

Electrodeposition of Iron from Kaolin Clay and the Effect of Mass Transport

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Abstract: The separation of iron from kaolin clay solutions using electro deposition was studied. Electrochemical studies of the iron electro-deposition were performed using the techniques of cyclic voltammetry, chronopotentiometry and chronoamperometry on a silver rotating disk electrode (RDE) as a working electrode. The effect of the kaolin solution pretreatment with ultrasonic method on the electrochemical reduction processes was studied. The influence of the disk speed of the electro-deposition performances was also studied. The morphology of the surface of the electro-deposit was observed by SEM. It was found that the ultrasonic pretreatment has an important effect on the reduction processes and on the morphology of the electrodeposited sample. The chemical composition of the electrode-posit was characterized by atomic absorption and ICP-ToFMS. It was shown that Fe₂O₃ content in the clay was 0.6% (weight). The voltammetric studies revealed that, during the electrochemical reduction processes of the kaolin solution, the iron reduction peaks were observed in the potential range from - 0.52V to -2.0V (E vs. SCE). Subsequently, the chronopotentiometry study showed that when a current of - 0.09A is applied to the electrochemical cell, the reduction of iron species occurred. It was also found that the variation of the amount of the electrodeposited iron is, of course, significantly dependent of the speed of the working electrode. For an electrode speed rate ranged from 1500 to 6500 rpm (revolutions per minute), an optimum amount of the electro deposited iron was obtained for an electrode speed of about 4000 rpm.

Keywords: Kaolin, reduction, electrochemistry, iron

1. INTRODUCTION

The great utility of kaolin clay for the manufacture of everyday products, makes a clay with a high commercial interest [2, 3]. Around the world the extraction of kaolin industry is growing fastly each year. However, the natural process of the formation of kaolinite requires long periods [4, 5]. Accordingly, it is a non-renewable resource. Most of the clay that exists naturally presents various impurities, so it becomes necessary to apply benefit techniques that reduce the amount of impurities.

Globally common mining techniques are applied for the benefit of kaolin as leaching, flotation and high intensity magnetic separation [6]. However, in recent years we have developed studies on the application of alternative techniques to resolve this problem,

such as bioleaching [7], electro-remediation [8, 9] and electro-deposition. In particular, electro-deposition technique is a highly selective for the recovery of metals in solution. However, the study of the electrochemical environment is essential if we want to establish the optimal conditions for carrying out the electro crystallization of metals. Previous work has shown that it is feasible to use this technique for the purification of kaolin leaving the iron in solution and allowing the separation of the solids [1]. However, the study of the effect of different variables on its performances is necessary to increase the effectiveness of the process as well as the conditions in which the electrodeposition of iron can be performed. The aim of the present research work is to study the influence of the agitation speed, as well as the pretreatment with ultrasound in iron deposits from solutions prepared with kaolin clay.

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2. EXPERIMENTAL METHODOLOGY

The solutions for which the electrochemical studies were performed were prepared in de-ionized water by adjusting the pH to 2. The solution with the sample was prepared by adding clay kaolin colored beige with particle size lower or equal to $2\mu\text{m}$ (called BG) in 20% of solids and imposing agitation convection for about 20 minutes.

Electrochemical studies were performed in a volume of 20 ml, with an arrangement of three electrodes, using cyclic voltammetry techniques and chronopotentiometry. The substrates used were as working electrode a silver plate as counter electrode and graphite rod as a reference a saturated calomel electrode (SCE). In conducting studies electrochemical potentiostat-galvanostat (PAR273A) was used. The techniques were applied through the equipment software.

After electrodeposition, the surface of the electrodes was analyzed by means of scanning electron microscopy (JEOL JSM840) which was coupled to EDS (Oxford Instruments ISIS300). Each electrode was also immersed in 10 ml of H_2SO_4 10% in volume, in order to dissolve the deposited iron. This solution was analyzed using atomic absorption spectrometer (Perkin-Elmer Analyst 200) to determine the amount of iron deposited on the surface. For the chemical analysis using by ICP-MS (Induced Coupled Plasma Mass Spectroscopy, 10 mg of the solid sample was dissolved using a mixture of hydrofluoric acid and boric acid for subsequent analysis by ICP-ToFMS (LECO, RENAISSANCE). The methods based on the Time Of Flight Inductively Coupled Plasma-Mass Spectrometry (TOF-ICP-MS) provide high precision and reliable element trace analysis detection in solids, liquid or gases samples of various materials and alloys. The detection limit of the methods ranges from the parts per million (ppm) (routine analysis for industrial production applications) to the parts per billion (ppb) or parts per trillion (ppt) levels for research and development purposes. It can also identify trace contamination and unknown chemical compounds in alloys. These methods help to solve many quality analysis problems because elemental trace analysis techniques are available for a wide range of materials and alloys.

Finally for microscopy and EDS analysis of the deposits after the treatment with ultrasound was used an equipment Jeol JSM-6300, this analysis was performed in the Universidad Autónoma del Estado de Hidalgo.

3. RESULTS AND DISCUSSION

The results of chemical analysis by atomic absorption shown in Table 1, which shows that the sample in which iron is present is an impurity in this type of clay. The observed ratio between the alumina (Al_2O_3) and silica (SiO_2) correspond with the formula of kaolinite which is 1:2.

We also identified the presence of iron oxides from ICP analysis and they showed that the sample contains 0.6% iron. Due to the colour of the clay, it is considered that the iron is in the form of Hematite (Fe_2O_3).

Table 1. Chemical composition of kaolin sample.

Sample	Al mg/L	Si mg/L	Fe mg/L
BG	816	1581	13,8

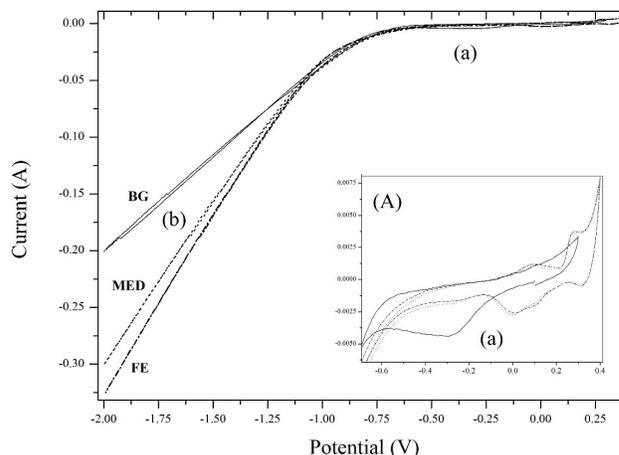


Figure 1. Voltammograms obtained for the solution of kaolin (BG), the dispersion medium (MED) and the dispersion medium contaminated with Fe_2O_3 (FE) at a scan rate of 25 mV s^{-1} .

Figure 1 shows voltammograms obtained in the solution prepared from kaolin (curve BG) at a scan rate of 25 mV s^{-1} , when the scanning starts in cathodic direction. For comparative purposes the same study was performed in the dispersion medium (MED curve), and the dispersion medium was contaminated with ferric oxide Fe_2O_3 (FE curve).

As shown in Figure 1, two main reduction processes occur in all three curves in zones (a) and (b). The reduction processes are observed on the MED curve in the potential range of 0.1 V to -0.52 V (in region (a) of the curve) and from -0.52 V to -2.0 V (in region (b) of the curve). Some reduction peaks are also observable on the curve related to the FE process. In this case the reduction peaks are present in region (a) in a potential range of 0.1 V to -0.56 V and in region (b) in the potential range of -0.56 to -2.0. The BG curve related to the kaolin solution also exhibits some reduction processes in the region (a) in the potential range of 0.1 V to -0.64 V and in region (b) in the potential range of -0.64 V to -2.0 V.

As seen in the magnification (A), the current peaks related to the reduction and the oxidation processes of the MED and FE curves are identical in the region (a) and are attributed exclusively to the reduction and oxidation of the dispersant medium (curves drawn in dashed lines). However, for the same curves in the region (b) a reduction process occurs with a different reduction peak current at a potential less than -0.6 V, this difference is attributed to the reduction of ferric oxide coupled with the hydrogen evolution on the surface of the electrode.

The BG curve shows the reduction processes of the kaolin solution. The current reduction peaks of this curve in the region (a) are seen in the range of the potential values which are similar to those of the previous curves. They are also attributed to the reduction reaction of the medium. On the other hand, in the region (b), the reduction current of the BG curve is lower than those of the MED and FE curves. This can be attributed to the presence of some solids in the kaolin solution which may change the quantity of the active reactant as iron ions at the electrode/electrolyte interface.

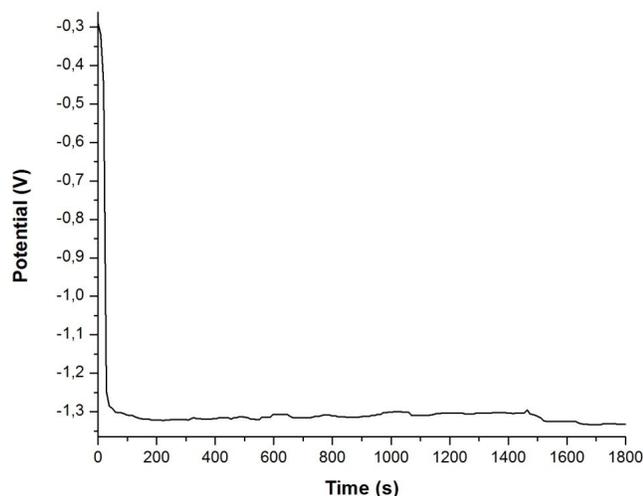


Figure 2. Transient chrono-potentiometry of the BG solution during 1800 seconds using a 3-electrode arrangement with a current of -0.09 A.

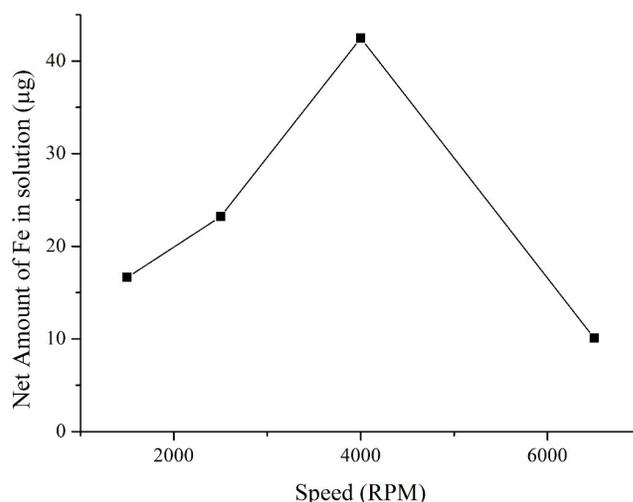


Figure 4. Graph the amount of iron deposited respect to the electrode rotation speed.

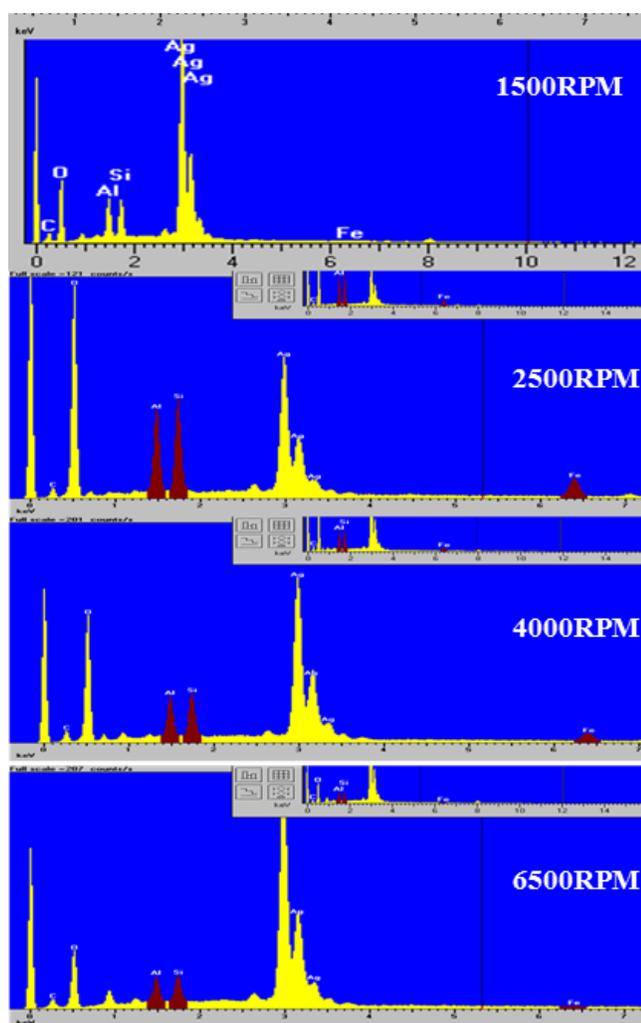


Figure 3. EDS spectra of the surface of the electrodes at different speeds of rotation.

However, as already mentioned above, these reduction currents are in this range of potential (of - 0.64 V to - 2.0V) in which the reduction of iron species in kaolin solution may take place. This process is carried out in the same potential region of the hydrogen evolution reaction. In order to corroborate this data, a chronopotentiometry study was carried out on the BG solution which is shown in Figure 2.

As shown in Figure 2, in the range of the iron reduction and the hydrogen evolution region an important fast is observed from -0.3 to -1.25 V in the interval from 0 to 12 s. Over 12 s the potential remains constant with time at a value of -1.3 V vs. SCE.

This behavior indicates the continuous decrease of the double layer electric charge capacity of the cathode/electrolyte interface with time. This behavior may be attributed to the reduction of the iron ions of the kaolin electrolyte.

To assess whether the reduction process of iron species is affected by the mass transport, the influence of the rotation speed of the electrode in the range of between 1500 and 6500 rpm was studied by imposing a reduction potential of -1.3 V for 2 hours on the working electrode.

Figure 3 shows the analysis by EDS of the deposits obtained at a rate speed of 1500, 2500, 4000 and 6500 rpm.

As shown in Figure 3, the spectrum of iron electrodeposited at the electrode surface is visible and its intensity changes with the rotation speed. The variation of the intensity of the peak exhibits a volcano behavior. These data are corroborated to the atomic absorption analysis of the dissolved iron in acid solution the electrodeposited at the rotating speeds of 1500, 200, 4000 and 6500 rpm respectively (Fig.4).

Effectively, the intensity of the peak and/or corresponding iron dissolved increases from 1500 RPM to 4000 rpm and then decreases for 6500 rpm. The amount of the electrodeposited iron increases from 1500 to 400 rpm and then decreases for 6500 rpm (Fig.4).

This indicates that the agitation of the solution during the electrodeposition process is related to the mass transport of iron species present electrodeposited at the electrode surface. By increasing the

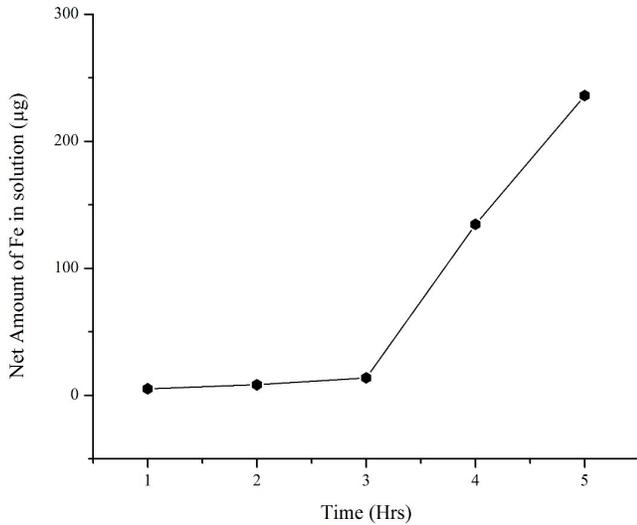


Figure 5. Graph of the amount of iron deposited at 2500 rpm, varying the time.

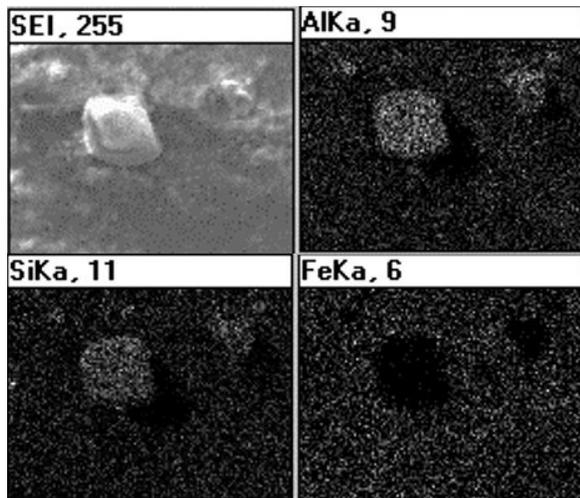


Figure 6. SEM Micrograph and elemental mapping of Al, Si and Fe of the deposit on the surface of the electrode after 4 hours of treatment.

speed to 6500 rpm, the mass transfer benefit decreases because the concentration of the iron ions transported in the double layer of the interface must be significantly higher than their concentration which is transformed in iron metal. Accordingly the optimum mass transport in this electrochemical process is obtained when the working electrode rotation speed is around 4000 rpm.

Based on these data, and taking into account that after 4000 rpm, the mass transport process might not be optimum, we studied the effect of the electro-deposition time on the mass of iron electro-deposited at the working electrode surface for a rotating speed 2500 rpm. As above, the amount of the electrodeposited iron on the working electrode surface was determined for atomic absorption. The variation of mass of the electrodeposited iron with time is

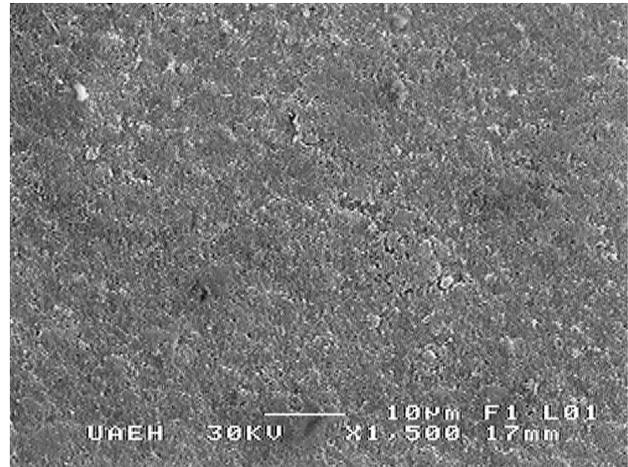


Figure 7. Micrograph of the electrode surface after an hour of treatment at 2500 rpm with 30 minutes of ultrasonic as pretreatment.

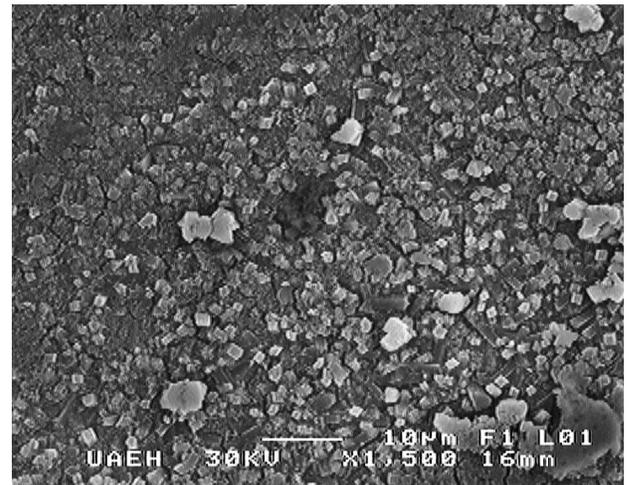


Figure 8. Micrograph of the electrode surface after an hour of treatment at 2500 rpm with 60 minutes of ultrasonic as pretreatment.

shown in Fig.5.

As shown in Figure 5 the amount of electro-deposited increases with time. This results indicates that the best iron recovery from the kaolin solution is obtained for to long electro-deposition time for a given rotating speed which value is in the rage where the process is controlled by the mass transport. Also, we may ensure that the cathode potential and the rotating speed of the working electrode are optimized to allow the iron electro-deposition process be carried out continuously and efficiently. This is essential to decrease the amount of iron from the bulk of kaolin solution.

Figure 6 shows a micrograph and mapping of elements of a section of the electrode surface after 4 hours of the electro-deposition process at a reduction potential of - 1.3 V and aa rotating speed of

2500 rpm.

In this Fig.6 we can see a particle of the clay in the foreground in the SEI box. The elemental mapping of aluminum and silicon (which are the principal elements of the kaolinite), confirms their presence in high concentration in boxes Alka and Sika of the same Fig.6. They are also scattered over the entire electro-deposit obtained on the working electrode surface. This is also the case of iron which is seen in box FeKa of Fig.6. This is another confirmation that the iron is electrodeposited on the working electrode surface during the purification process of the kaolin.

Another experimental parameter which may have an effect on the performances of the iron electro deposition might be the ultrasonic pretreatment of the electrolyte. Figs. 7 and 8 show the micrographs of the surface of electro-deposit obtained for a rotating disk of 2500 rpm prior to ultrasonic pretreatment of the electrolyte during 30 and 60 minutes.

Fig.7 shows the SEM micrograph of the electro-deposit prior to ultrasonic pretreatment of the electrolyte during 30. The EDS analysis of the electrodeposited layer showed that it contains 3.21% (weight) iron. The surface layer is composed of iron and kaolinite particles. Figure 8, small cubic crystals are observed on the whole electrode surface. The corresponding EDS analysis showed that in this case the deposited surface layer is composed of 33.12% (weight) of iron. The increase of the iron content in the electrodeposited with the time of the ultrasonic pretreatment of the kaolin solution is due to the increase of the ionic impurities at the working electrode surface. Increasing the ultrasonic pretreatment time accelerates the dissolution of the large particles to impurities which become free in the electrolyte and be transported easily to the working electrode surface. This is supported by Franco et al. [10] who indicated that under ultrasonic pretreatment, the characteristics of the flat kaolin particles are arranged in the direction of the ultrasonic waves.

4. CONCLUSIONS

Based on the results obtained in this work, it may be concluded that:

- i) The results obtained through chemical analysis indicated that the kaolin solution contains iron oxide which is a typical impurity in kaolin clay. It was shown that Fe_2O_3 content in the clay was 0.6% (weight);
- ii) The electrochemical studies showed that kaolin solution presents various reduction processes of iron species in clay, in the range of potential - 0.56 to - 2.0 V vs. SCE;
- iii) If a reduction potential of - 1.3 V vs. SCE is applied to the working electrode, a deposit of metallic iron occurs on the surface of the electrode;
- iv) The electro-deposition of iron is controlled by mass transport. The amount of iron increases with the working electrode rotating speed and the optimum mass transport was obtained for 4000 rpm;
- v) For a working electrode speed of 2500 rpm, the mass electrodeposited of iron increases with the deposition time; thus reducing the amount of iron impurities present in the solution;
- vi) The concentration of the electrodeposited iron in the electrodeposited layer increases with the time of the ultrasonic pretreatment of the kaolin solution before

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REFERENCES

- [1] Flores Segura, J.C., et al., *Purification of Kaolin Clays by Means of Electrochemical Techniques*, in *Recent developments in metallurgy, materials and environment* M.I. Pech-Canul., et al., Editors. 2012, Editorial Cinvestav IPN. p. 145-154.
- [2] Murray, H.H., *Chapter 5 Kaolin Applications*, in *Developments in Clay Science*, H.M. Haydn, Editor. 2006, Elsevier. p. 85-109.
- [3] Murray, H.H., *Applied Clay Science*, 17, 207 (2000).
- [4] Domínguez, E.A., et al., *Applied Clay Science*, 47, 290 (2010).
- [5] Murray, H.H., *Chapter 3 Geology and Location of Major Industrial Clay Deposits*, in *Developments in Clay Science*, H.M. Haydn, Editor. 2006, Elsevier. p. 33-65.
- [6] Murray, H.H., *Applied Clay Mineralogy: Occurrences, Processing and Applications of Kaolins, Bentonites, Palygorskite-sepiolite, and Common Clays*. 2006: Elsevier Science.
- [7] Guo, M.-r., et al., *Applied Clay Science*, 48, 379 (2010).
- [8] Sanjay, K., et al., *Colloids and Surfaces A*., 222, 259 (2003).
- [9] Wang, J.-Y., et al., *Journal of Hazardous Materials*, 136, 532 (2006).
- [10] Franco, F., L.A. Pérez-Maqueda, and J.L. Pérez-Rodríguez, *Journal of Colloid and Interface Science*, 274, 107 (2004).