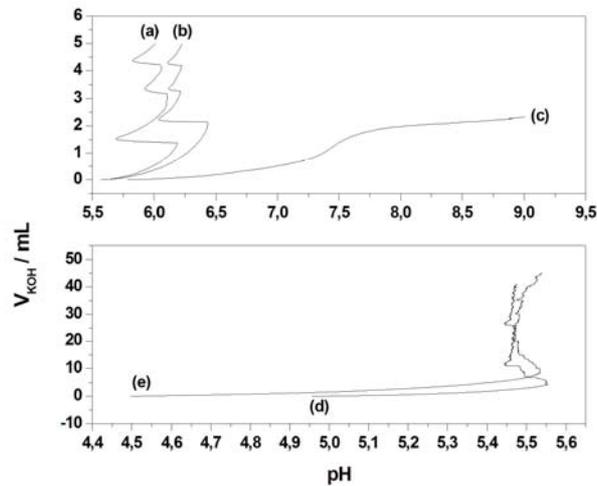

Figure 1. Potentiometric titration curves at 25°C. (a) I = 0.1M KCl / 10^{-3}M Cu^{2+},
(b) I = 0.1M KNO$_3$ / 10^{-3}M Cu^{2+}, (c) I = 0.1M KNO$_3$ / 10^{-4}M Cu^{2+}, (d) I = 0.1M KNO$_3$ / 10^{-2}M Cu^{2+}
and (e) I = 0.1M KNO$_3$ / 10^{-2}M Cu^{2+} + 0.05g TiO$_2$

In aqueous solutions, Cu^{2+} ions participate in various equilibria forming soluble and insoluble species. Therefore we studied the Cu^{2+} speciation using a program for the computation of chemical equilibria in aqueous media (Papelis *et al.*, 1988). The relevant ionic equilibria as well as the corresponding formation constants at 25°C and zero ionic strength are presented in Table 1.

Figure 2, indicates that the dominant copper species is that of Cu^{2+} for an extensive pH range at 0.1M KNO$_3$ and 25 °C.

Table 1. Equilibria of Cu^{2+} ions and their corresponding formation constants, at $25^{o}C$ and zero ionic strength (NIST Version 6, 2001)

$[Cu(H_2O)_6]^{2+} + OH^- \leftrightarrow [Cu(OH)(H_2O)_5]^+ + H_2O$ $\qquad$ $logk_4 = 6.5$ $\quad$ (4)

$[Cu(H_2O)_6]^{2+} + 2OH^- \leftrightarrow [Cu(OH)_2(H_2O)_4]^0_{(aq)} + 2H_2O$ $\qquad$ $logk_5 = 11.8$ $\quad$ (5)

$2[Cu(H_2O)_6]^{2+} + 2OH^- \leftrightarrow [Cu_2(OH)_2(H_2O)_{10}]^{2+} + 2H_2O$ $\qquad$ $logk_6 = 17.4$ $\quad$ (6)

$3[Cu(H_2O)_6]^{2+} + 4OH^- \leftrightarrow [Cu_3(OH)_4(H_2O)_{14}]^{2+} + 4H_2O$ $\qquad$ $logk_7 = 35.2$ $\quad$ (7)

$[Cu(H_2O)_6]^{2+} + 3OH^- \leftrightarrow [Cu(OH)_3(H_2O)_3]^- + 3H_2O$ $\qquad$ $logk_8 = 14.5$ $\quad$ (8)

$[Cu(H_2O)_6]^{2+} + 4OH^- \leftrightarrow [Cu(OH)_4(H_2O)_2]^{2-} + 4H_2O$ $\qquad$ $logk_9 = 15.6$ $\quad$ (9)

$2[Cu(H_2O)_6]^{2+} + OH^- \leftrightarrow [Cu_2(OH)(H_2O)_{11}]^{3+} + H_2O$ $\qquad$ $logk_8 = 8.2$ $\quad$ (10)

$[Cu(H_2O)_6]^{2+} + NO_3^- \leftrightarrow [Cu(NO_3)(H_2O)_5]^+ + H_2O$ $\qquad$ $logk_8 = 0.5$ $\quad$ (11)

$[Cu(H_2O)_6]^{2+} + 2NO_3^- \leftrightarrow [Cu(NO_3)_2(H_2O)_4]^0_{(aq)} + 2H_2O$ $\qquad$ $logk_9 = -0.4$ $\quad$ (12)
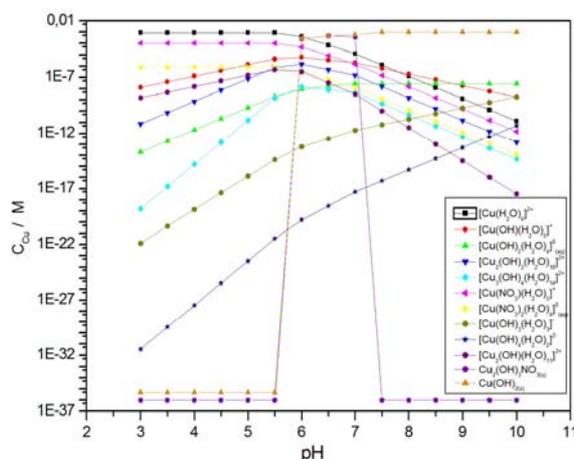

Figure 2. Concentration of copper species existing in an aqueous solution of $I = 0.1M$ KNO_3, $25\ ^oC$ and $10^{-3}M$ initial copper concentration, as a function of pH

In order to study the pH value where $Cu_2(OH)_3NO_{3(s)}$ or/and $Cu(OH)_{2(s)}$ precipitation takes place at the homogeneous solution, titration experiments at three different Cu^{2+} concentrations were performed at the same value of ionic strength. It may be seen (Fig. 1(c)) that for relatively low copper concentrations (10^{-4} M) no precipitation takes place. At higher copper concentrations (10^{-3} M), copper precipitates at a pH value equal to 6.5, while at a concentration equal to 10^{-2} M, precipitation occurs at pH 5.6. Those experimental results are consistent with the theoretical data, too. It may be observed that even in the case of the highest copper concentration, the decrease of pH because of the copper precipitation is negligible due to the shift to the left of equilibria (4) - (10) (Table 1).

In addition to the homogeneous precipitation studied above, the titania's contribution to a possible surface precipitation was checked. In this case (Fig. 1(e),(d)) it was found that TiO_2 causes probably $Cu_2(OH)_3NO_{3(s)}$ and / or $Cu(OH)_{2(s)}$ precipitation but at a quite less extent, since the pH value where precipitation occurs (Fig.1(e)) is slightly lower than that of the homogeneous precipitation (Fig.1(d)). The greater quantity of basic solution needed to reach the pH value where precipitation starts, in the presence of titania, is attributed to the simultaneous proton removal due to the deprotonation of the surface (pH > pzc).

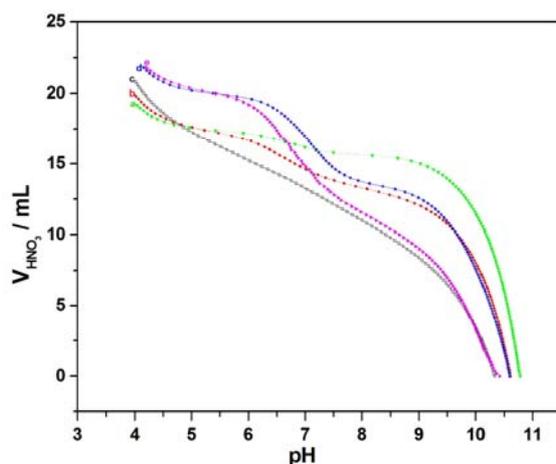*Figure 3*. Potentiometric titration curves at $25^{o}C$, I = 0.1M KNO_3, (a) 0.8g TiO_2, (b) 0.4g TiO_2, (c) blank, and I = 0.02M KNO_3, (d) blank and (e) 0.2g TiO_2

The determination of the point of zero charge, pzc, of titania was achieved through the potentiometric titrations experiments of two suspensions containing different solid mass (0.8 g and 0.4 g respectively at 150 mL KNO_3), as well as of a blank KNO_3 solution (Fig. 3). The pzc of titania is the common intersection point of the titration curves (Bourikas *et al.*, 2003), which in this case corresponds at a pH value equal to 4.8. In addition, potentiometric titration experiments of a suspension containing 0.2 g TiO_2 and a blank KNO_3 solution, were repeated at ionic strength 0.02M KNO_3. The common intersection point of the titration curves obtained was almost identical with the previous one.
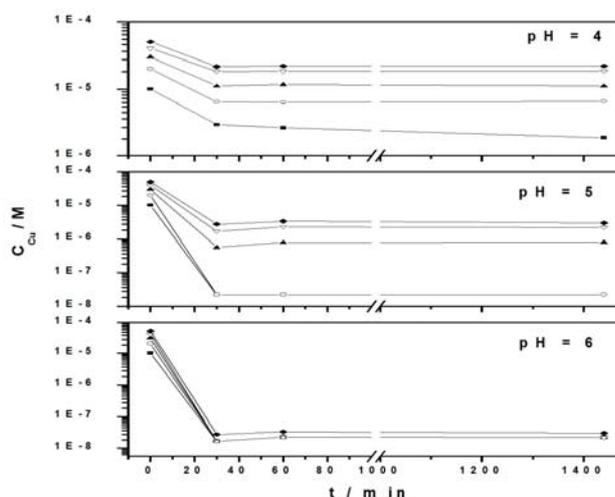

Figure 4. Decrease of Cu^{2+} concentration with time due to copper adsorption on to TiO_2 surface

Concerning the kinetic study of copper adsorption on the TiO_2 surface, Figure 4 indicates that it is a rapid process which is accomplished in the first thirty minutes of the impregnation. In addition, it can be observed, that at pH values higher than pzc, where the surface of the oxide is negatively charged, almost the whole quantity of Cu^{2+} ions is adsorbed, independently of the Cu^{2+} initial concentration, while at pH values lower than pzc, where the titania surface is positively charged, an appreciable quantity of Cu^{2+} species is adsorbed.
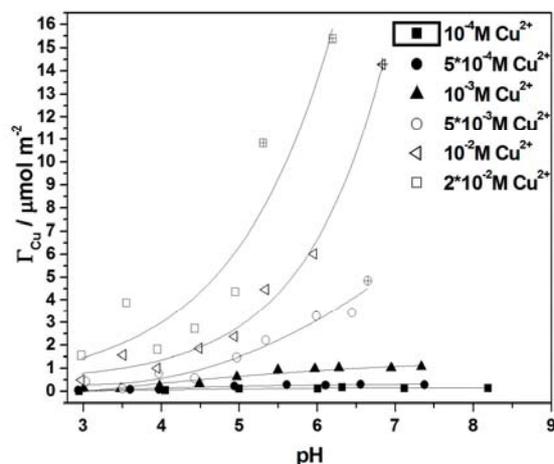
Figure 5. Adsorption edges obtained for various initial Cu(II) concentrations (C$_{in}$) in the suspension. Crossed symbols correspond to Cu(II) surface precipitation on titania.

The inspection of the equilibrium adsorption results provides valuable information for the mode of interfacial adsorption. The adsorption edges curves obtained for various initial Cu(II) concentrations at a pH range 3 to 8, are illustrated in Figure 5. It can be seen that even at low pH values (pH < pzc), where the surface is positively charged, an appreciable quantity (Γ/ μmol m^{-2}) of the Cu^{2+} ions is adsorbed. This indicates that copper adsorption does not take place only through electrostatic forces but through coordination bonds or hydrogen bonds as well. At higher pH values (pH > pzc), where TiO$_2$ surface is negatively charged, the adsorption of the positively charged Cu^{2+} ions increases, due to the increased electrostatic interactions. It should be stated here that the Cu^{2+} adsorption was studied at relatively low pH values (pH < 6, in the case of 10^{-2} M Cu^{2+}) due to the copper precipitation, which was identified by XRD analysis. In addition, the study of the influence of ionic strength to the adsorption of Cu^{2+} on the TiO$_2$ surface pointed out that the ionic strength does not affect the adsorption. This strongly suggests retention of the Cu(II) species through coordinative bonds (Figure 6).
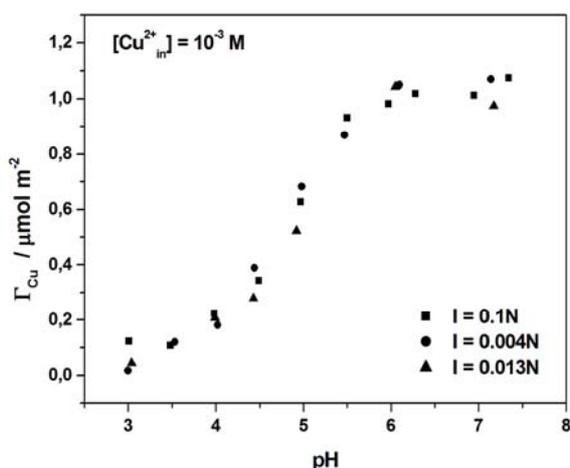

Figure 6. Adsorption edges curves obtained for various values of ionic strength and the same initial Cu(II) concentration (C$_{in}$) in the suspension
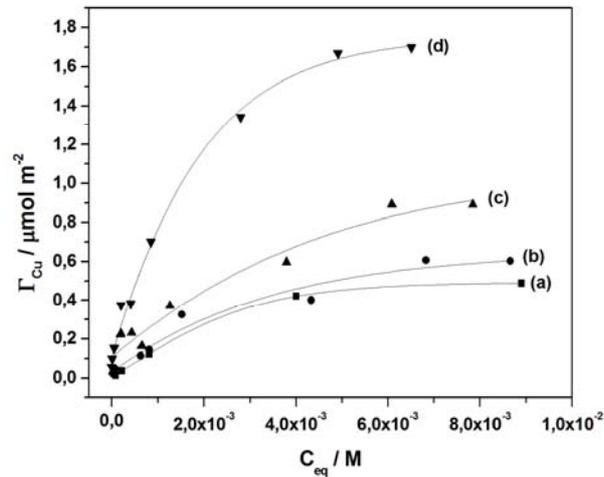
Figure 7. Adsorption isotherms curves at 25°C, I = 0.1M KNO$_3$.
(a) pH = 3, (b) pH = 4, (c) pH = 4.5 and (d) pH = 5.

The results of the adsorption isotherm experiments are shown in Figure 7. One may observe an increase of the adsorption by increasing the pH. The experimental results were fitted on the basis of the extended Langmuir adsorption model, according to the following equation:

$$\frac{1}{\Gamma} = \frac{1}{\Gamma_m} + \frac{1}{k\Gamma_m exp\left(\frac{\lambda\Gamma}{RT}\right)C_{eq}} \tag{1}$$

where Γ, Γ_m, k and C_{eq} represent the surface concentration, the maximum surface concentration of the adsorbed Cu(II), the adsorption constant and the equilibrium concentration of the Cu(II) species in the suspension, respectively. λ equals to E/Γ_m, where E is the energy of the lateral interactions exerted between the adsorbed Cu^{2+} species. The fitting of the adsorption isotherm results corresponded at pH = 4.5 is illustrated in figure 8. As it may be observed, an excellent fitting was attained, resulting in the determination of the values of the maximum adsorbed quantity (Γ_m), the adsorption constants (k) and the energy of the lateral interactions (E), at different pH values (Table 2).
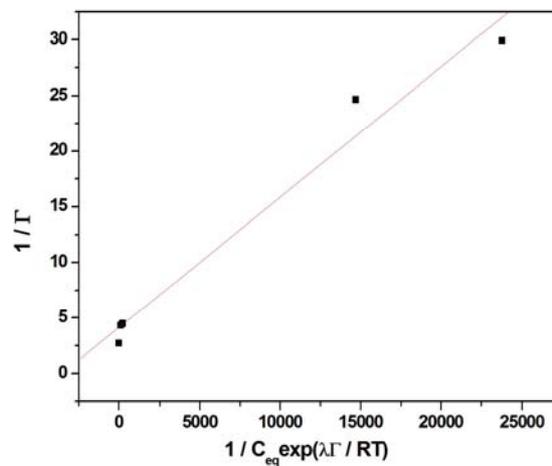

Figure 8. Fitting of the adsorption isotherm results corresponded at pH = 4.5

Table 2. Lateral interaction energy (E), adsorption constants (K) and
maximum surface concentration (Γ_m), at various pH values

pH	E ($J\ mol^{-1}$)	K ($mol^{-1}L$)	Γ_m ($\mu mol\ m^{-2}$)
3	2554	342	0.48
4	211	1344	0.52
4.5	79	1553	0.71
5	15	1989	1.47

Table 2 shows that if the pH increases the energy of the lateral interactions decreases. This is due to the fact that at low pH values, the amount of the adsorbed onto the surface copper species is very low and as a result water dipoles interfere, resulting in attractive interactions between the adsorbed Cu(II) species. On the contrary, when the pH value increases, the surface becomes less positive increasing the density of the adsorbed Cu^{2+} ions. As a result, the lateral interactions between the adsorbed Cu^{2+} ions, becomes less positive. Moreover, Table 2 shows that the value of the adsorption constants increases by increasing the pH value. This may be attributed to the more negatively charged surface of titania, as pH increases, which results in more intense attractive interactions with the positively charged Cu^{2+} ions. An alternative explanation for the observed changes of the K and E values is that these phenomenological parameters are mean values of the corresponding parameters for the various Cu^{2+} species retained at the interface and that interfacial speciation is pH dependent.

CONCLUSIONS

Adsorption of copper species on the titania surface is a rapid process, which is not affected by the ionic strength value. By increasing the pH, the adsorbed amount of Cu^{2+} ions and the value of the adsorption constant increase, whereas the value of the lateral interaction energy decreases. The results indicate that the Cu^{2+} species are presumably retained at the interface by coordinative bonds.

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