BIRNESSITE ELECTRODEPOSITED ONTO SnO_2SUBSTRATE: APPLICATION TO THE REMOVAL OF METHYL ORANGE

Wafa CHOUCHENE [a], Cyrine ANNABI [a], Manel ZAIED [b], Sophie PEULON [c], Annie CHAUSSE [c], Nizar BELLAKHAL [a]

[a] *UR de Catalyse, Electrochimie de Nanomatériaux et Leurs applications et de Didactique, Institut National des Sciences Appliquées et de Technologie (INSAT), B.P. N°676, 1080 Tunis, Tunisie.*
[b] *Laboratoire de Valorisation des Ressources Naturelles et des Matériaux de Récupération Centre de Recherche en Sciences des Matériaux Pôle Technologique de BorjCedria B.P.95 - 2050 Hammam-Lif.Tunisie.*
[c] *Laboratoire Analyse et Modélisation pour la Biologie et l'Environnement (LAMBE), (CNRS-CEA-Université d'Evry UMR 8587), boulevard François Mitterrand, 91 025 Evry, France.*

(Submitted: 18 April 2014, accepted: 24 December 2014)

ABSTARCT: Degradation of methyl orange (MO) , also called the Heliantine , organic azo dye belongs to a class of highly toxic dyes (indigo) was studied by thin layers of birnessite electrodeposited onto a transparent semiconductor substrate (SnO_2) at room temperature. The experimental results showed that 68% of the MO solution was completely discolored by thin layers of birnessite, and the decay kinetic always follows a pseudo-first-order reaction. An electrochemical activation of samples of birnessite and a non-spontaneous discoloration of MO have been successfully tested and a great improvement was reported in the treatment. These results suggest that birnessite thin layers may be envisaged as a new non-toxic material for treatment of colored wastewater.

Keywords: Thin layers manganese oxide, Birnessite, Dyes, Discoloration.

RESUME : La dégradation de l'orange de méthyle (OM), aussi appelé l'Hélianthine, colorant organique de type azoïque appartient à une classe de colorants hautement toxiques (indigoïdes) a été étudiée par des couches minces de birnessite électro déposés sur un substrat semi-conducteur transparent (SnO_2) à température ambiante. Les résultats expérimentaux ont montré que 68% de la solution d'OM a été complètement décoloré par les couches minces de birnessite, et la cinétique de dégradation suit toujours une réaction de pseudo-premier ordre. Une activation électrochimique d'échantillons de birnessite et une décoloration non-spontanée d'OM ont été testées avec succès et une grande amélioration a été signalée dans le traitement. Ces résultats suggèrent que les couches minces de birnessite peuvent être envisagées comme un nouveau matériau non toxique pour le traitement des eaux usées colorées.

Mots Clé: Couches mincesd'oxyde de manganèse, birnessite, colorants, décoloration.

INTRODUCTION

The increase in industrial and agricultural activities in developing countries requires the use of high quantities of synthetic chemicals such as pesticides, insecticides, dyes and chemical additives. Many industries, including textiles, use various dyes and generate a considerable amount of colored wastewater causing damage to the ecological system[1-3]. Moreover, most dyes are stable to light and are not biodegradable[4,5], that is why the dyes in wastewater are considered as a serious environmental problem. Several methods are proposed to remove organicpollutants: such as biological, physical, and chemical or electrochemical[6-9].

Because of their very large production amounts and use, the development of new processes of organic compounds degradation, which are non-toxic, low-cost and efficient, able to eliminate these pollutants from contaminated water seems to be very

* Corresponding author, e-mail address : wafachouchene7@yahoo.fr

important. Several studies were reported on the destruction of persistent organic pollutants (POPs) with electro-fenton process that seem to be interesting in decontamination of wastewater without adding harmful chemical reagents to the solution to be treated. In addition to this process, thin layers of birnessite have been successfully applied to various POPs [10-12]. Thus in this study birnessite($Mn^{III}_2Mn^{VI}_5O_{13}$, $5H_2O$)as the major mineral phase in many soils was evaluated [13].The birnessite is considered as the most interesting manganese oxide because of its high absorption capacityand its redox properties[14-17]. In fact, it was shown the good reactivity of birnessite thin films towards methylene blue, a cationic phenothiazine dye and towards Indigo Carmine, an anionic dye belonging to a highly toxic class of dyes (indigoid) [14,18]. These results encouraged us to further investigate the possibility to use thin films of birnessite in the degradation of other dyes such as methylorange (dimethylamino-4-4 azobenzene-sulfonatesodium). To understand the mechanism of degradation of the MO dye various analytical techniques such as X-ray diffraction (XRD) and UV-visible spectroscopy were used.

MATERIALS AND METHODS

1. Chemicals and analytical procedures

The 100 mL of a solution containing Na_2SO_4 (0.4 $mol.L^{-1}$) and $MnSO_4$ (1.6×10^{-3} $mol.L^{-1}$) (Sigma Aldrich, 98% purity) were prepared just before measure with a combined pH electrode (WTW SenTix 97/T; pH-meter WTW - Multiline P4). Analytical grade NaOH and H_2SO_4 (Sigma Aldrich) were used to adjust the initial pH of the solution. For all experiments, the solutions were gently stirred continuously during electrodeposition, without deaeration.

The electrochemical measurements were performed at room temperature using a voltalab 80 controlled by a computer using the GPES software package. A classical electrochemical cell with three electrodes was used. The reference electrode was an ESM electrode (REF621 Radiometer analytical, E_{ref} = 0.656 V/ESH). All potential values cited in the text are referred to this reference electrode. The counter electrode is a platinum wire. The working electrode is a glass plate covered withtin dioxide (SOLEMS, 120 Ω/cm^2, 15 mm × 30 mm) used as received. The surface in contact with electrolyte was delimited by an adhesive mask.

2. Analysis Procedures

The analysis of thin layers was determined by XRD using a MRD KRO diffractometer with radiation (K_α (λ = 1.5456 A°) equipped with a curved position sensitive detection. The Analyses of solutions of dyes were performed by UV-vis spectroscopy (Unico 2820 UV/Vis spectrophotometer).

RESULTS AND DISCUSSION

1. Electrodeposition and characterization of birnessite thin layers

A complete study concerning the electrodeposition of manganese compounds by oxidation of Mn^{2+}onto SnO_2 has been already conducted [19]. Standard samples of thin layers of birnessite were electrodeposited by chronoamperometry in neutral aerated solution containing sodium sulphate and manganese sulphate at E = 0.6 V with Q = 1.5 C onto a surface equal to 4.5 cm^2 (time around 2700 s, $J_{average}$ = 0.26 mA/cm^2). Theelectro-oxidation ofMn^{2+}in neutralaerated sulfate solution leads to the formation of birnessite (Mn_7O_{13}, $5H_2O$) [14]. After electrodeposition, thin films were rinsed with Milli-Q water and dried in ambient air during some hours. Samples can be electrodeposited and stocked some hours before interaction experiments because birnessite is a very stable compound[20]. In these conditions, the mass of the material, electrodeposited on SnO_2, is equal to m = $(0.76 \pm 0.1).10^{-3}$ g, and the thickness evaluated to e = (0.46±0.1)µm. These results were calculated with the density of birnessite generally reported (d = 3.0 g/cm^3). During electrodeposition, Q increases linearly due to a

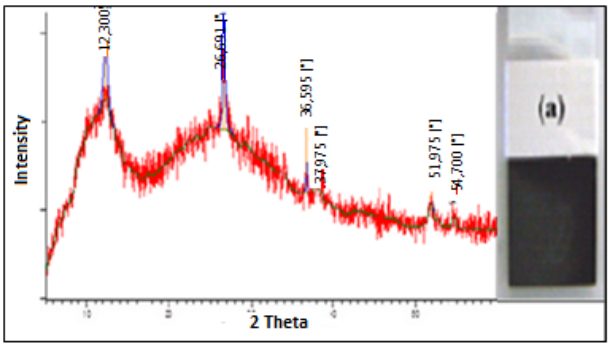

Figure 1:XRD patterns of a thin layer of birnessite electrodeposited onto SnO_2 before interaction with a solution of OM (Na_2SO_4 (0.4 M) / $MnSO_4$ (0.0016 M), E = 0.6 V/ECS, t = 2700s, pH = 6, Q = 1.5 C, S =4.5cm^2, agitation = 350 tr/min)

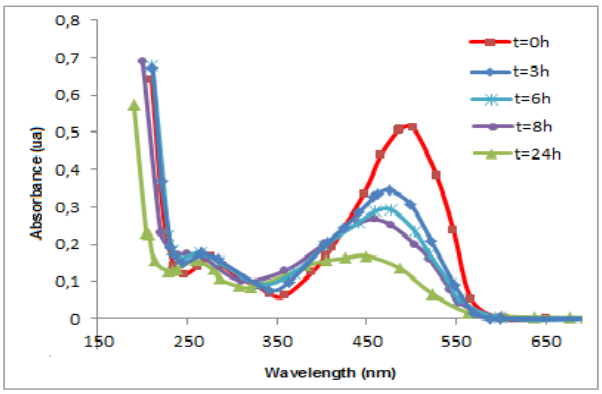

Figure 2: Evolution of theUV-visible spectrum of the solution of Methyl Orange (C= 3.10^{-5} mol.L^{-1}, pH =3, t = 2700 s, Q = 1.5 C, S = 4.5 cm^2, agitation = 350 tr/min) as a function of the duration of treatment.

good electronic conduction of the deposited film [19]. The figure 1 shows XRD patterns obtained on the adherent black solid electrodeposited in standard conditions (picture a, inset Figure 1). According to JCPDS 23-1239 card (Mn_7O_{13}, $5H_2O$) birnessite and SnO_2 were identified. The peaks are well defined indicating a very good crystallinity.

2. Reactivity of birnessite thin layers towards methyl orange solutions

2.1. Influence of initial pH

It has been shown in previous studies [20] that the Methyl Orange is only degradable in an acid medium. This phenomenon can be explained by the changing structure of our dye as a function of pH. Indeed, Methyl Orange, like all azo dye, switches between two molecular structures depending on pH: the azo structure and quinoid structure. In acidic media, there is a large majority of quinoid structure of Methyl Orange in the solution. According to the experimental results, the quinoid structure is more likely to be degraded because it is easier to break a single covalent bond rather than a double bond. It is worthy to note that in most previous studies of degradation of Methyl Orange, the optimal pH of the treatment is 2 [21,22]. At this value, the birnessite is positively charged and sulfonic groups of Methyl Orange are responsible of fixing the dye due to electrostatic attraction [23]. Unfortunately, this pH was found to be too aggressive for our birnessite thin layer that is why pH equal to 3 has been chosen for the rest of our experiments.

2.2. Evolution of UV-Visible spectra

Figure 2 shows results obtained during interaction, in the dark, between one thin layer of birnessite electrodeposited in standard conditions (S = 4.5cm^2 and Q= 1.5 C), and 10 mL of MO solution containing3.10^{-5}mol.L^{-1}. After 24 h, of interaction, sample solution was discolored, and all peaks characteristic to MO (496 nm and 276 nm) have disappeared, while the solution in interaction with SnO_2 (S = 4.5cm^2) alone is always orange without any modification of UV-vis spectra, these results shows the positive effect of the birnessite with regards to SnO_2. The thin layer of birnessite after interaction stays very adherent, black without any aspect modification.

2.3. Kinetic studiesof thedegradationofMethylOrange

The kinetic of discoloration of Methyl Orange by thin layers of birnessite was studied at pH 3 by varying the contact time between the sample and the dye solutions at a fixed volume and MO concentration (V = 10 mL and C = 3.10^{-5} mol.L^{-1}). Figure 3 shows that the discoloration of our dye is fast at the beginning of the process (a reduction of approximately 33% after 3hours of interaction) then eventually it become slow. The inset shows

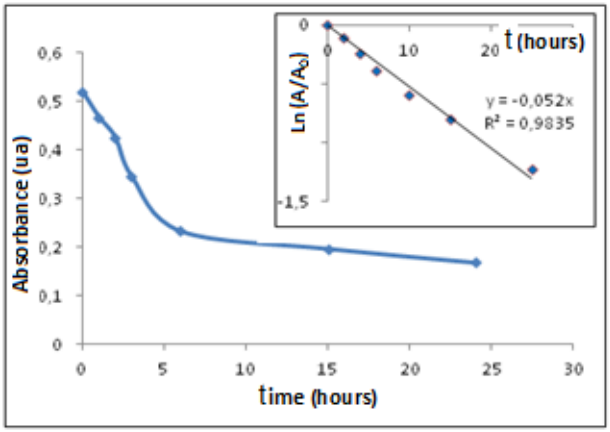

Figure 3: Kinetics of degradation of Methyl Orange (C= 3.10^{-5} mol.L^{-1}, pH = 3, t = 2700 s, Q = 1.5 C, S=4.5cm^2, agitation = 350 tr/min)
The inset presents the applying the equation of the first order kinetic model to degradation

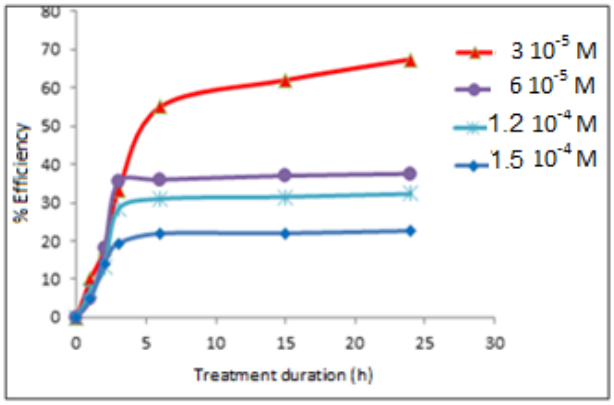

Figure 4: Influence of the concentration of dye solutions on the effectiveness of treatment (pH = 3, t = 2700 s, Q = 1.5 C, S = 4.5 cm^2, agitation = 350 tr/min)

also that the discoloration reaction follows pseudo-first order kinetic with R^2 value of 0.9835in good agreement with kinetic degradations of organic pollutants by manganese oxides [24-27].

2.4. Influence of MO concentration

The effect of MO concentration was evaluated in the range that varied between 3.10^{-5} mol.L^{-1} and $1.5.10^{-4}$ mol.L^{-1}. Figure 4 shows the discoloration efficiency (%), calculated according to Eq (1), versus time for various concentrations of MO.

Discoloration efficiency (%) = (A_0 (496 nm) - A (496 nm)) / A_0 (496 nm) × 100 Eq (1)

With A_0 (496 nm): initial absorbance atλ_{max}= 496nm and A (496 nm): absorbance at λ_{max}=496 nm at t (h).

Results obtained showed that, when the initial dye concentration is3.10^{-5} mol.L^{-1} treatment is effective at about 67% and the solution is completely discolored after 24 hours. However at a concentration of $1.5.10^{-4}$ mol.L^{-1}, only 20% of the color disappeared even after 48 h. The results show that the effectiveness of treatment decreases with increasing concentration. In addition, the efficiency for each concentration increases linearly after the first 6 hours of treatment. As can be seen in Figure 4, MO discoloration decreased with increase in initial MO concentration, suggesting that the reactive adsorption sites were saturated. In fact, it has been well established that oxidative degradation of organic matter by manganese oxides is via a surface mechanism [28-30]. It should be indicated that the interaction experiments were performed with samples made under optimum conditions (Q = 1.5 C and S = 4.5 cm^2) according to previous studies [14,31].

2.5. Study of the electrochemical reactivation of the birnessite

It has been shown previously [28] that using samples of birnessite which were in contact with aqueous solution of methyl orange, are no longer functional. In fact, the surface of the sample is saturated by organic molecules adsorbed and Mn(III) and Mn(IV) of our birnessite are reduced to Mn(II). These experiments aim to activate electrochemically the used samples in order to use them again. The electrochemical activation consists on imposing an oxidizing potential of 0.7 V/SCE to the used birnessite, for a period of 3 hours. The formation of the birnessite's potential was slightly exceeded to assure the oxidation of manganese.

The activated samples were placed in contact again with the MO dye, using the same previous experimental condition (figure 5). By comparing the values found for a sample freshly synthesized and an electrochemically activated sample, we note that the activation has significantly improved the treatment efficiency. After the first three hours,

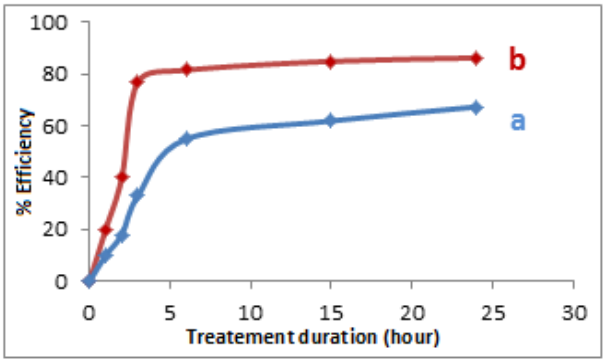

Figure 5: Effectiveness of discoloration MO solution ($C= 3.10^{-5}$ mol.L^{-1}, pH = 3, t = 2700 s, Q = 1.5 C, $S=4.5cm^2$, agitation = 350 tr/min)with a birnessite sample (a) new and (b) after electrochemical activation

discoloration reached 77% efficiency for an activated sample against 33% for a new sample. At the end of treatment, 87% of dye was removed after activation against 68% only for a sample of fresh birnessite. This phenomenon could be explained as follows: the electrochemical activation assured the oxidation of Mn(II) of the birnessite to Mn(III) and Mn(IV). This makes the layer of birnessite more responsive and more efficient for the oxidation of MO molecules [3,32,33]. That is why the treatment is clearly improved. Indeed, the birnessite (initially containing 60%Mn(III) and 40% Mn(IV)) becomes richer with Mn (IV) (75%) and therefore more oxidizing [34].

3. Proposition of a schema depicting the reaction of degradation of MO onto birnessite surface

The oxidative degradation of organic matter by Mn oxides via a surface mechanism has been well established [14,35].The mechanism for the total transformation of methyl orange may be based on electronic transfers (oxidation) and broken azo links with formation of free radicals [36-39]. It was found that the intensity of absorption band that correspondsto aromatic ring (276 nm) has increased after 24 hours of interaction.

Initially, MO has been adsorbed onto external surface of the birnessite instead of being intercalated into the structure. This result suggests the presence of reactive sites onto birnessite external surface [14,40-42]. The adsorption step must be very fast and quantitative. The electron transfers between MO adsorbed and birnessite occurs within the surface bound to Mn(III, IV), followed by release of organic oxidation products and Mn (II) arising from reductive dissolution of Mn oxides [29-31].The surface of birnessite is getting saturated after approximatively 3 hours of interaction for all the initial dye concentrations tested (Figure 4). That's why the electrochemical activation, by oxidizing Mn(II) to Mn(III,VI) in the surface birnessite has improved the treatement.

4. Study of the non-spontaneous discoloration of dye: Imposition of an oxidizing potential

We focus in these experiments on the study of the efficacy of treatment after imposition of an oxidation potential to the Methyl Orange. The discoloration could be attributed to the adsorption on birnessite, on one hand and to the oxidation on the other hand. The birnessite will act as a catalyst for the reaction of discoloration. First of all, the oxidation potential of our MO dye was determinated by cyclic voltammetry. This potential will be furthermore, applied to an aqueous solution of MO with a sample of the birnessite as anode. Figure 6 shows results obtained after 3 hours of treatment. The non-spontaneous degradation achieved an efficiency rate of 87% against 33% for spontaneous degradation without the imposition of potential. A 53% improvement is observed. This could be expected since there were two mechanisms of discoloration: adsorption on the outer layers of thebirnessite and decomposition of the other molecule (MO) via oxidation.

CONCLUSION

This works describes the successful use of birnessite thin layers to remediate aqueous solution containing methyl orange under standard conditions (room temperature without deaeration, a conventional cell). It was shown that thin layers of birnessite,

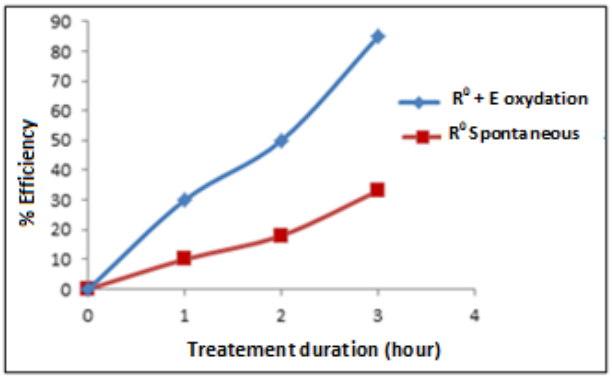

Figure 6: Comparison of results from a spontaneous discoloration and non-spontaneous discoloration ($C= 3.10^{-5}$mol.L^{-1}, pH= 3, t=2700s, Q = 1.5 C, S = 4.5 cm^2, agitation = 350 tr/min).

electrodeposited on SnO_2 in neutral aerated sulphate solutions at room temperature, can discolor aqueous solutions of MO at about 68% after 24 hours. The experiments made before and after interaction by UV spectroscopy and XRD allowed us to propose a mechanism of discoloration of MO. The fact that the birnessite thin layers can degrade spontaneously Methyl Orange, a representative of a highly toxic class of dyestuff, without energy supply. Furthermore, an electrochemical activation of the birnessite and a non-spontaneous degradation of MO have greatly ameliorated the efficiency of the treatment 87% of the MO solution was discolored after 24 hours. These results suggest that birnessite thin layers appear as a very interesting material for the development of a simple and ecological method of wastewater remediation.

REFERENCES

[1] Al. N. Chowdhury, Md. Sh. Azam, Md. Aktaruzzaman, A. Rahim, *J. Hazard. Mater*., (**2009**) 1229-1235.
[2] D. Brown, Ecotoxicol. *Environ. Saf*., (**1987**) 139-147.
[3] J. Tang, Z. Zou, J. Yin, J. Ye, *Chem. Phys. Lett*., (**2003**) 175-179.
[4] M.G. Coelho, G.M. de Lima, R. Augusti, D.A. Maria, J.D. Ardisson, *Appl. Catal. B: Environ*., 96 (**2010**) 67-71.
[5] F.J. Green (Ed), *Aldrich Chemical*, Milwaukee., (**1990**) 403 pp.
[6] G. Crini, Bioresour. *Technol*., 97 (**2006**) 1061-1085.
[7] H.S. Awad, N.A. Galwa, *Chemosphere*., 61 (**2005**) 1327-1335.
[8] G. Crini, Bioresour. Technol., (**2006**) 1061-1085.
[9] H.S. Awad, N.A. Galwa, *Chemosphere*.,(2005) 1327-1335.
[10] E. Brillas, B. Boye, I. Sirés, J.A. Garrido, R.M. Rodríguez, C. Arias, P.L. Cabot, C. Comninellis, *Electrochim. Acta*., (**2004**) 4487-4496.
[11] A. Kesraoui, N. Oturan, N. Bellakhal, M. Dachraoui, M.A. Oturan, *Appl. Catal*. B-Environ., 78 (**2008**) 334-341.
[12] S. Hammami, N. Oturan, N. Bellakhal, M. Dachraoui, M.A. Oturan, *J. Electroanal. Chem*., 610 (**2007**) 75-84.
[13] J.P. Viricelle, A. Pauly, L. Mazet, J. Brunet, M. Bouvet, C. Varenne, C. Pijolat, *Mater .Sci. Eng*., 26 (**2006**) 186-195.
[14] M. Zaied, S. Peulon, N. Bellakhal, B. Desmazieres, A. Chausse, *Appl. Catal.* B: Environ., 101 (**2011**) 441-450.
[15] L. Mao, K. Arihara, T. Sotomura, T. Ohsaka, *Electrochim. Acta*., 49 (**2004**) 2515-2521.
[16] E. Machefaux, A. Verbaer, D. Guyomard, *J. Pow. Sour.*, 157 (**2006**) 443-447.
[17] X.H. Feng, L.M. Zhai, W.F. Tan, F. Liu, J. Z. He, *Environ. Pollut*., (**2007**) 366.
[18] A.N. Chowdhury, M.S. Azam, M. Aktaruzzaman, A. Rahim, *J. Hazard. Mater*., 172 (**2009**) 1229-1235.
[19] N. Larabi-Gruet, S. Peulon, A. Lacroix, *Electrochim. Acta*., 53 (**2008**) 7281-7287.
[20] J. Zhao, X. Wang, L. Zhang, X. Hou, Y. Li, C. Tang, *J. Hazard. Mater*., 188 (**2011**) 231-234.
[21] K. Yong, W. Zhi-liang, W. Yu, Y. Jia, C. Zhi-dong, *New Carb Mater*., 26 (**2011**) 459-464.
[22] Y. Badra, M.A. Mahmoud, *J. Phys. Chem*., 68 (**2007**) 413-419.
[23] M.J. Scott, J.J. Morgan, *Environ. Sci. Technol*.,30 (**1996**) 1990-1996.
[24] M.X. Zhu, Z. Wang, L.Y. Zhou, *J. Hazard. Mater*., 150 (**2008**) 37-45.
[25] J.Y. Shin, M.A. Cheney, *Colloids Surf*., 242 (**2004**) 85-92.
[26] K.H. Kang, D.M. Lim, H.S. Shin, *Water. Sci. Technol*., 58 (**2008**) 171-178.
[27] V. Subramanian, H. Zhu, B. Wei, *Journal of Power Sources*., 159 (**2006**) 361-364.
[28] B.M. Tebo, J.R. Bargar, B.G. Clement, G.J. Dick, K.J. Murray, D. Parker, R. Verity, S.M. Webb, Annu. Rev. *Earth Planet. Sci*., 32 (**2004**) 287-328.
[29] Al. N. Chowdhury, Md. Sh. Azam, Md. Aktaruzzaman, A. Rahim., *J. Hazard. Mater*., 172 (**2009**) 1229-1235.
[30] A.T. Stone, J.J. Morgan,.Environ. *Sci. Technol*., 18 (**1984**) 450-456.
[31] M. Zaied, E. Chutet, S. Peulon, N.Bellakhal, B. Desmazieres, M. Dachraoui, A. Chausse,. *Applied Catalysis* B: Environmental,. 107 (**2011**) 42- 51.

[32] Y.K. Zhou, M. Toupin, D. Belanger, T. Brousse, F. Favier, *J. Phys. Chem. Solids*., 67 (**2006**) 1351-1354.
[33] R. Han, W. Zou, Y. Wang, L. Zhu, *J. Environ. Radioact.*, 93 (**2007**) 127-143.
[34] J.E. Post, D.R. Veblen, *Am. Mineral*., 75 (**1990**) 477-489.
[35] I. Othman, R.M. Mohamed, F.M. Ibrahem, J. Photochem. Photobiol, A: Chem., 189 (**2007**) 80-85.
[36] K.A. Barrett, M.B. Mc Bride, *Environ. Sci. Technol*., 39 (**2005**) 9223-9228.
[37] M.A. Cheney, J.Y. Shin, D.E. Crowley, S. Alvey, N. Malengreau, G. Sposito,. *Physicochem. Eng. Aspects*., 137 (**1998**) 267-273.
[38] M.A. Cheney, G. Sposito, A.E. McGrath, R.S. Criddle, *Colloids Surf*., 107 (**1996**) 131-140.
[39] J.W. Park, J. Dec, J.-E. Kim, J.M. Bollag,. *Environ. Sci. Technol*., 33 (**1999**) 2028-2034.
[40] M.A. Al-Ghouti, Y.S. Al-Degs, M.A.M. Khraisheh, M.N. Ahmad, S.J. Allen, *J. Environ.Manage*.,90 (**2009**) 3520-3527.
[41] A. Ithurbide, S. Peulon, F. Miserque, C. Beaucaire, A. Chausse, *Radiochim. Acta*., 97 (**2009**) 177-180.
[42] A. Ithurbide, S. Peulon, F. Miserque, C. Beaucaire, A. Chausse, *Radiochim. Acta*., 98 (**2010**) 563-568.