Journal of Science and Technology **54** (4B) (2016) 123-131

A RESPONSE SURFACE METHODOLOGY APPROACH FOR THE OPTIMIZATION OF CU^{2+} REMOVAL USING RICE HUSK–DERIVED ACTIVATED CARBON

Long Giang Bach[1], **Bui Thi Phuong Quynh**[1], **Van Thi Thanh Ho**[2],
Nguyen Thi Thuong[1], **Dinh Thi Thanh Tam**[1], **Trinh Duy Nguyen**[1],
Tran Van Thuan[1, *]

[1] *NTT Institute of High Technology, Nguyen Tat Thanh University, 298–300A Nguyen Tat Thanh, Ho Chi Minh City, Vietnam*

[2] *Hochiminh City University of Natural Resources and Environment, 236B Le Van Sy, Ho Chi Minh City, Vietnam*

[*] Email: *tranvt@outlook.com*

Received: August 2016; Accepted for publication: 10 November 2016

ABSTRACT

In this study, we have used the potassium hydroxide (KOH) as an eco–friendly and favorable activating agent to develop the porous and defect structure of activated carbon. Otherwise, the response surface methodology (RSM) has been applied to investigate the effects of the adsorption parameters including initial concentration, adsorbent dosage, and pH of solution on the percentage of Cu^{2+} removal. The *RSM*–based two order regression polynomial models were found to be statistically significant by values of the coefficients of determination (R^2) closer than 1.0 and the P–values < 0.0001 from analysis of variance (ANOVA). Under the predicted optimum conditions, actual experiments were confirmed to optimize the percentage of Cu^{2+} removal efficiency (97.5 %) and maximum adsorption capacity (24.45 $mg.g^{-1}$) from Langmuir equation. Based on experimental results, a treatment process can be easily designed using rice husk for the fabrication of activated carbon to remove toxic metal ions from the polluted water.

Keywords: removal of Cu^{2+}, rice husk, response surface methodology, activated carbon.

1. INTRODUCTION

Heavy metals are generally considered as one of the main causes for adverse effects on human health and ecosystems due to their high cumulative toxicity in groundwater [1]. Among the well–known elements, copper is a carcinogenic and non–biodegradable transition metal and it is commonly detected in fertilizer manufacture, mineral processing industrial effluent, the leak of chemical pollutants and tan–house [2]. The accumulation of copper accounts for typically serious infections such as neurological disorders, respiratory failure, and birth defects [3]. Traditional techniques have been developed for the elimination of copper–contaminated water, for example, chemical precipitation, oxidation/reduction and membrane filtration [4].

Nevertheless, obstacles of these treatment processes could prohibit their potential applications including very high operational cost, moderate removal efficiency and the generation of hazardous sludge. Meanwhile, adsorption is recognized as an effective mechanism for the removal of pollutants because of its high performance and outstanding recyclability [5]. In recent years, adsorption onto activated carbon has been proven as a promising means of treatment for the removal of heavy metal ions from aqueous solution. However, commercial activated carbon is very expensive in the market, and hence its widespread applications are limited towards economic aspects [6]. These difficult challenges can be solved by using abundant biomass source as raw material for the fabrication strategy of activated carbon.

Activated carbon (AC), a microcrystalline and non–graphitic material, could be prepared from zero–costly and locally available agricultural wastes [7]. Among the agricultural products, rice is a well–known and widespread plant and it is massively cultivated in some tropical countries. Combustion and discharge of rice husk without pretreatment can lead several environmental problems. According to the previous publication, main components of the rice husk are cellulose, hemicelluloses and lignin [8]. Hence, the transformation and conversion of non–toxic and renewable rice husk into low–cost and high–performance activated carbon has paid much attention of scientists and environmental organizations all over the world. The present work aims to investigate influential factors of the removal of Cu^{2+} by adsorption onto rice husk – derived activated carbons using the response surface methodology (RSM). The quadratic regression equations were established to evaluate the effect of several variables including initial Cu^{2+} concentration, the dosage of AC and pH of the solution on the Cu^{2+} removal efficiency. Otherwise, the predicted optimum conditions–based experiment was employed to find the maximum percentage of Cu^{2+} removal.

2. MATERIALS AND METHODS

2.1. Chemicals and instruments

All chemicals for this study were commercially purchased from Merck and used as received without any further purification unless otherwise noted. All activated carbon samples were pretreated by heating at 105 ^oC for 3 h. The scanning electron microscope (SEM) was recorded by instrument S4800, Japan and used an accelerating voltage source of 10 kV with a magnification of 7000. The FT–IR spectra were recorded by using the Nicolet 6700 spectrophotometer instrument

2.2. Production of activated carbon from rice husk (RSAC)

The rice husk was carbonized at 500 ^oC (10 ^oC/min) under N_2 atmosphere (400 cm^3/min). The char was soaked with KOH solution (char KOH = 1:1 by weight) for 1 day, then KOH–impregnated char was heated to 600 ^oC beneath N_2 atmosphere. The sample was repeatedly washed with deionized water until filtered water obtained a neutral solution. Finally, the synthesized AC was slowly dried at 105 ^oC, and then smoothly ground for storage (27.8 % of AC yields).

2.3. Adsorption batch

The activated carbon (0.8–9.2 g/L) was poured in an Erlenmeyer flask containing 50 mL of Cu^{2+} aqueous solution (8–92 ppm). After absorption equilibrium obtained, the adsorbent was removed from the mixture. The residual concentrations were confirmed by AAS and Cu^{2+} removal was calculated as follows:

$$Cu^{2+}\ \text{removal}\,(\%) = \frac{C_o - C_e}{C_o}.100 \tag{1}$$

where, C_o and C_e are the Cu^{2+} initial and equilibrium concentrations (ppm), respectively.

2.4. Experimental design with RSM

In this study, we used the RSM as a mathematical method to optimize experimental variables through second order polynomial regression equations. Central composite design (CCD) is used to establish given 20 experiments (Table 1) with five level including the low (–1), high (+1) and rotatable (±α).

Table 1. Independent variables matrix and their encoded levels

No	Independent factors	Code	Levels				
			–α	–1	0	+1	+α
1	Initial concentration (ppm)	x_1	8	25	50	75	92
2	Adsorbent dosage (g/L)	x_2	0.8	2.5	5	7.5	9.2
3	pH of solution (–)	x_3	0.6	2	4	6	7.4

3. RESULTS AND DISCUSSION

3.1. Textural characterization of activated carbon

The surface functional groups of activated carbon influences significantly on the absorbability such as ion exchange, catalysis, and adsorbent. The spectra of Fourier transform infrared spectroscopy was used to analyze the characteristics of material surface (Figure 1a). Generally, the rice husk–derived activated carbon possessed complex surface with various kinds of functional groups. In detail, the strong absorption band located at 3450 cm^{-1} – 3400 cm^{-1} was typically attributed to the –OH stretching vibrations of hydroxyl functional groups. A double peak around 2900 cm^{-1} was correspondent to C–H vibrations in alkane compounds. The oxygen–nitrogen asymmetric and C≡C bonding vibrations were confirmed by the presence of the peaks, which positioned at 1541 cm^{-1} and 2353 cm^{-1}, respectively. The unsaturated carbon bonds (C=C) in aromatic rings or olefin were also confirmed by stretching band at 1640 cm^{-1}. According to previous studies, KOH activation plays a crucial role in the formation of higher pore volumes and surface areas and evolution of the oxygen–containing group species [9]. Under electrostatic attraction between active sites containing a lone pair of electron and metal sites containing a positive charge, Cu^{2+} ions was captured by the mechanism of ion–exchange on the surface of activated carbon [10]. Moreover, the surface morphology of the as–synthesized activated carbon was recorded by a means of scanning electron microscope and micrographs (size 2 µm–100 µm) was shown in Figure 1b at a magnification of 60000. It is clear that the structure of activate carbon possesses the high porosity and amorphous surface.

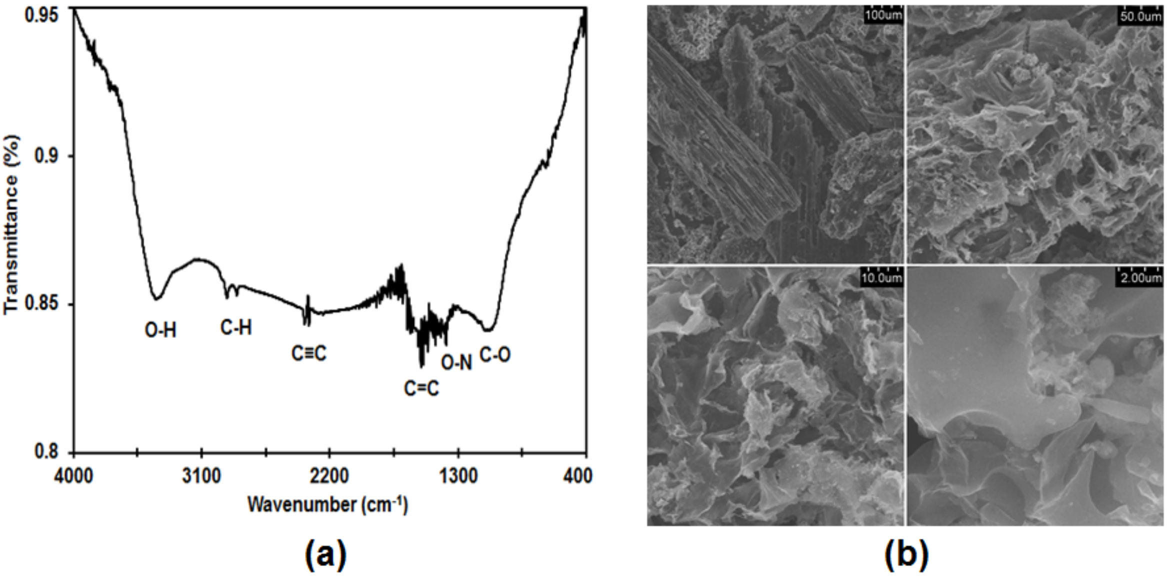

Figure 1. FT–IR spectra (a) and SEM micrograph (b) of the activated carbon.

3.2. Assessment of experimental results with Design–Expert

The percentage of Cu^{2+} removal from the synthetic wastewater using the response surface methodology approach was presented in Table 2. The ranges of investigation parameter were designed as follows: initial concentration from 8 ppm to 92 ppm, an adsorbent dosage from 0.8 g/L to 9.2 g/L and pH of the solution from 0.6 to 7.4. The correlation between the responses and variables was described by the following quadratic equations:

$$\begin{aligned} Cu(II)\,removal\,(\%) = 93.1 - 5.2x_1 + 12.73x_2 + 24.20x_3 + 0.84x_1x_2 \\ + 3.99x_1x_3 - 7.21x_2x_3 - 2.75x_1^2 - 7.9x_2^2 - 15.09x_3^2 \end{aligned} \quad (2)$$

Herein, the significance of quadratic model could be evaluated by ANOVA data obtained from the response surface methodology approach through output parameters. According to Table 3, the proposed model for Cu^{2+} removal was statistically significant (95 % confidence level) due to the values of probability > F were less than 0.0001 and determination of coefficient R^2 was closer 1.0. The adequate precision (AP) ratio was used to measure to noise ratio. This ratio greater than 4.0 indicated an adequate signal and the proposed model could be used to navigate the design space. In addition, the predicted and actual values positioned at the straight line revealed high fitness of model (Figure 2a). Otherwise, lack of fit (LOF) value was statistically insignificant to indicate the model fitted data well.

Table 2. Matrix of observed and predicted values

No	Variables			Response (Cu^{2+} removal)	
	x_1 (C_i, ppm)	x_2 (dosage, g/L)	x_3 (pH)	Actual (%)	Predicted (%)
1	25	2.5	2	30.2	33.2
2	75	2.5	2	14.1	13.2

3	25	7.5	2	69.2	71.4
4	75	7.5	2	53.7	54.7
5	25	2.5	6	86.5	88.1
6	75	2.5	6	83.6	84.0
7	25	7.5	6	93.9	97.4
8	75	7.5	6	97.1	96.7
9	8	5	4	98.9	94.0
10	92	5	4	75.3	76.5
11	50	0.8	4	50.4	49.3
12	50	9.2	4	94.6	92.1
13	50	5	0.6	11.6	9.7
14	50	5	7.4	92.8	91.1
15	50	5	4	91.1	93.1
16	50	5	4	94.9	93.1
17	50	5	4	92.8	93.1
18	50	5	4	93.0	93.1
19	50	5	4	95.1	93.1
20	50	5	4	90.9	93.1

Table 3. ANOVA for response surface quadratic models

Response	Source	Sum of squares	Degree of freedom	Mean square	F–value	Prob. > F	Comment
Cu^{2+} removal (%)	Model	15013.94	9	1668.22	193.37	< 0.0001^{s}	Mean = 75.47
	x_1	369.02	1	369.02	42.78	< 0.0001^{s}	CV = 3.89
	x_2	2212.71	1	2212.71	256.49	< 0.0001^{s}	$R^2 = 0.9943$
	x_3	7996.34	1	7996.34	926.91	< 0.0001^{s}	$R^2_{(adj.)} = 0.9891$
	x_1 x_2	5.61	1	5.61	0.65	0.4387^{n}	AP = 42.231
	x_1 x_3	127.20	1	127.20	14.74	0.0033^{s}	
	x_2 x_3	416.16	1	416.16	48.24	< 0.0001^{s}	
	x_1^2	109.04	1	109.04	12.64	0.0052^{s}	
	x_2^2	902.27	1	902.27	104.59	< 0.0001^{s}	
	x_3^2	3281.43	1	3281.43	380.37	< 0.0001^{s}	
	Residuals	86.27	10	8.63			
	LOF	70.20	5	14.04	4.37	0.0658^{n}	
	PE	16.07	5	3.21			

Note: ^{s} significant at $p < 0.05$ and ^{n} not significant at $p > 0.05$, LOF: lack of fit, PE: pure error

3.3. Effect of independent variables on the removal of Cu^{2+}

With *P*–values < 0.0001 referring to Table 3, the initial concentration (x_1), adsorbent dosage (x_2) and pH of the solution (x_3) influenced significantly on the percentage of Cu^{2+} removal. Herein, the response surface was plotted with a variation of two parameters while the other parameter maintained at zero level (Figure 2).

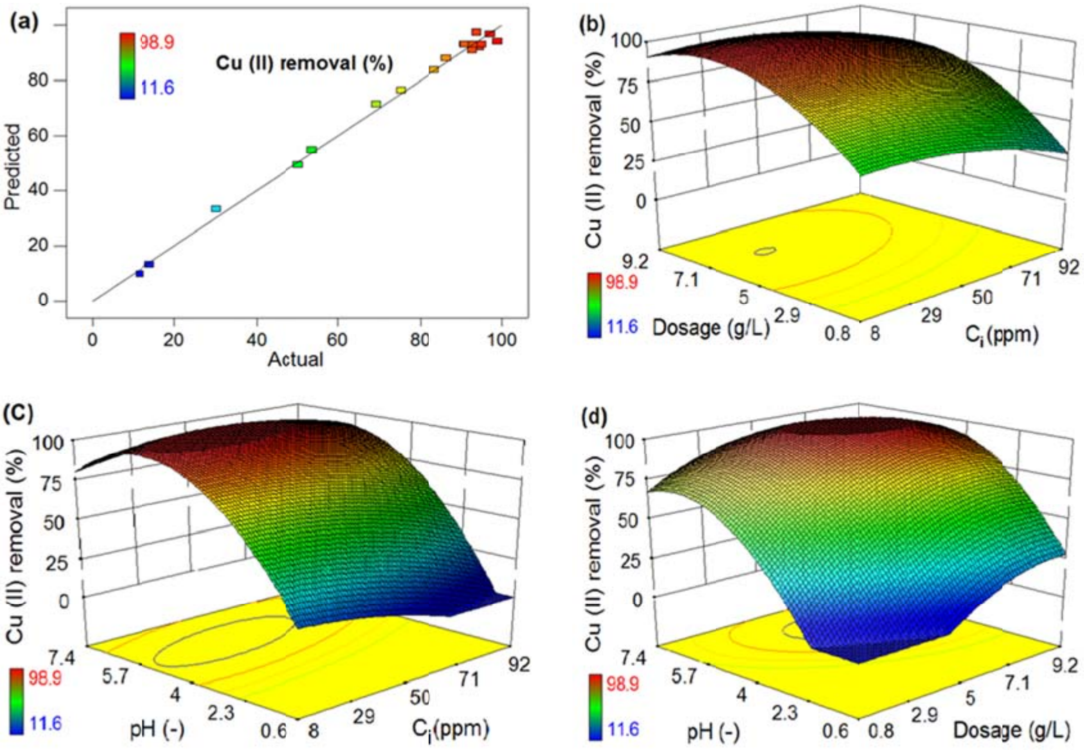

Figure 2. Actual versus predicted plot (a) and response surfaces (b–d) for regression model of the percentage of Cu^{2+}) removal.

The optimization of Cu^{2+} removal efficiency was undertaken using the statistical program DX9 to approach the optimum points for the operational conditions and to obtain the maximum percentage of Cu^{2+} removal through equation (2). According to the observation in Figure 2b, both adsorbent dosage and initial concentration of Cu^{2+} influenced slightly on the removal of Cu^{2+} from aqueous solution. The maximum percentage of Cu^{2+} removal (100 %) could be obtained at a higher value of activated carbon dosage (> 5 g/L) and lower value of initial concentration (<75 ppm). Figure 2c revealed the dependence of Cu^{2+} removal on both initial concentration and pH of the solution at a dosage of 5 g/L. It was clear that the variation of initial concentration of Cu^{2+} had a negligible impact on the removal efficiency while pH of solution influenced strongly on the Cu^{2+} removal efficiency. At strongly acidic environment (pH < 2), the adsorption of Cu^{2+} onto the activated carbon was unfavorable. This phenomenon can be explained due to the competition in term of adsorption between Cu^{2+} ions and H^+ on the active sites containing a lone pair of the electron [11]. Meanwhile, Cu^{2+} adsorption could be improved clearly (100 %) by increasing the value of pH from 4 to 6. However, Cu^{2+} removal efficiency was slightly reduced at a higher value of pH (> 7.0). Finally, the effect of AC dosage and pH on the removal of Cu^{2+} was observed in Figure 2d. A wide range for the value of pH (4 – 7) and dosage (3–8 g/L) was favorable for the adsorption. To confirm the optimum points from DX9, a model experiment were employed at the following conditions: C_i = 67.1 ppm, dosage = 5.1 and pH = 5.8 (Table 4). Thereby, the experiment for the percentage of Cu^{2+} removal was obtained 97.5 %. This result was nearly closer to the predicted values of 100.5 %. These above results demonstrate the high compatibility of the proposed models with the experimental data.

Table 4. Model confirmation

Sample	C_i (ppm)	Dosage (g/L)	pH (–)	Desirability	Cu^{2+} removal (%)	
					Predict	Test
TWAC	67.1	5.1	5.8	1.00	100.5	97.5

3.4. Isotherm modeling and adsorbent recyclability

Adsorption parameters can be obtained by using well–known isotherm equations, which gives crucial information about behaviors, mechanisms, and properties of adsorbent. The constants of isotherm models for the adsorption process and the respective correlation coefficient (R^2) are summarized in Table 5. Based on the isotherm equations, high obtained values of R^2 for adsorption models of Cu^{2+} are observed to be 0.9954, 0.9937 and 0.9443 for Langmuir, Freundlich, and Tempkin, respectively and the data fitness as order: Langmuir > Freundlich > Tempkin. For the Langmuir model, adsorption constant R_L less than 1.0 indicates that Langmuir adsorption is recognized as a favorable process. Therefore, Langmuir model can be used to describe the adsorption behavior of Cu^{2+} onto the surface of activated carbon and Cu^{2+} adsorption process is proposed to occur mainly monolayer adsorption. The maximum adsorption in this study acquired to be 24.45 mg.g^{-1}, which was higher than previous studies (Table 6).

Table 5. Isotherm parameters for the adsorption

Isotherm	Equation	Parameters	Value of parameters
Langmuir	$\frac{1}{q_e}=\frac{1}{q_mK_L}.\frac{1}{C_e}+\frac{1}{q_m}$	K_L (L.mg^{-1})	0.1680
		q_m (mg.g^{-1})	24.45
		R_L	0.0608
		R^2	0.9954
Freundlich	$\ln q_e = \ln K_F + \frac{1}{n}\ln C_e$	K_F	0.2263
		[(mg.g^{-1}).(L.mg^{-1})]$^{1/n}$	0.9346
		1/n	0.9937
		R^2	
Temkin	$q_e = B_1 \ln K_T + B_1 \ln C_e$	K_T (L.mg^{-1})	0.1362
		B_1	5.3117
		R^2	0.9443

The regeneration was employed to investigate the recyclability of rice husk–derived activated carbon. The steps for this procedure as follows: 3 × 50 mL hydrochloric acid (1.4 M) was used to wash Cu^{2+}–adsorbed activated carbon [12]. Then, desorption adsorbent was completely dried at 378 K for 12 h and could be used as an adsorbent for the further study. As a result, the removal percentage of Cu^{2+} of the recycled RSAC was decreased from 97 % (1st) to 82.4 % (6th). Therefore, RSAC can be used for the removal of Cu^{2+} several times without a considerable decrease of adsorption capacity (Figure 3). The present results revealed the great potential in the use of rice husk as a raw material source for adsorption of Cu^{2+} from wastewater.

Table 6. Comparison of absorption capacity of Cu^{2+} treatment by several adsorbents

Source	Cu^{2+} treatment				Ref
	C_o (ppm)	Dosage (g/L)	pH	q_m (mg/g)	
Sugarcane	75	5.1	6.0	4.87	[3]
Coconut tree sawdust	200	4	6.0	3.89	[13]
Eggshell	200	4	6.0	34.48	[13]
Sugarcane bagasse	200	4	6.0	21.28	[13]
Rice husk	67.1	5.1	5.8	24.45	*This work*

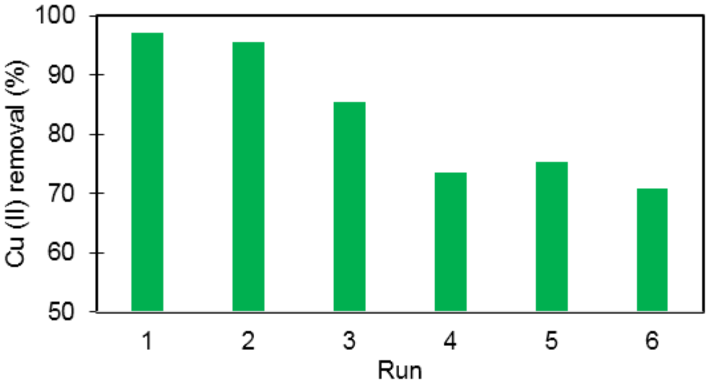

Figure 3. Reuse test of the activated carbon,

4. CONCLUSIONS

The present study focused on the promising of the rice husk as a zero–costly and available precursor for the fabrication of porous activated carbon for the purposes of wastewater treatment. The characteristic profiles admitted the highly porous, amorphous, various kinds of essential functional groups and defective structure of rice husk–derived active carbon. Three parameters for the adsorption process of Cu^{2+} onto activated carbon have been investigated including initial concentration, adsorbent dosage, and pH of the solution. The optimization of Cu^{2+} removal using the response surface methodology has found out the optimum points as follows: C_i = 67.1 ppm, dosage = 5.1 g/L and pH = 5.8. Moreover, isotherm models were checked and revealed the high satisfactory ($R^2 > 0.9$) by all adsorption equations, where the Langmuir equation showed high capacity of monolayer adsorption (24.45 $mg.g^{-1}$). The recycling results up to six times proved a great potential for application of activated carbon from rice husk for pollution treatment.

Acknowledgements. This research is funded by Foundation for Science and Technology Development Nguyen Tat Thanh University, Ho Chi Minh City, Vietnam.

REFERENCES

1. Ahiduzzaman M. and Islam A. – Preparation of porous bio–char and activated carbon from rice husk by leaching ash and chemical activation, SpringerPlus, **5** (2016) 1248–1262
2. Tran V. T., Quynh B. T. P., Phung T. K., Ha G. N., Thuong N. T., and Bach L. G. – Preparation of activated carbon from sugarcane bagasse using $ZnCl_2$ as an efficient activation for the removal of Cu^{2+} ion from aqueous solution: Application of response surface methodology, Journal of Science and Technology (VAST), **3A** (2015) 276–283
3. Tran V. T., B. Quynh T. P., Trinh N. D. and Bach L. G., A comparative study on the removal efficiency of metal ions (Cu^{2+}, Ni^{2+}, and Pb^{2+}) using sugarcane bagasse–derived $ZnCl_2$–activated carbon by the response surface methodology, Adsorption Science & Technology, accepted (2016) DOI: 10.1177/0263617416669152
4. Amarasinghe B. and Williams R. – Tea waste as a low cost adsorbent for the removal of Cu^{2+} and Pb^{2+} from wastewater, Chem. Eng. J. **132** (2007) 299–309
5. Sadaawy and Abdelwahab O. – Adsorptive removal of nickel from aqueous solutions by activated carbons from doum seed (Hyphaenethebaica) coat, Alexandria Eng. J. **53** (2014) 399–408
6. Esfandiar N., Nasernejad B., Ebadi T. – Removal of Mn(II) from groundwater by sugarcane bagasse and activated carbon (a comparative study): Application of response surface methodology (RSM), J. Ind. Eng. Chem. **20** (2014) 3726–3736
7. Hu–Chun T., He–Ran Z., Bo Lia J. and Wen–Yi D. – Biomass based activated carbon obtained from sludge and sugarcane bagasse for removing lead ion from wastewater. Bioresour. Technol. **192** (2015) 611–617
8. Ping L., Gambier F. and N. Brosse – Wood adhesives from agricultural by–products: Lignins and tannins for the elaboration of particleboards, Cellul. Chem. Technol. **46** (7) (2012) 457–462
9. Chandra T., Mirna M., Sunarso J., Sudaryanto Y., Ismadji S. – Activated carbon from durian shell: Preparation and characterization, J. Taiwan Inst. Chem. Eng. **40** (2009) 457–462
10. Yennam R., Namrata G. and Ramgopal U. – Ni(II) adsorption characteristics of commercial activated carbon from synthetic electroless plating solutions, Desalin Water Treat. **1** (2015) 1–12
11. Esfandiar N., Nasernejad B., Ebadi T. – Removal of Mn (II) from groundwater by sugarcane bagasse and activated carbon (a comparative study): Application of response surface methodology (RSM), J. Ind. Eng. Chem. **20** (2014) 3726– 3736
12. Huang Y., Li S., Chen J., Zhang X., Chen Y. – Adsorption of Pb(II) on mesoporous activated carbons fabricated from water hyacinth using H_3PO_4 activation: Adsorption capacity, kinetic and isotherm studies, Appl. Surf. Sci. **293** (2014) 160–168.
13. Putra W. P., et al. – Biosorption of Cu (II), Pb (II) and Zn (II) ions from aqueous solutions using selected waste materials: Adsorption and characterisation studies, Journal of Encapsulation and Adsorption Sciences, **4** (2014) 25–35.