EFFECT OF MICROBIAL BIOMASS PRESENCE ON PALM SHELL ACTIVATED CARBON FOR THE ADSORPTION OF Cu, Cd AND Zn

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ARTICLE HISTORY	ABSTRACT

Concentration of heavy metals present in industrial wastewaters should be reduced to permissible discharge level to prevent their harmful environmental effect. Adsorption provides effective removal of metals from wastewater. Palm shell activated carbon (PSAC) and microbial biomass of Bacillus subtilis (BS) and Aspergillus niger (AN) are low cost adsorbents. Their ability to adsorb Cu(II), Cd(II) and Zn(II) ions from wastewater in batch mode was investigated in this study. Combination of PSAC with microbial biomass resulted in the decrease of pH_{pzc}, surface area and porosity of the adsorbents compared to the original PSAC. However, the concentration of surface functional groups and negative charge density increased. Each biosorbent exhibited selective adsorption affinity. Thus, BS-PSAC showed highest sorption of zinc ions, 0.27mol/L; AN-PSAC showed the highest removal of copper, 0.51mol/L; and cadmium was best removed by original PSAC, 0.28mol/L. The adsorption capacity of the original and biomodified PSACs was higher at pH 5-6; positive $\Delta H^{\bullet}$ values indicated endothermic nature of adsorption process. Kinetics data showed that adsorption followed pseudo-second-order reaction model.Overall, the results demonstrated that modification of PSAC with microbial biomass selectively improved adsorption efficiency of heavy metals removal from wastewater.

Keywords: *palm shell, activated carbon, biosorbent, microorganisms, heavy metals.*

1. INTRODUCTION

Heavy metals such as copper, zinc and cadmium are utilized in many manufacturing processes. Presence of these metals in industrial effluents and their negative impact on aqua environment is a serious issue for many developing countries. Adsorption is preferable method to reduce heavy metals concentration to the permissible discharge level, in terms of its initial cost, simplicity of design, ease of operation and insensitivity to other toxic substances (Meshko, Markovska, Mincheva & Rodrigues, 2001). Commercial petroleum based activated carbon is well recognized for high capacity adsorption; however, it is expensive material reaching US$ 22/kg (Lin & Juang, 2009). In recent years, it was shown that various agricultural wastes can be utilized for production of activated carbons. Palm shells, by-product of large palm oil sector in Malaysia, are successfully used to commercially produce good quality activated carbon. Many microorganisms biomass also showed impressive metal adsorption capacities. Thus, biomass of *Aspergillus niger* and *Bacillus subtilis*, commonly used in commercial production of antibiotics and enzymes, respectively, showed high

adsorption capacities for various heavy metals (Khambathy, Mody, Basha & Jha, 2009; Wang & Chen, 2009; Liu, Liao, He, Li, Wang, Hu, Guo & He, 2013). The objective of this study was evaluation of adsorption capacities of commercial palm shell activated carbon (PSAC) alone and in combination with biomass of *A.niger* and *B.subtilis* to remove copper, cadmium and zinc at different pH, metal concentration, temperature and time.

2. EXPERIMENTAL

2.1 Adsorbents characterization

Commercial granular palm shell activated carbon (PSAC) prepared through physical steam activation was provided by "Bravo Green" (Malaysia). Particles size of PSAC between 1.0–2.0 mm was used in all experiments. BET surface area (Thermo Electron, USA) at $p/p°$ = 0.04 to 0.3 and 77K, total acidity (Boehm, 1994), pH_{pzc} (Rivera-Utrilla, Bautista-Toledo, Ferro-Garcia & Moreno-Castilla, 2001), FTIR spectra (Perkin-Elmer, USA) and SEM images (Hitachi, Japan) were obtained for all tested biosorbents. *B. subtilis* was cultured in nutrient broth (Merck, Germany) at 30°C, 220 rpm for 24 hours. The biomass was separated via centrifugation at 5000 rpm for 15 minutes. *A. niger* was grown in liquid medium containing sucrose, peptone and yeast extract (20,10 and 3g/L, respectively) at 30°C, 220 rpm for a week. Fungal biomass was easily separated through a strainer and blended to obtain homogeneous mass. 2 mL (1.9 g) of wet microorganism's biomass (fungal or bacterial) was resuspended in 40 mL of Milli-Q water for further usage in the biomodification procedure.

2.2 Biomodification procedure

40 mL of cell suspension was added to a 50 mL centrifuge tube containing 1.2 g of original PSAC; the content was stirred on a vortex mixer for 2 min and then it was placed on a shaker (LabTech, Korea) at 50 rpm for 72 hrs to allow biomass attachment on the activated carbon surface. The resulted material was filtered and rinsed using Milli-Q water; it was dried at 80°C overnight and then kept for adsorption experiments. Three biosorbents were tested: palm shell activated carbon biomodified with *B.subtilis* (BS-PSAC), palm shell activated carbon biomodified with *A.niger* (AN-PSAC) and original untreated PSAC.

2.3 Adsorption experiments

$Zn(NO_3)_2$, $Cd(NO_3)_2$ and $Cu(NO_3)_2$ (R&M Chemical, UK) were used to prepare 0.1 M respective stock solutions in 0.15 M $NaNO_3$ (Merck, Germany) blank solution. The use of the background electrolyte is linked to the earlier studies on electrodeposition published elsewhere (Issabayeva, Aroua & Sulaiman, 2006). The initial metal ions concentration varied between 30 to 300 mg/L. pH varied from 3 to 6 by adding 0.1 M NaOH or HCl. The batch adsorption experiments were carried out in 250 mL conical flasks with 100 mL solution of required metal ions concentration placed on an orbital shaker at 220 rpm, 27°C (room temperature) for 24 hours. Mass of respective adsorbent was 250 mg/flask in all tests. All samples were filtered (0.45 µm, Fioroni, France) and metal concentrations were measured using ICP-OES (Optima 7000 DV, Perkin Elmer, USA). For determination of kinetics data, the experiments were carried out in 48 hours period where samples were taken in 20 min interval in the first two hours and ones an hour in the followed four hours period; additional samples were taken in 24 and 48 hours. Initial concentration of metal ions in all tests was 50

mg/L. For determination of thermodynamic properties 303, 313 and 323K temperatures were tested; metal ions concentration varied from 30 mg/L to 200 mg/L.

2.4 Adsorption data evaluation

The following equations were used for data evaluation. Langmuir isotherm model equation (Langmuir, 1916):

$$\frac{C_e}{q_e} = \frac{1}{b\,q_{max}} + \frac{C_e}{q_{max}} \qquad (1)$$

where, q_e- amount of metal absorbed (mg/g) at equilibrium; q_{max} -maximum adsorption capacity (mg/g); b- Langmuir constant (L/mg); C_e -equilibrium concentration of the metal in the solution (mg/L.) The linear form of Freundlich (Freundlich, 1906) isotherm model:

$$log\ q_e = log\ K_f + (\frac{1}{n})\,log\ C_e \qquad (2)$$

where, K_f-Freundlich adsorption constant; n_f- Adsorption intensity constant.
Kinetics parameters were determined using linear forms of pseudo-first-order reaction model (Lagergren, 1898):

$$log(\ q_e - q_t\ ) = log\ q_e - \frac{K_1}{2.303}t \qquad (3)$$

where, q_e -amount of metal adsorbed on the carbon (mg/g) at the equilibrium; q_t - amount of metal uptake (mg/g) at time t (min.); k_1= rate constant, (min^{-1}); and pseudo-second-order reaction (Ho & Mckay,1998) model:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e}t \qquad (4)$$

where, k_2 = rate constant (g/mg min), and $h = k_2 q_e^2$ = initial sorption rate (mg/g min). Thermodynamic parameters (ΔG^o, ΔH^o and ΔS^o) were calculated from the variation of the thermodynamic equilibrium constant K° over temperature range (Chen, Li, Zhao, Tan & Wang, 2007). K° obtained from the Langmuir's equation by the plots of $\frac{c_e}{q_e}$ versus C_e (Moradi, Zare & Yari, 2011):

$$\frac{C_e}{q_e} = \frac{1}{K^\circ} + \frac{C_e}{Q^\circ} \qquad (5)$$

where, C_e - equilibrium concentration (mg/L); q_e -amount of heavy metal absorbed (mg/g) at equilibrium; Q° =maximum adsorption (µmol/g); K° - equilibrium constant. The Van't Hoff equation was used to determine the value of the equilibrium constant at different temperature:

$$\frac{d(ln\,K^\circ)}{dT} = \frac{\Delta H^\circ}{RT^2} \qquad (6)$$

lnK˚ can be obtained through:

$$ln\,K^\circ = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \qquad (7)$$

The ΔH^o and ΔS° values were calculated from the slopes and intercepts of the linear plots of *lnK˚* versus *1/T*, respectively.
ΔG° is obtained using the following equations:

$$\Delta G^\circ = -RT\,ln\,K^\circ \qquad (8)$$

Eq. 7 combined with Eq. 8 gives:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \qquad (9)$$

where, ΔH^o-enthalpy change (kJ mol^{-1}); ΔS^o - entropy change (kJ mol^{-1} K^{-1}); ΔG^o - Gibbs free energy (kJ mol^{-1}); R- Ideal gas constant (8.3145 J mol^{-1} K^{-1}); T -temperature (K).

3. RESULTS AND DISCUSSION

3.1 Surface Characteristics of Adsorbents

The comparison of the surface characterization data for the three adsorbents showed that surface area (m^2/g) decreased in the following order: original PSAC (716.89) > BS-PSAC (688.88) > AN-PSAC (530.67). Such decrease is associated with a partial blockage of carbon pores by the microbial biomass as the bacterial cells are smaller in size (0.25–*1.0 µm* in diameter) compared to the fungal cells (40-60 µm in diameter). The bacterial cells may penetrate deeper into the carbon matrix; whereas larger fungal cells tend to accommodate on the outer surface of PSAC. Measurements of total acidity (µmol/g) of the biosorbents showed presence of carboxylic functional groups; their concentration increased as follows: PSAC (0.124) < BS-PSAC (0.196) < AN-PSAC (0.268) as a result of microbial biomass presence. pH of point of zero charge (pH$_{pzc}$) decreased from 9.25 to 8.60 and 6.60 for original, BS-PSAC and AN-PSAC, respectively, as a result of the surface charge displacement towards the charge of the microorganism's biomass. FT-IR spectrum for all biosorbents (Figure 1) was similar with the following identified bands: a broad band at 3429 - 3434 cm^{-1} for O-H stretching, 1635 - 1638 cm^{-1} band for C=C stretching, and 1077 - 1110 cm^{-1} band for C-O stretching. -OH and C-O functional groups are involved in the chemical bonding and responsible for the metal ions adsorption (*Skoog & Leary,* 1992). Presence of microbial biomass in the PSAC matrix was also confirmed by SEM images (Figure 2) where clear fragments of the bacterial and fungal cells attached to the carbon structure can be observed. Although the total surface area for two hybrid adsorbents decreased, their total acidity is higher compared to the original PSAC which anticipates a higher metal removal. Overall, factors such as size of microbial cells, ionic strength (Yee, Fein & Daughney, 2007) and support-material's structure (Jeyachandran, Narayandassa, Mangalaj, Bao, Li, Liao, Zhang & Chen, 2006) affect the process of integration of the microbial biomass within carbon matrix and therefore the adsorption capacities.
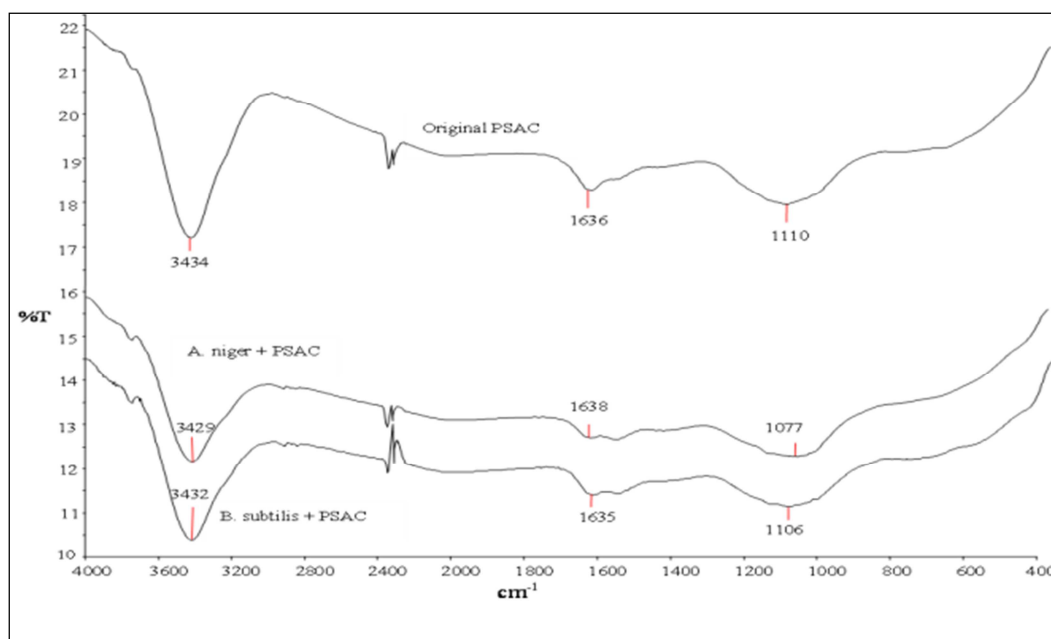

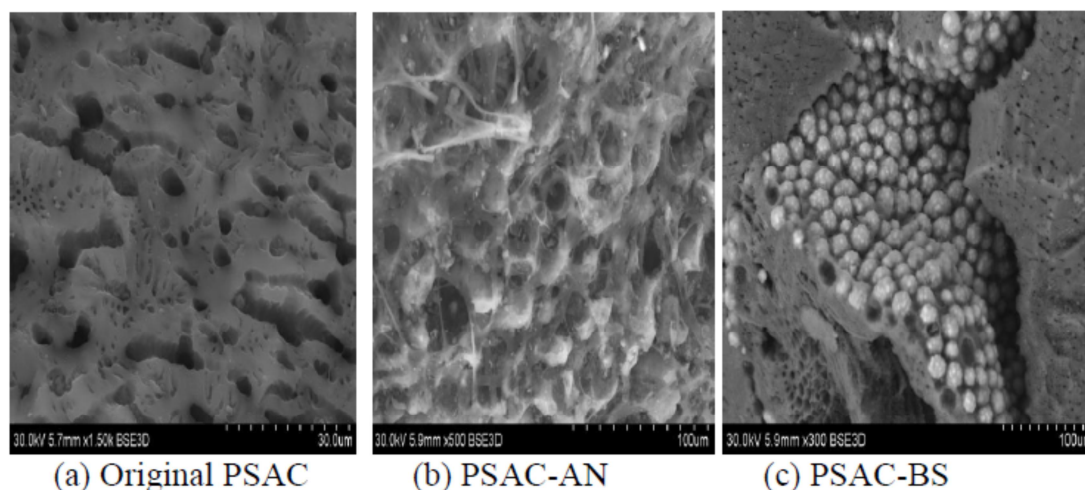Figure 1:FT-IR spectra of the original and biomodified PSACs

Figure 2: SEM images of the biosorbents (a) original palm shell activated carbon;
(b) PSAC biomodified with *A.niger*; and (c) PSAC biomodified with *B.subtilis*

3.2 Effect of pH and metal initial concentration on adsorption capacity

Batch adsorption experimental data were evaluated using Langmuir and Freundlich isotherm models. Tables 1 and 2 present the parameters of both models, respectively. The correlation coefficients for Langmuir model were higher than for Freundlich model suggesting primarily monolayer adsorption of metal ions onto the biosorbents. The values of q_{max} in Table 1 are given in mol/g for the comparison purpose as the three metals have different molecular weight. The results showed that adsorption of copper increased when pH increased from 3 to 5. The highest adsorption of copper was by AN-PSAC, 0.51 mol/L. However, at pH 6 adsorption of copper decreased for all biosorbents , which is associated with a tendency of metals to precipitate at higher pH. Wang, Chong-Wei Cui and Xing (2016) reported 0.37 mol/g adsorption capacity for copper by the straw fermented with *A. niger*, which was noted as remarkable in comparison to the untreated straw.

Table 1: Langmuir model data for metals adsorption at different pHs

	q_{max} (mmol/g)				b (L/mg)				R^2			
pH	3	4	5	6	3	4	5	6	3	4	5	6
Cu^{2+}												
PSAC	0.12	0.34	0.35	0.27	0.01	0.05	0.07	0.85	0.99	0.97	0.91	0.97
AN-PSAC	0.17	0.30	0.51	0.40	0.34	0.05	0.01	0.03	0.91	0.97	0.92	0.95
BS-PSAC	0.10	0.29	0.32	0.29	0.12	0.01	0.02	0.02	0.91	0.89	0.88	0.91
Cd^{2+}												
PSAC	0.11	0.20	0.26	0.28	0.03	0.03	0.03	0.02	0.87	0.99	0.95	0.91
AN-PSAC	0.10	0.12	0.13	0.16	0.01	0.05	0.03	0.03	0.88	0.97	0.96	0.91
BS-PSAC	0.13	0.19	0.23	0.19	0.01	0.02	0.02	0.02	0.97	0.99	0.96	0.97
Zn^{2+}												
PSAC	0.11	0.19	0.23	0.26	0.08	0.13	0.10	0.04	0.97	0.94	0.94	0.95
AN-PSAC	0.05	0.11	0.23	0.15	0.09	0.14	0.02	0.04	0.92	0.95	0.91	0.98
BS-PSAC	0.19	0.22	0.27	0.22	0.02	0.09	0.02	0.05	0.99	0.95	0.94	0.94

The adsorption of cadmium gradually increased with increase of pH showing noticeable increase at pH 5 and reaching the highest removal at pH6 by the original PSAC (0.28 mol/L).

The adsorption of Cd by BS-PSAC was slightly lower, 0.23 mol/g, at pH 5. AN-PSAC showed the lowest Cd adsorption of 0.16 mol/g.

The highest adsorption of zinc was shown by BS-PSAC, 0.27 mol/g. The original PSAC showed adsorption capacity of 0.26 mol/g for Zn at pH6, and AN-PSAC adsorbed 0.23 mol/g of Zn at pH 5. Comparison of the adsorption data for the three metals shows that higher pH promotes adsorption of metal ions removal. It can be explained by the lower electrostatic repulsion forces between the sorbate species and the adsorbent surface functional groups at higher pH (Rao, Ramana, Seshauah, Wang & Chien, 1990); whereas decrease of pH promotes protonation of the active surface sites and results in the increased repulsion of metal ions as both H^+ and Me^{2+} compete for the same adsorption sites.

The bacterial and fungal cell walls contain a variety of functional groups, such as carboxylic, hydroxyl, phosphoric, amines and phosphordiesters originating from peptidoglycan, teichoic and teichuronic acids, lipopolysaccharides, phospholipids and other bio-constituents of cell membrane (Yun, Vijayaraghavan & Won, 2011). Besides, the carbohydrate-based polymers, also regarded as cell-wall glycopolymers (CWGs), present in microorganism cell wall, often have highly variable structures and tend to have very selective species-specific interactions (Weidenmaier & Peschel, 2008). Due to the specific interactions between various functional groups and metal ions, the total concentration of the acidic groups of a biosorbent may not be directly linked to the higher adsorption capacity. Thus, the results showed that each biosorbent exhibited a selective adsorption affinity: BS-PSAC showed the highest sorption of zinc ions, 0.27mol/L; whereas AN-PSAC showed the highest removal of copper, 0.51mol/L; and cadmium was best removed by the original PSAC, 0.28 mol/L. It also should be considered that the microbial biomass preparation procedure could result in the partial or complete decomposition of some oxygen surface functional groups and surface-active components that reduced the overall adsorption capacity of the biosorbents due to the increased alkalinity of the carbon surface (Shafeeyan, Daud, Houshmand & Shamiri, 2010).

In terms of the initial metal concentration, all biosorbents showed a similar trend: initial adsorption of a metal increased as its initial concentration in the solution increased. It is associated with the enhancement of the driving force to overcome the mass transfer resistance between the aqueous and adsorbent phases and resulting higher collisions rate between the adsorbate and adsorbent surface groups (Kumar, Vincent, Krithika & Kumar, 2010). Adsorption of zinc by the PSAC and AN-PSAC significantly decreased at the initial concentrations of 170 mg/L and 200 mg/L, respectively. Copper and cadmium adsorption by PSAC also decreased when concentration increased above 220 mg/L. It was observed that among the three biosorbents, the original PSAC showed higher susceptibility towards the increase of metal ions concentration, suggesting that presence of the microbial biomass in PSAC promoted further adsorption of metal ions.

3.3 Effect of temperature on adsorption of metals

Table 3 presents thermodynamic parameters estimated for the obtained at different temperatures experimental data. Positive values of enthalpy, $\Delta H°$, confirm the endothermic nature of adsorption process and presence of strong interaction between adsorbent and metals (Ho & Mckay, 1998). The negative values for the degree of freedom, $\Delta G°$, indicate spontaneity of the adsorption process. Also progressive decrease of $\Delta G°$ values over the rising

temperature implies the increment of the adsorption efficiency (Ibrahim, 2011). Parameter for entropy, $\Delta S°$, reflected the affinity between the adsorbent and adsorbate, its values increased in the following order: Cu removal by AN-PSAC, Cd removal by PSAC and Zn removal by BS-PSAC, which corresponds to the highest adsorption capacities by the same biosorbents.

Table 2. Freundlich model data for metals adsorption at different pHs

pH	K_f				n_f				R^2			
	3	4	5	6	3	4	5	6	3	4	5	6
Cu^{2+}												
PSAC	0.29	5.54	6.51	7.78	1.84	4.16	4.30	5.76	0.97	0.88	0.76	0.73
AN-PSAC	2.90	5.96	2.68	2.37	3.62	4.96	2.51	2.32	0.50	0.91	0.95	0.92
BS-PSAC	1.49	3.00	2.91	2.60	4.79	3.89	3.21	3.12	0.29	0.70	0.90	0.88
Cd^{2+}												
PSAC	1.39	2.95	3.62	5.56	2.48	2.79	2.61	3.68	0.67	0.97	0.90	0.79
AN-PSAC	0.48	1.83	2.45	4.04	1.81	2067	3.04	3.81	0.89	0.90	0.80	0.78
BS-PSAC	0.56	1.48	1.99	2.46	1.88	2.10	2.27	2.64	0.99	0.96	0.98	0.92
Zn^{2+}												
PSAC	2.17	3.96	4.78	4.51	4.17	4.36	4.43	4.20	0.67	0.47	0.63	0.82
AN-PSAC	5.84	4.56	1.30	2.14	9.14	11.57	2.31	11.27	0.13	0.22	0.84	0.79
BS-PSAC	1.00	2.91	3.74	3.23	2.35	3.16	4.00	3.62	0.93	0.77	0.81	0.72

The effect of elevated temperature is associated with the accelerated mobility of metal ions and higher frequency collisions with the adsorbent's surface groups that promotes rapid adsorption. Besides, higher temperature promotes the enlargement of pathways in carbon matrix (Han, Lu, Zou, Daotong, Shi & Jiujun, 2006).

Table 3 Thermodynamic parameters of metal ions removal by PSAC biosorbents.

Metal/Adsorbent	$\Delta G°$, (kJ mol^{-1})			$\Delta H°$, (kJ mol^{-1})	$\Delta S°$, (J mol^{-1} K^{-1})
	303K	313K	323K		
Cu^{2+}					
PSAC	-2.47	-2.66	-2.86	3.32	19.12
AN-PSAC	-1.11	-1.84	-2.57	21.08	91.24
BS-PSAC	-1.70	-2.61	-3.52	25.95	73.24
Cd^{2+}					
PSAC	-1.68	-1.63	-2.58	28.06	94.86
AN-PSAC	-0.06	-0.36	-0.65	8.78	29.18
BS-PSAC	-0.09	-0.32	-0.55	6.86	29.18
Zn^{2+}					
PSAC	-0.23	-0.44	-0.66	6.29	21.50
AN-PSAC	-0.05	-0.25	-0.46	6.10	20.30
BS-PSAC	-1.12	-1.81	-1.81	20.56	69.24

3.4 Effects of contact time on metal adsorption

A common trend observed for all biosorbents was that the initial sorption was rapid and mostly attained within the first 120 minutes; after that the sorption continued in a slower steadier rate indicating saturation of the adsorption sites, which corresponded to about 40% of heavy metals removal. Such trend is associated with the availability of numerous surface sites at the beginning of adsorption and their gradual saturation by the metal ions over a lapse of time. The saturation of the adsorption sites was first observed for copper; then for zinc and

lastly, for cadmium. Such saturation order also reflected a stronger affinity between cadmium ions and original PSAC, for which the highest adsorption capacity was obtained. On the other hand, BS-PSAC was saturated faster with copper ions, and AN-PSAC exhibited clear affinity towards copper with the corresponding highest adsorption capacity. The measurements of metals concentrations after 24 and 48 hours showed insignificant changes in the metals removal for all biosorbents. Overall, the results showed that nearly complete saturation of adsorption sites of the tested biosorbents could be achieved within the first two hours. Table 4 presents kinetics data for all biosorbents at pH 5 determined using pseudo-first and pseudo-second-order reaction models. Comparison of calculated q_e values showed good agreement between pseudo-second-reaction order model and experimental q_e values for all three biosorbents.

Table 4 : Kinetics data for metals adsorption onto PSAC ($[C_{Me}]$=50 mg/L,pH 5).

	Pseudo-first-order rate constants				Pseudo-second-order rate constants		
	$q_e,exp,$(mg/g)	$K_1,$(1/min)	$q_e,cal,$(mg/g)	R^2	$K_2,$ (g/mg min)	$q_e,cal,$(mg/g)	R^2
			Original PSAC				
Cu^{2+}	13.15	5.07×10^{-3}	6.84	0.96	1.41×10^{-3}	14.35	1.00
Cd^{2+}	9.29	8.52×10^{-3}	6.58	0.93	1.80×10^{-3}	10.63	1.00
Zn^{2+}	9.41	0.02	8.45	0.96	2.95×10^{-3}	10.45	1.00
			AN-PSAC				
Cu^{2+}	5.81	4.61×10^{-3}	3.30	0.96	3.00×10^{-3}	6.24	1.00
Cd^{2+}	8.61	5.99×10^{-3}	3.33	0.93	2.23×10^{-3}	10.11	1.00
Zn^{2+}	6.10	8.06×10^{-3}	3.09	0.93	3.70×10^{-3}	6.83	1.00
			BS-PSAC				
Cu^{2+}	10.05	0.01	3.56	0.97	6.27×10^{-3}	10.53	1.00
Cd^{2+}	7.78	0.02	5.56	0.98	0.01	7.95	1.00
Zn^{2+}	5.81	0.02	3.32	0.85	5.40×10^{-3}	6.46	1.00

Also, R^2 values for the pseudo-second-reaction order model were higher and consistent as compared to the pseudo-first-order reaction model results. Such results confirmed that adsorption of copper, cadmium and zinc involved chemisorption mechanism (Ho & Mckay, 1998; Shafeeyan, Daud, Houshmand & Shamiri, 2010; Robalds, Naja & Klavins, 2016).

4. CONCLUSION

Adsorption results showed that combination of *B.subtilis* and *A.niger* biomass with PSAC resulted in the changes of physico-chemical properties of the obtained biosorbents. Each metal expressed specific affinity towards certain biosorbent: cadmium towards PSAC, copper towards BS-PSAC and zinc towards AN-PSAC. Overall, the combination of microbial biomass with activated carbon improved adsorption capacity of the tested biosorbents and outlined certain affinity between the adsorbate and the biosorbent.

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