

Magnetite Nanocomposites, Application for Decontamination of Wastewaters

S.G. Muntean*, M.A. Nistor*, A.A. Andelescu*, M.E. Radulescu-Grad* and R. Ianos*,**

*Institute of Chemistry Timisoara of Romanian Academy, 24 Av. Mihai Viteazul, 300223 Timisoara, Romania,
e-mail: sgmuntean@acad-icht.tm.edu.ro

** University Politehnica Timisoara, Faculty of Industrial Chemistry and Environmental Engineering, 300223, Parvan 6, Timisoara, Romania

Abstract: The present work describes the application of magnetic nanoparticles embedded within a matrix of activated carbon as adsorbent for acid dyes and Cu(II) removal from wastewaters, in selected working conditions. The effects of process variables: pH solution, adsorbent ratio and dose, initial concentration of pollutant, and contact time was investigated in order to determine the optimal parameters of the process. Pseudo-second order kinetic model was fitted to the kinetic data, and adsorption isotherm analysis was used to elucidate the adsorption mechanism. The experimental results suggest that as-prepared magnetite/carbon nanocomposites has the potential applications in the water purification management.

Keywords: magnetic nanocomposites, adsorption, complex acid dye, metal ions

1. Introduction

The wastewaters discharged from various industries causes serious environmental problems [1]. The textile dyes are persistent substances with strong color, poor biodegradability, and high capacity to modify the environment [2, 3]. Metal complex dyes are compounds with a lot of applications leather finishing, stationery printing inks, inks, dyes for metals and plastic etc. Importance present copper complex dyes, used in dyeing of cellulose materials, and sensitized solar cells [4-6]. Metal ions are not biodegradable, cannot be metabolized or decomposed, and are highly persistent in the environment [7]. Copper, widely used in many industries, contaminates the surface water and groundwaters [8]. In this context the availability of clear water for various activities is becoming the most challenging task for researchers and engineers worldwide.

Among different methodologies reported for wastewaters management, adsorption proved to be a superior technique for dye and metal ions removal from aqueous phase, in terms of cost, availability of a wide range of adsorbents, low harmful secondary products, facile regeneration of the adsorbents and high effectiveness [9-11].

In the last years magnetic nanoparticles were applied with very good results as adsorbent materials due to their unique physical and chemical properties [12-14].

The objective of the present study was to investigate the adsorption capacity of new magnetite nanomaterial for the removal of complex dyes and metal ion from aqueous solution. The effects of process variables on the adsorption process were studied, and the kinetics and adsorption isotherm were evaluated.

2. Experimental

A complex dye Acid orange 7, AO7+Cu, and a metal ion (Cu^{2+}) were used as adsorbate. The azo-dye with metallic ion complex (AO7-Cu) was synthesized using AO7 as ligand. The synthesis and characterization of AO7-Cu were previously reported by our group [15].

The CuSO_4 was purchased from Reactivul Bucuresti, and were used as received without further purification.

Working dye solutions were prepared with distilled water, using different concentrations of complex dye and metal, in order to replicate industrial colored wastewaters.

The magnetic nanoparticles embedded within a matrix of activated carbon (MP) were synthesized by a simple and cost-effective combustion technique. The detailed procedure about the preparation route and sample characterization is presented in [16].

Batch experiments were carried out by adding magnetic nanocomposites to model wastewaters and maintained under a constant shaking speed of 180 rpm. After reaching the equilibrium, the adsorbent was separated by a magnet, and the pollutant concentration in solution was spectrophotometrically (CECIL CE UV-Vis Spectrophotometer, SensAA atomic absorption spectrometer) determined.

Using experimental data the adsorption capacity (1) and the removal percentage (2) were calculated.

$$q_t = \frac{(C_0 - C_t) \cdot V}{W} \quad (1)$$

$$R = \frac{C_0 - C_e}{C_0} \cdot 100 \quad (2)$$

3. Results and Discussion

The selected nanocomposites materials had different magnetite/carbon ratios: 1/1 (MP 1), 1/2 (MP 2) and 1/5 (MP 3), and exhibited a ferrimagnetic behavior. As the Fe_3O_4 /carbon ratio decreased from 1/1 to 1/5, the BET surfaces increased from $360 \text{ m}^2/\text{g}$ to $706 \text{ m}^2/\text{g}$, and the micropore volume increased from 0.096 to $0.212 \text{ cm}^3/\text{g}$ [16]. Regarding these values our goal was to test these materials as adsorbents.

The structure of Acid Orange 7 copper complex (AO7-Cu) is presented in Figure 1:

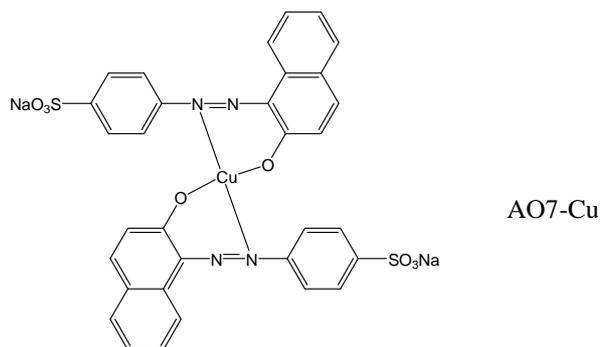


Figure 1. Molecular structure of investigated complex dye

3.1. Effect of initial solution pH

pH solution is an important factor, significantly affecting the adsorption of dyes and metal ions. The analysis were performed at different pH values between 2.5 and 11 in case of AO7-Cu, and between 3 and 8 for $\text{Cu}(\text{II})$, using HCl (0.1 mol/L) or NaOH (0.1 mol/L) solutions. The pH values above 8 for copper solution were not considered due to the precipitation of heavy metals [17].

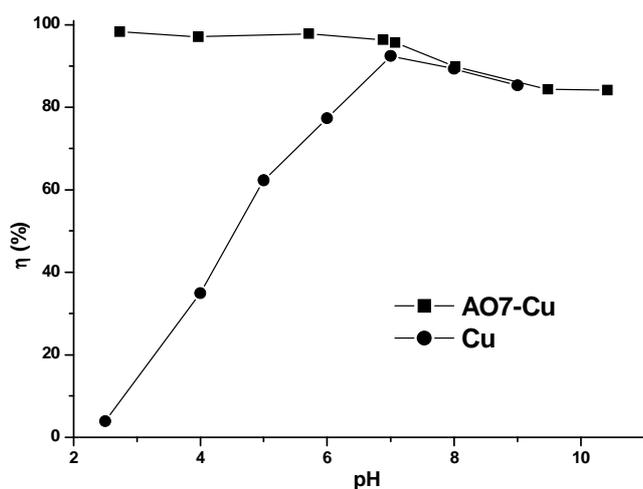


Figure 2. Effect of solution pH on adsorption onto MP 3

The results presented in Figure 2, for AO7-Cu dye complex indicate that the removal percentage decreased with increasing of solution pH. At low pH value, the adsorption mechanism of anionic dyes (AO7-Cu) is controlled by electrostatic attractions between the positively charged surface of adsorbent, as a result of the protonation process, and the negatively charged dye molecules.

When the pH values were increased from 2 to 6, the removal percentage of $\text{Cu}(\text{II})$ increased from 3.92 to 92.46%. Moreover a decrease of removal percentage of $\text{Cu}(\text{II})$ was observed in the range of pH 6 – 8.5. It is known that the chemical speciation of copper ions is influenced by the pH. According to the chemical speciation diagram of copper, $\text{Cu}(\text{II})$ is the dominant species at $\text{pH} < 5$ [18].

According to these results, the adsorption studies were further conducted at the natural pH for AO7-Cu 6.4, and at pH 5 for Cu^{2+} ion.

3.2. Effect of adsorbent type

The effect of magnetite/carbon ratio on the removal efficiency is presented in Figure 3. As can be observed, the increase of the carbon content from sample 1 to sample 3 continually increases the removal efficiency for investigated sorbates.

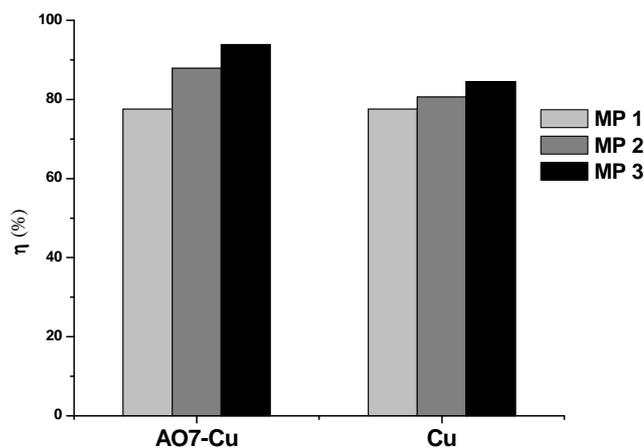


Figure 3. Effect of support's type on adsorption

Nanopowder MP 3 that showed the best adsorption capacity was used as adsorbent for the removal of AO7-Cu dye and Cu^{2+} .

3.3. Effect of adsorbent dose

The effect of adsorbant dose was studied in the range of 0.5 g L^{-1} to 3 g L^{-1} . The results presented in Figure 4 revealed that the removal efficiency increases with the increase of the adsorbent mass from 0.5 g/L to 3 g/L .

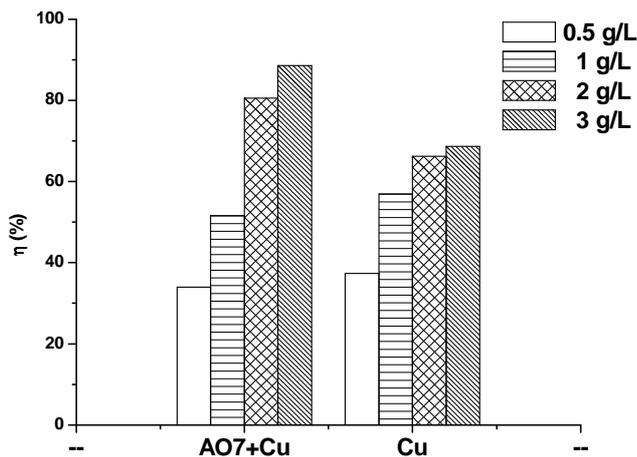


Figure 4. Effect of adsorbent dose on adsorption process

These results can be attributed to the availability of more adsorption sites as the adsorbent dose increased. Further studies were carried out using a 2 g L⁻¹ adsorbent dose.

3.3. Influence of initial concentration

To study the influence of the initial concentration of dye adsorption process, the concentrations were varied between 10 and 150 mg / L, at 25 ° C and optimum pH. As it can be seen in Figure 5, the adsorption was very fast during the first 25 minutes, and near the equilibrium, remains almost constant. This is due to saturation of the active centers available for the sorbate on the adsorbent surface.

The amount of adsorbed pollutant increased with the increases of the initial concentration, indicating that the pollutant removal is concentration dependent.

3.4. Kinetic studies

The experimental results obtained for the influence of initial concentration were analyzed using the first-order Lagergren (3) and the pseudo second-order kinetic models (4).

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{3}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{4}$$

The correlation coefficients were used to determine the best fitting kinetic model, and the obtained results are presented in Figures 6 and 7, and Table 1.

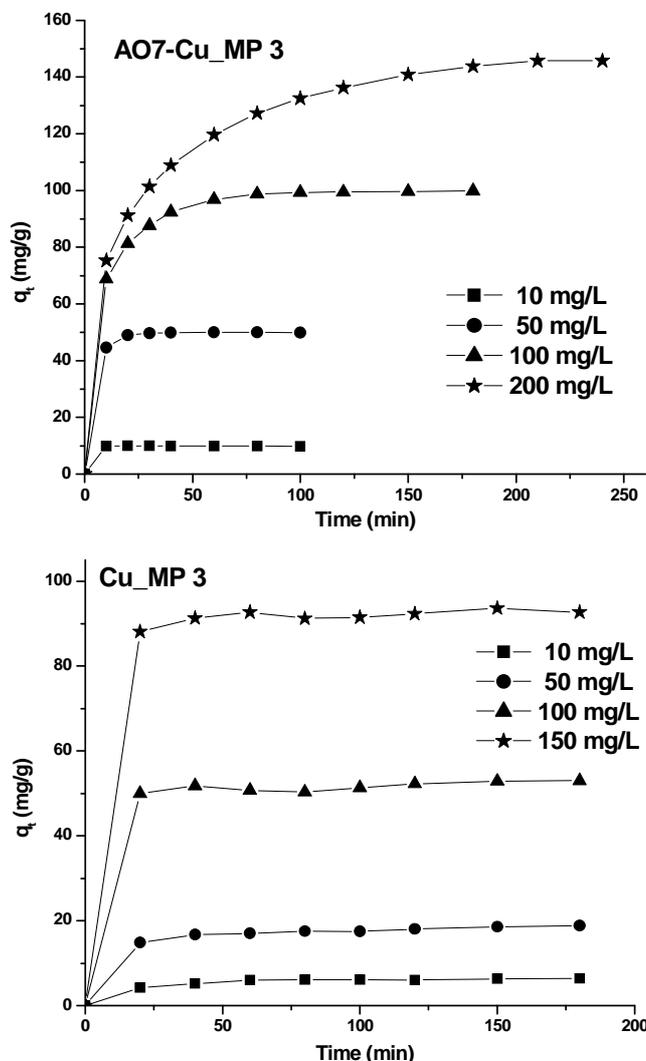


Figure 5. Effect of the pollutant initial concentration on adsorption onto MP 3 (adsorbent dose 2 g/L, 25°C, optimum pH)

TABLE 1. Comparison of experimental and calculated q_e values, and kinetic parameters for adsorption of AO7-Cu and Cu²⁺ onto MP 3

Sorbent	C ₀ (mg/L)	q _{e,exp} (mgg ⁻¹)	First order kinetic model		Second order kinetic model	
			q _{e,calc} (mgg ⁻¹)	k ₁ · 10 ³ (min ⁻¹)	q _{e,calc} (mgg ⁻¹)	k ₂ · 10 ³ (g/mg min)
AO7-Cu	10	9.94	2.28	15.7	9.78	242.7
	50	49.96	4.61	6.98	50.00	22.3
	100	99.79	54.43	1.88	103.19	2.02
	150	148.17	71.60	0.77	156.25	0.41
Cu ²⁺	10	7.61	3.37	21.76	6.77	13.42
	50	22.50	9.12	22.45	19.46	8.39
	100	55.44	14.06	28.09	53.42	7.26
	150	108.74	21.32	34.75	93.89	6.25

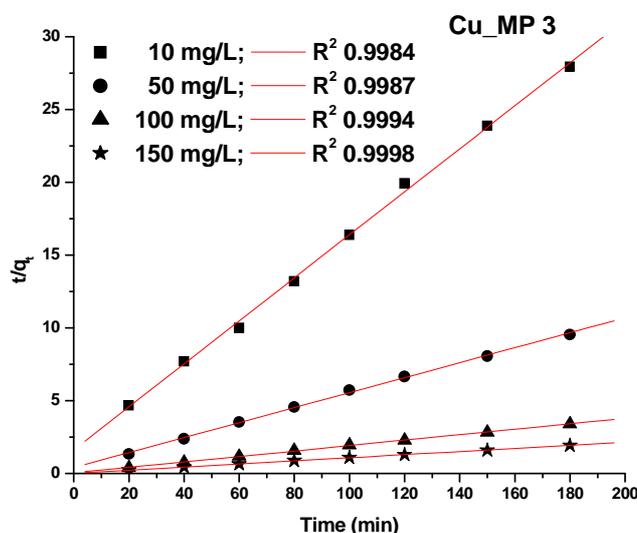
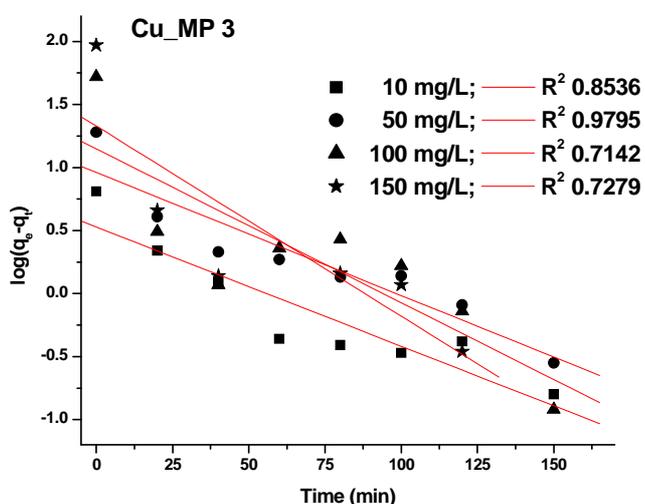
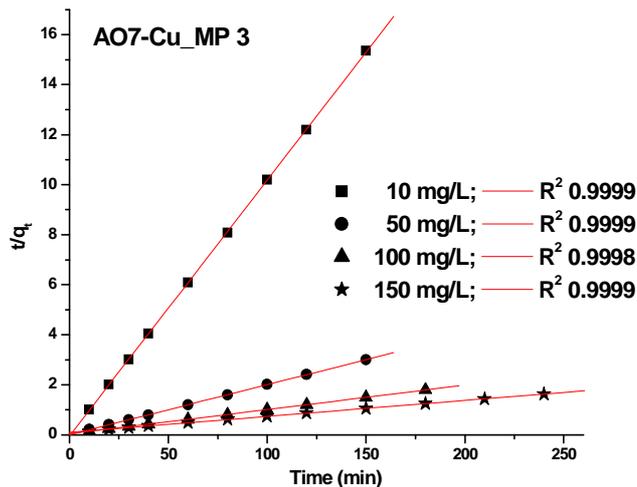
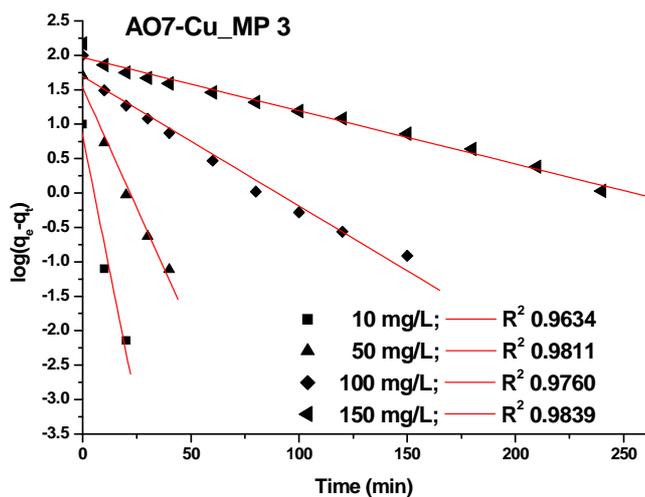


Figure 6. First order kinetic model fitting for the adsorption of AO7-Cu and Cu²⁺ onto MP 3

Figure 7. Pseudo-second order kinetic model fitting for the adsorption of AO7-Cu and Cu²⁺ onto MP 3

The obtained data gave poor fits when the the first order kinetic model was used (Figure 6) and very good fits with the pseudo-second order kinetic model.

The theoretical values of adsorption capacity were close to the experimental values in case of pseudo-second order kinetics ($R^2 > 0.99$).

Also, a decrease of the pseudo-second order constant rate k_2 was observed, indicating that the necessary time for reaching the equilibrium increased with raising initial dye concentration, which is in agreement with experimental obtained data.

3.5. Equilibrium studies

Equilibrium adsorption studies were carried out for a better understanding of the adsorption process. The experimental data obtained at equilibrium, was analyzed with Freundlich, Langmuir, and Sips adsorption models.

$$q_e = K_F C_e^{1/n} \tag{5}$$

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{6}$$

$$q_e = \frac{q_m K_S C_e^{1/n}}{1 + K_S C_e^{1/n}} \tag{7}$$

The parameters that describes the theoretical models were determined using ORIGIN version 6.1., and the statistical criteria were the standard deviation (SE) and the squared multiple regression coefficient (R^2).

Results are presented in Figure 8 and Table 2.

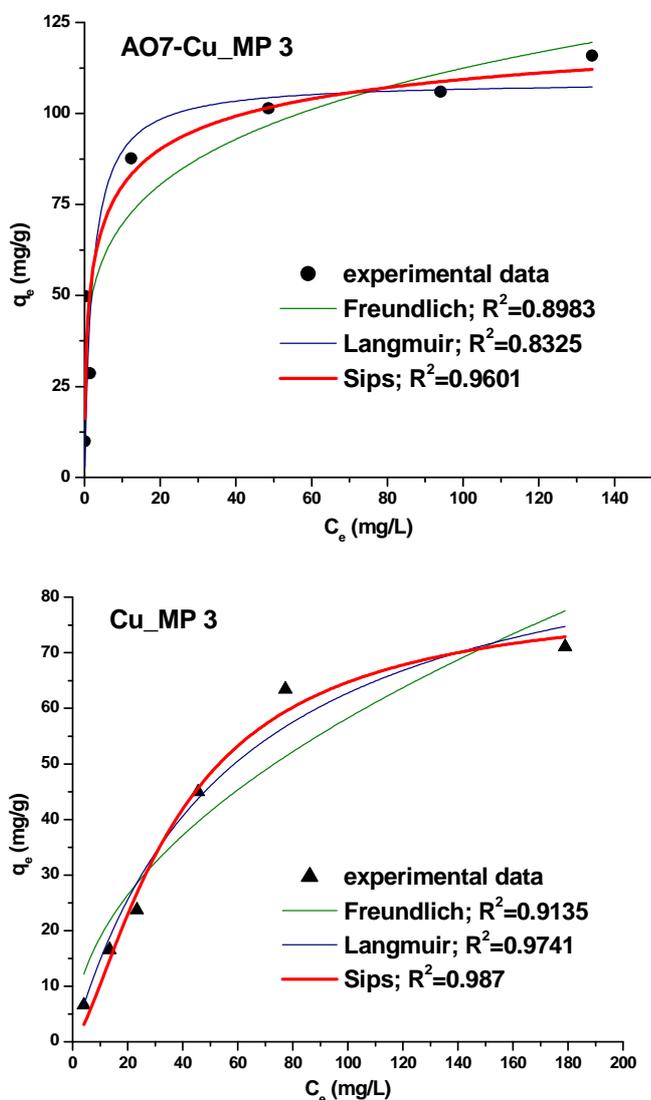


Figure 8. Isotherm plots for the adsorption of AO7-Cu and Cu(II) onto MP 3

The best isotherm model that fits the experimental data with lower error was the Sips isotherm model. That means that an adsorption process is going on after a combined model of Freundlich and Langmuir: diffused adsorption at low dye concentration, and a monomolecular adsorption with a saturation value - at high adsorbate concentrations.

The maximum adsorption capacity of the MP 3 for AO7-Cu dye, and Cu(II) was determined from the Sips isotherm curves.

TABLE 2. Adsorption isotherm constants for the investigated pollutants adsorption on MP 3

Isotherm model	Parameter	AO7-Cu	Cu(II)
Freundlich	K_F ($\text{mg}^{1-(1/n)}\text{L}^{1/n}$)	43.11	6.06
	n	7.81	2.03
Langmuir	q_m (mg/g)	108.96	98.66
	K_L (L/mg)	0.46	$1.75 \cdot 10^{-2}$
Sips	q_m (mg/g)	135.92	80.56
	K_s (L/mg)	0.22	$2.64 \cdot 10^{-2}$
	n	2.18	0.68

4. Conclusions

New magnetic adsorbents with varied carbon content were successfully applied for removal of complex dye and copper ions from wastewaters.

The removal efficiency of investigated pollutants depends on pH solution, and increases with increasing the carbon content, with initial dye concentration, and the dose of magnetite/carbon nanocomposites.

The adsorption process can be conducted at normal temperature and natural solution pH with minimal working costs, which is important for a potential application in real systems.

The high adsorption capacity and excellent separation capability, indicates that the as-prepared magnetite/carbon nanocomposites are excellent adsorbent materials for removal of pollutants.

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REFERENCES

- Xu P., Zeng G.M., Huang D.L., Feng C.L., Hu S., Zhao M.H., Lai C., Wei Z., Huang C., Xie G.X. and Liu Z.F. *Sci. Total Environ.*, 424, **2012**, 1-10.
- Nogueira A.E., Castro I.A., Giroto A.S. and Magriotis Z.M., *J. Catal.*, **2014**, Article ID 712067.
- Zhou Z., Lin S., Yue T. and Lee T.C., *J. Food Eng.* 126, **2014**, 133-141.
- Turcaa C.V. and Sebe I., *U.P.B. Sci. Bull., Series B*, 74(1), **2012**, 109-118.
- Chhowala T.N. and Desai K.R., *Int. J. Sci. Res.*, 4(2), **2015**, 901-905.
- Colombo A., Dragonetti C., Roberto D., Valore A., Biagini P. and Melchiorre F., *Inorg. Chem. Acta*, 407, **2013**, 204-209.

7. Wang X., Guo Y., Yang L., Han M., Zhao J. and Cheng X., *J. Environ. Anal. Toxicol.* 2, **2012**, 154-160.
8. Yang J.K., Park H.J., Lee H.D. and Lee S.M., *Coll. Surf. A: Physicochem. Eng. Aspects*, 337, **2009**, 154-158.
9. Hora S.G., Simu G., Bugariu L., Popa A. and Rad R., *Molec. Cryst. Liq. Cryst.* 416, **2004**, 137-144.
10. Muntean S.G., Paska O., Coseri S., Simu G.M., Grad M.E. and Iliu G., *J. Applied. Polym. Sci.*, 127, **2013**, 4409.
11. Muntean S.G., Radulescu-Grad M.E. and Sfarloaga P., *RSC Adv.*, 4(52), **2014**, 27354- 27362.
12. Gomez-Pastora J., Bringas E. and Ortiz I., *Chem. Eng. J.* 256, **2014**, 187-204.
13. Liu X., An S., Wang Y., Yang Q. and Zhang L., *Chem. Eng. J.*, 262, **2015**, 517-526.
14. Pacurariu C., Paska O., Ianos R. and Muntean S.G., *Clean Technol. Envir. Pol.*, 18(3), **2016**, 705-715.
15. Radulescu-Grad M.E., Muntean S.G., Todea A., Verdes O. and Andelescu A. *Chem. Bull "Politehnica" Univ. (Timisoara)*, 60(74), **2015**, 37-40.
16. Ianos R., Pacurariu C. and Mihoc G., *Ceram. Int.*, 40, **2014**, 13649-13657.
17. Kyzas G.Z., Bikiaris D.N., Kostoglou M. and Lazaridis N.K., *E3S Web of Conferences*, 1, **2013**, 25004.
18. Bahnika S., Sarma H.P. and Bhattacharyya K.G., *Int. F. Environ. Sci.*, 6(5), **2016**, 737-745.

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