

## Wollastonite Ceramic/CuO Nano-Composite for Cadmium Ions Removal from Waste Water

Nabila Ammar<sup>1</sup>, Ahmed Fahmy A. Youssef<sup>2</sup>, S. H. Kenawy<sup>3\*</sup>, E.M.A. Hamzawy<sup>4</sup>, M.A. El-Khateeb<sup>1</sup>

<sup>1</sup>Water Pollution Control Department, National Research Center, <sup>2</sup>Chemistry Department, Cairo University, <sup>3</sup>Ceramic Department, <sup>4</sup>Glass Department, National Research Center, Dokki, Cairo, Egypt.

**N**ANO-PARTICLES, within 29-45 nano-meters, based on wollastonite were prepared with/without CuO through wet method. The adsorption process was occurred on nano-particles powder ceramic at different conditions (pH, contact time and dose) for removing of cadmium ions from waste water. The SEM of nano-particles after treatment of waste water revealed that, surface texture of the blank adsorbents changes totally due to the adsorption of cadmium ions on the particles. At optimum operating conditions (at pH 9) cadmium ions removal reached 98.88% after measurement by ICP and EDX techniques. The obtained results showed that the produced ceramic nano-particles could be used efficiently for removal of cadmium ions with reasonable simple and low cost technique.

**Keywords:** Wollastonite, Ceramic, Nano materials, Water treatment, Adsorption.

### Introduction

The heavy metals (HM) release into the environment has a potential threatening effect to water, soil quality as well as to plant, animal and human health, directly and indirectly. Heavy metals adversely affect the fertility of soils, production of plants, animals and the entire environment if exceed certain limits [1]. Furthermore, these metals could be soluble in aquatic media in the environment and consequently, may be easily absorbed by the cells of living creatures. Thus, by entering the food chain, HM could be bio-accumulated in higher levels of food chain. When HM absorbed above the recommended dose, could cause severe health hazards [2, 3]. Heavy metals could be bio-accumulated through different trophic levels and unlike organic toxicants considered non-biodegradable [4, 5]. Over the last two decades there was an extensive use of Cd worldwide for production of batteries compared with its use for other applications. There were several international agreements and legislation to regulate and monitor the emission of Cd to the environment consequently; minimizing human and environmental threat of Cd which could cause failure of kidney in all mammals [6, 7]. Also, Cd has particular environmental interest as one of the toxic heavy metals, because it could

be accumulates in soils via agricultural usage of fertilizers, sewage residues, disposal of Cd-polluted wastes (industrial as well as municipal). Cadmium is an outstanding human cancer-causing agent and may cause hypertension, bone injuries and lung deficiency [8, 9].

Adsorption among the available remedial technologies is the most popular because of its simplicity and low cost. Different natural (e.g. metal oxides, bentonites, natural zeolites) and synthetic (resins, modified zeolites, synthetic hydroxides /oxides/hydroxides, metal phosphates and silicates) materials have been tested in adsorption process for removal of heavy metal from wastewater with various efficiencies [10, 16]. In addition, significant research work has been done on different waste materials to improve and investigate proper sorbents for water and wastewater treatment, blast furnace slug [17, 18], biomass [19, 20], fly ash [21], and bagasse fly ash [22, 23], among other have been investigated as sorbents for removal of heavy metal with various levels of achievement.

Nano-metal oxides are a highly valuable material with various applications in catalysts [24], gas sensors [25], optical, electrical and mechanical devices (Yi et al. 2011), cosmetics

\*Corresponding author e-mail: ksayed6631@gmail.com  
DOI : 10.21608/ejchem.2017.1289.1076

and sunscreens [26]. Nano-metal oxides such as hydrous manganese oxides, iron, aluminum, titanium oxides and zinc oxide are extensively used for removal of heavy metal ions from water and wastewater. These nano-metal oxides can be manufactured by different techniques such as microwave-assisted route [27], chemical vapor deposition (CVD), different hydrothermal techniques and sol-gel method [28].

The main objectives of this study are the synthesis a nominal nano-calcium silicate (wollastonite) ceramic doped with CuO as metal oxide using a very simple technique. As well as, investigate the adsorption capacity of the produced nano-composite as an adsorbent material to remove of Cd ions from water samples.

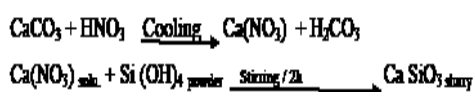
## Materials and Methods

### Materials

Nominal nano-calcium silicate ceramic (wollastonite) was prepared from calcium carbonate (El-Gomhorya Company for Chemicals, Egypt 99%), silicon hydroxide gel (Fluka) and copper carbonate ( $\text{CuCO}_3$ ). The source of Cd(II) used in the adsorption studies was high purity cadmium chloride hexahydrate ( $\text{CdCl}_2 \cdot 6\text{H}_2\text{O}$ ), (Chem-Supply-Merck).

### Synthesis of Nominal nano-calcium silicate ceramic

Nominal calcium silicate ceramic (wollastonite) was prepared from pure calcium carbonate, silicon hydroxide (silica gel) and copper carbonate ( $\text{CuCO}_3$ ), was used as precursors for CuO was doped (0.0 - 7g/ 100 g  $\text{CaSiO}_3$  powder).  $\text{CaCO}_3$  was dissolved in stoichiometric amount of nitric acid ( $\text{HNO}_3$ ). The freshly prepared calcium nitrate [ $\text{Ca}(\text{NO}_3)_2$ ] was dissolved in appropriate amount of distilled water gently with slow stirring. The silicon hydroxide gel was added slowly to the calcium nitrate under vigorous stirring for 2h to ensure good mixing. The CuO dopant, freshly prepared from  $\text{CuCO}_3$  with distilled water to gave  $\text{Cu}(\text{OH})_2$  was added under continues vigorous stirring for 1 hr. The homogenous composite was dried at  $100^\circ\text{C}$  overnight followed by calcined at  $550^\circ\text{C}/2\text{h}$ . The following equations explain the steps of produce



X-ray investigations of the  $\text{CaSiO}_3$  with /CuO calcined at  $550^\circ\text{C}$  in air for 2h was conducted using XRD (BRUKER, D8 ADVANCED Cu target, Germany). XRD was carried out in the range from 20 to  $60 2\theta^\circ$ . The morphology of the sample was checked via scanning electron microscopy (SEM) coupled with energy-dispersive spectroscopy EDX, (SEM Model Quanta FEG 250).

### Removal of the metal ions using the nano-ceramic sorbent

A batch sorption method was used to study the efficiency of the nano-ceramic for the removal of Cd ions. The influences of initial metal ion concentration, adsorbent dose, contact time and pH of solution on the sorption of Cd ions were examined. A Jar test procedure was used for ensuring homogeneity of the metal ions salts in solutions. The metal ions were estimated in the samples after filtration with filter papers Whatman® (No. 41). Control samples without adsorbent were used for comparison between sorption and precipitation of metal ions. All experiments were repeated three times, the percentage of metal ions removal by the nano-ceramic was measured for all samples using inductive coupled plasma optical emission spectrometry (Agilent ICP-OES 5100) according to standard methods for the examination of water and wastewater [APHA, 2012].

## Results and Discussion

### Characterization of nano-ceramic sorbent

The X ray diffraction pattern of calcined  $\text{CaSiO}_3/\text{CuO}$  powder was shown in Fig. 1. The identified phases were wollastonite ( $\text{CaSiO}_3$ , ICDD, 01-076-0925) and for tenorite ( $\text{CuO}$ , ICDD, 00-005-0661).

The SEM micrograph of the calcined  $\text{CaSiO}_3/\text{CuO}$  powder before soaking in waste water was shown in Fig. 2. The photograph show cluster of nano-particles within 29–45 nm nano-meter, however some connected barrier of nano-particles which make boxes or pores were clearly visible in the all sample field (Fig.2). Micrograph of the sample, illustrate some tiny particles as well

as particles of a somewhat larger size indicating some of crystallinity. Figure 2 shows that, the particles are near uniform spherical, the irregular surface of the particles increases the surface area and the particle size can be estimated in the range of 29–45 nm. The resulting microstructure and the pore size distribution of the obtained ceramic

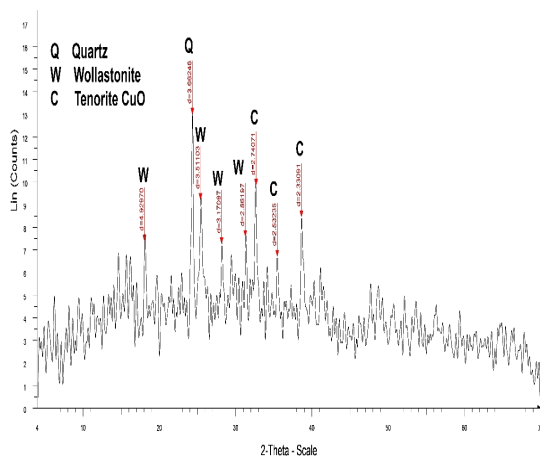


Fig. 1. X ray diffraction patterns of CuO- doped wollastonite treated at 550°C/2hr.

are particularly important for potential adsorption applications.

The pH has significant effect on adsorption, as it affects the surface charge of adsorbent and also chemical speciation of the adsorbate. Adsorption of Cd ions was studied at different pH ranging from 3 upto 9 where,  $\text{Cd}^{2+}$ ,  $\text{Cd}(\text{OH})$ ,  $\text{Cd}(\text{OH})_2$ , and  $\text{Cd}(\text{OH})_{2(\text{s})}$  are the forms of cadmium present in de-ionized water. In these experiments adsorbate concentration was 25 mg/L, ceramic mass was 0.75 g at contact time varying from 0 to 60 min.

Figure 3 shows the effect of pH on adsorption

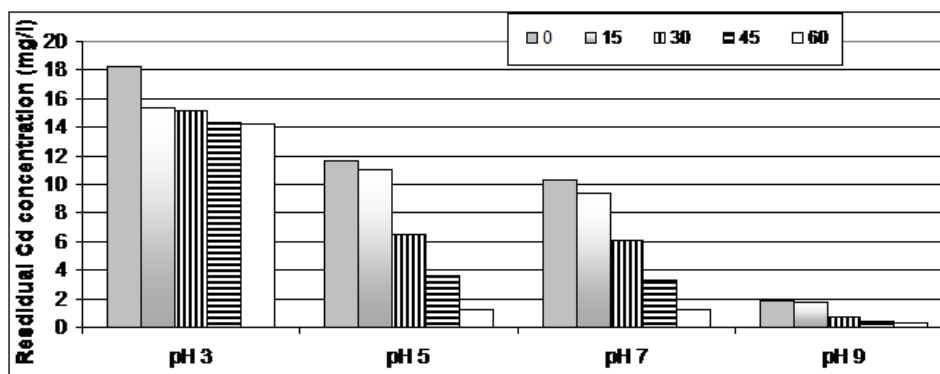


Fig. 3. Effect of pH value on the removal efficiency of Cd ions by using the nano-ceramic (initial Cd concentration was 25 mg/l).

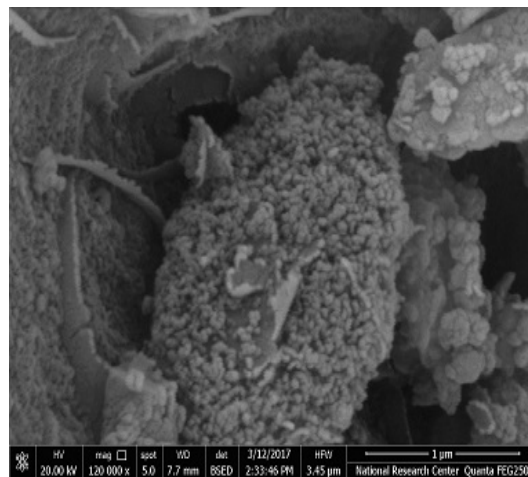


Fig. 2. SEM of the Nano-ceramic before Cadmium adsorption.

process (initial Cd concentration was 25 mg/l). It can be seen that, adsorption increases with increasing the pH of the solution. The removal efficiency increased from 43.2 % at pH 3 to 98.88 % at pH 9. Where, at lower pH values  $\text{H}^+$  ions compete with Cd(II) ions for binding sites on the absorbent surface. However, as the pH increases there is a reduction in competition between  $\text{H}^+$ ,  $\text{Cd}^{2+}$  and  $\text{Cd}(\text{OH})^+$  ions and as a result, metal uptake by the absorbent increases. The experimental results indicate that, Cd(II) removal was predominantly controlled by adsorption upto a pH 8. It was showed that [29], the Cd(II) ion predominates at pH below 7 and it begins to precipitate out as  $\text{Cd}(\text{OH})_2$  at pH values just above 9. Based on the results, further experiments were conducted at pH 9.

#### Effect of contact time

Adsorption of Cd ions was studied at different contact time ranging from 0 to 120 min. with

25 mg/L of adsorbate concentration, the nano-ceramic mass was 0.75 g and pH 9. Figure 4 shows the influence of contact time on the efficiency

of the nano-ceramic for the removal of Cd(II) ions. It can be noted that, the removal efficiency increased from 92.4 % to 98.88 % and almost

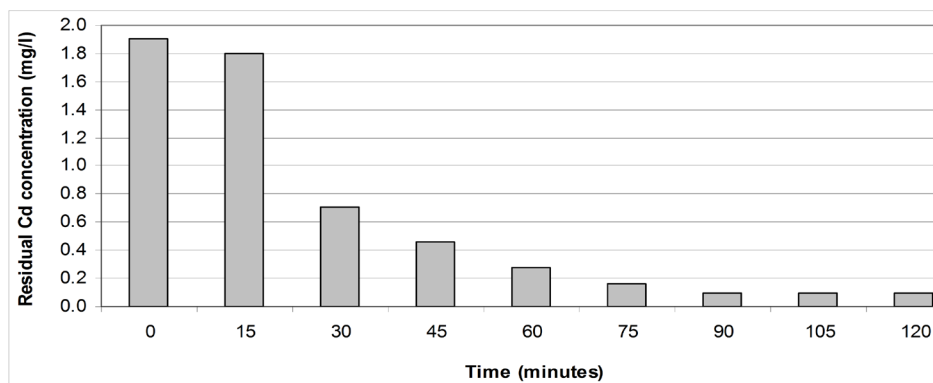


Fig. 4. Effect of contact time on the removal efficiency of Cd ions by using the nano-ceramic at pH: 9 and T: 298 (initial Cd concentration was 25 mg/l).

remain constant from 60 until 120 min. Therefore, the equilibrium adsorption time is 60 min.

#### *Effect of adsorbent dosage on adsorption*

The effect of adsorbent dose was studied using 25 mg/L of adsorbate concentration, at pH 9 with nano-ceramic mass varied from 0.25 to 1.0 g/L with 0.25 mg/l intervals, at contact time ranging from 0 to 60 min.

The general trend indicates that, 0.25 to 0.75 g/L of sorbent dose uptake huge percent of Cd(II) (Fig. 5) where, it can be observed that the removal efficiency increased from 96.04 - 98.88 % and nearly remain constant from 0.75 - 1.0 g/L. The reason for the increasing of removal efficiency could be attributed to the increasing of adsorbent

dose that means increase of the total available surface area of the adsorbent particles. Beyond 0.75 g/L, the removal remained almost unaffected by the adsorbent dosage so, at 0.75 g/L, the adsorbent surface becomes saturated with Cd(II).

#### *The SEM of Cd on the nano-ceramic sorbent*

The SEM micrograph of the Cd loaded on nano-calcium silicate (wollastonite) doped with CuO is shown in Fig. 6. The photos show light coated nano-particles of Cd-metal on the surface of ceramic. It could be noted from Fig.6, that the surface morphology and porosity of the nano-ceramic (wollastonite) doped with CuO were drastically changed after loading of cadmium as compared with the surface shape of the blank adsorbents. The EDS microanalysis indicates the

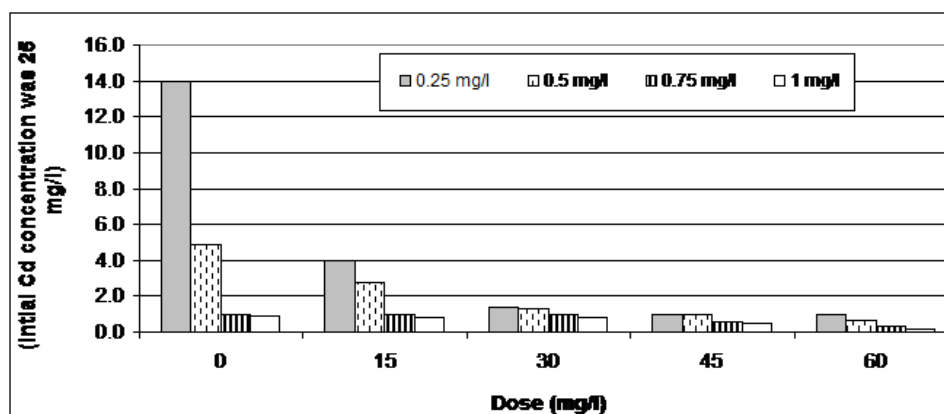


Fig. 5. Effect of adsorbent dosage of the nano-ceramic on the removal efficiency of Cd ions at pH: 9 and T: 298 (initial Cd concentration was 27.4 mg/l).

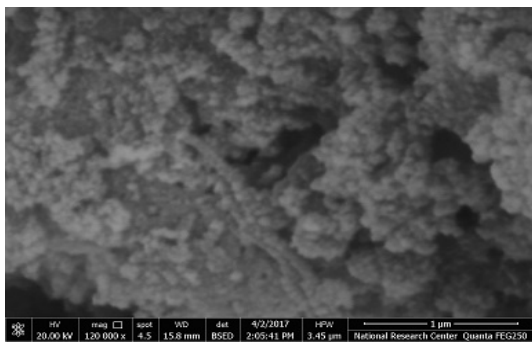


Fig. 6. SEM of the nano-ceramic sample after cadmium adsorption.

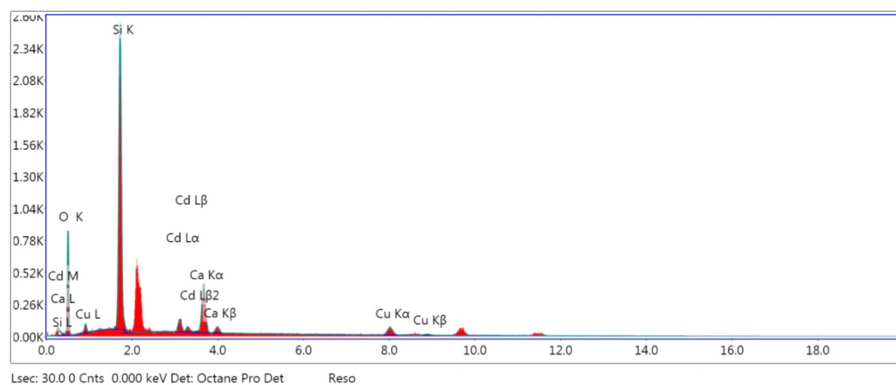


Fig.7. Energy dispersive spectrum (EDS) of the Cd-loaded nano-Calcium Silicate doped with CuO.

averaging was 0.5 to 1.0  $\mu\text{m}$  with particles forming larger agglomerates.

### Conclusions

- Nano-Calcium Silicate doped with nano-copper is found to be beneficial for removing of heavy metal such as Cd from an aqueous solution. The studied material was synthesized using very simple technique (co-precipitation method) from low cost starting chemicals. The prepared ceramic doped with CuO was investigated using different tools.
- Higher uptakes (98.88% of Cd(II)) from aqueous solution is possible using wollastonite as an adsorbent provided the initial concentration of the Cd(II) in the wastewater is around 25 mg/l. This material could be used for industrial wastewater treatment.
- The pH has been found to be a master variable controlling the adsorption of Cd(II) by the oxides present in wollastonite. The adsorption is maximum around pH 9.0

presence of cadmium cations after adsorption onto surface of nano-ceramic doped with CuO (Fig.7).

The aforementioned results were in agreement with previous work where, the synthesized nano-structured calcium silicates showed that the synthesized material based on an amorphous materials without a defined structure. In our work the particle size were ranged from 29-45 nano-meter synthesized using commercially inorganic materials, while for the previous work the mean particle size

and it has been concluded that surface complexation involving  $\text{H}^+$  exchange and chemical precipitation contribute towards maximum uptake.

### References

1. American Public Health Association, Standard methods for the examination of water and wastewater, 22nd ed., Washington, DC: APHA, (2012).
2. Antonio, J.R.C., Samuel, P.D.M., Joao, M.S., Josue, M.F., Gilberto, D.S. and Alcinea, C.O., Nanosized aluminum derived oxides catalysts prepared with different methods for styrene production, *Chemical Engineering Journal* **209**(1), 345–355(2012).
3. Ayangbenro, A.S. and Babalola, O.O., A new strategy for heavy metal polluted environments: a review of microbial biosorbents, *International Journal of Environmental Research and Public Health* **14**(94), (2017); doi:10.3390/ijerph14010094
4. Chubar N., Carvalho J.R. and Correia M.J.N., Cork Biomass as Biosorbent for Cu(II), Zn(II) and

- Ni(II), *Colloids Surfaces A: Physicochemical and Engineering Aspects*, **230**(1), 57-65, (2003).
5. Ciccu R., Ghiani M., Serci A., Fadda S., Peretti R. and Zucca A., heavy metal immobilization in the mining-contaminated soils using various *Industrial Wastes, Minerals Engineering*, **16**(3), 187-192(2003).
  6. Dimitrova, S.V. and Mehandriev, D.R., Lead removal from aqueous solutions by granulated blast-furnace slag, *Water Research*, **32**(11), 3289-3292 (1998).
  7. Epifani, M., Comini, E., Diaz, R., Arbiol, J., Siciliano, P., Sberveglieri, G. and Morante, J.R., Oxide nanopowders from the low-temperature processing of metal oxide sols and their application as gas-sensing materials. *Sens Actuators B, Chem* **118**(1-2), 105-109(2006).
  8. Farid, G., Sarwar, N., Saifullah and Ahmad, A., Abdul Ghafoor and Rehman M., Heavy metals (Cd, Ni and Pb) contamination of soils, plants and waters in madina town of faisalabad metropolitan and preparation of gis based maps, *Advances in Crop Science and Technology*, 4:199(2015), doi:10.4172/2329-8863.1000199.
  9. Garg, U., Kaur, M.P., Jawa, G.K., Sud, D. and Garg, V.K., Removal of cadmium(II) from aqueous solutions by adsorption on agricultural waste biomass, *Journal of Hazardous Materials.*, **154**, 1149, (2008).
  10. Gundogan, R., Acemioglu, B. and Alma, M.H., Copper(II) Adsorption from Aqueous Solution by Herbaceous Peat, *Journal of Colloid and Interface Science.*, **269**(2), 303(2004).
  11. Hegazi, H.A., Removal of heavy metals from wastewater using agricultural and industrial wastes as adsorbents, *Housing and Building National Research Center (HBRC) Journal*, **9**, 276-282(2013).
  12. Ho, Y.S. and Mckay, G., The sorption of Lead(II) ions on peat, *Water Research*, **33**, 578(1999).
  13. Kaji, M., Role of experts and public participation in pollution control: the case of Itai-itai disease in Japan, *Ethics in Science and Environmental Politics*, **12**, 99-111(2012).
  14. Lagashetty, A.K., Havanoor, V.A., Basavaraja, S., Balaji, S.D. and Venkataraman, A., Microwave-assisted route for synthesis of nanosized metal oxides. *Science and Technology of Advanced Materials*, **8**(6), 484-493, (2007)
  15. Lu, B., Chen, S. and Kawamoto, K., Direct hydrothermal synthesis of nanosized mesoporous ramsdellite manganese oxide with high surface area, *Materials Research Bulletin* **47**(11), 3619-3624 (2012).
  16. Mahdavi, S., Jalali, M. and Afkhami, A., Heavy metal removal from aqueous solutions using TiO<sub>2</sub>, MgO, and Al<sub>2</sub>O<sub>3</sub> nanoparticles, *Chemical Engineering Communications* **200**(3),448-470, (2013).
  17. Mckay, G. and Ho, Y.S., Pseudo-second-order model for sorption processes. *Process Biochemistry*, **34**, 451-465(1999)
  18. Mobasherpour, I., Salahi, E. and Pazouki, M., Removal of divalent cadmium cations by means of synthetic nano-crystallite hydroxyapatite, *Desalination*, **266**, 142-148(2011).
  19. Pagnanelli, F., Veglio, F. and Toro, L., Modelling of the Acid-Base Properties of Natural and Synthetic Adsorbent Materials Used for Heavy Metal Removal from Aqueous Solutions, *Chemosphere*, **54**(7), 905-915(2004).
  20. Park, K.T., Gupta ,V.K., Mohan, D. and Sharma, S., Removal of chromium(VI) from electroplating industry wastewater using bagasse fly ash—a sugar industry waste material, *The Environmentalist*, **19**(2), 129-136(1999).
  21. Ramos, R.L., Rangel-Mendez, J.R., Mendoza-Barron, J., Fuentes-Rubio, L. and Guerrero-Coronado, R.M., Adsorption of cadmium (II) from aqueous solution onto activated carbon. *Water Science and Technology*, **35**, 205-211(1997).
  22. Reed, B.E. and Matsumoto, M. R., Modelling of cadmium adsorption by activated carbon using langmuir and freundlich expressions, *Separation Science and Technology*, **28**, 2179(1993).
  23. Sekhar, K.C., Kamala, C.T., Chary, N.S., Sastry A.R.K., Nageswara Rao, T. and Vairamani, M., Removal of lead from aqueous solutions using an immobilized biomaterial derived from a plant biomass, *Journal of Hazardous Materials*, **108**(1-2), 111-117(2004).
  24. Shin, E.W., Karthikeyan, K.G. and Tshabalala, M.A., Adsorption mechanism of cadmium on juniper bark and wood, *Bioresource Technology*, **98**(3), 588-594 (2007), doi:10.1016/j.biortech.2006.02.024

25. Tomoyuki, K. and Asa, K., Ultraviolet-screening zinc oxide excellent in transparency and composition containing the same, US patent No 6, 171, 580(2001).
26. Tripathi, A. and Ranjan, M.R., Heavy Metal Removal from Wastewater Using Low Cost Adsorbents, *Journal of Bioremediation and Biodegradation*, **6**, 315(2015), doi:10.4172/2155-6199.1000315
27. Xu, Y. and Axe, L., Synthesis and Characterization of iron oxide-coated silica and its effect on metal adsorption, *Journal of Colloid and Interface Science*, **282**(1), 11-19 (2005).
28. Yi, Y., Yang, Z. and Zhang, S., Ecological risk assessment of heavy metals in sediment and human health risk assessment of heavy metals in fishes in the middle and lower reaches of the Yangtze River basin, *Environmental Pollution*, **159**, 2575–2585, (2011).
29. Zhu, R., Yu, R., Yao, J., Mao, D., Xing, C. and Wang, D., Removal of Cd<sup>2+</sup> from aqueous solutions by hydroxyapatite, *Catalysis Today*, **139**, 94–99(2008).

(Received 6/7/2017;

accepted 21/8/2017)

### متوالفات نانو سيراميكيات الولوستونيت/اكسيد النحاس لازالة ايونات الكاديوم من المياه الملوثة

نبيلة عمار<sup>١</sup>، أحمد يوسف<sup>٢</sup>، سيد قناوي<sup>٣</sup>، عصمت حمزاوي<sup>٤</sup> و محمد الخطيب<sup>٥</sup>  
<sup>١</sup>قسم تلوث المياه - المركز القومي للبحوث، <sup>٢</sup>قسم الكيمياء - جامعة القاهرة، <sup>٣</sup>قسم السيراميك و <sup>٤</sup>قسم الزجاج -  
 المركز القومي للبحوث - القاهرة - مصر.

تم تحضير حبيبات نانو ولوستونيت مطعم بأكسيد النحاس باستخدام طريقة الترسيب. وكان حجم الحبيبات يتراوح بين ٢٩-٤٥ نانومتر. وقد تمت عملية الادمصاص لايونات الكاديوم عند درجات مختلفة من الالاس الهيدروجيني وكذلك علي فترات زمنية محددة وايضا عند تركيزات مختلفة من ايونات الكاديوم. وقد اظهر الفحص باستخدام الميكروسكوب الماسح الاليكتروني ان حبيبات النانو للعينات بعد الادمصاص تغطية كاملة لكل حبيبات النانو بأيونات الكاديوم مما ادي الي تغيير النسيج السطحي للحبيبات. وقد لوحظ انه عند الالاس الهيدروجيني المثالي وهو (٩) ان حوالي ٩٨,٨٪ من ايونات الكاديوم قد ازيلت بواسطة تقنية ال ICP و EDX. ومما سبق اظهرت النتائج المتحصل عليها امكانية استخدام حبيبات السيراميك النانومترية بكفاءة عالية لازالة ايونات الكاديوم من المياه الملوثة مع الاخذ في الاعتبار ان طريقة التحضير للسيراميك بسيطة ورخيصة للغاية.