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Improved biosorption potential of *Thuja orientalis* cone powder for the biosorptive removal of Basic Blue 9

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ABSTRACT

This study focused on the development of an efficient and practical biosorbent, a low cost and promising plant waste with cellulose–lignin polymeric structure, for the treatment of dye containing solutions. *Thuja orientalis* biomass was modified by citric acid and its biosorption potential was investigated with respect to pH (2.0–10.0), contact time (1–60 min), sorbent dosage (0.01–0.05 g), initial dye concentration (10–725 mg L^{-1}) and flow rate (0.5–4.0 mL min^{-1}). Modification significantly increased the biosorption of dye by 30% as compared with unmodified biomass. Kinetic data followed the pseudo-second-order model while the equilibrium data were well predicted by the Langmuir isotherm model. Maximum dye biosorption capacities for natural and modified biomasses were found to be 91.03 and 203.21 mg g^{-1} at 30 °C, respectively. Modified biosorbent exhibited very good regeneration potential up to 10 cycles and it was successfully used for the decolorization of synthetic solution in dynamic flow mode. Zeta potential measurements, IR, SEM and EDX analysis were used to characterize the possible dye–biosorbent interactions. Overall, the present study underlines the alternative use of modified *T. orientalis* cones for removal and recovery applications of cationic dye, Basic Blue 9.

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1. Introduction

Synthetic dyes are extensively used in various industrial applications such as textile, leather, tanning, paper production and food technology. The release of colored effluents to the aquatic environment without adequate treatment causes public concern, legislation problems and is a serious challenge to environmental scientists. Synthetic origin and complex aromatic structures of dyes make them stable and difficult to remove using traditional wastewater treatment technologies. Decolorization of dye containing industrial effluents is of great importance because of the toxic, mutagenic and carcinogenic nature of the synthetic dyes or their metabolites. As the colored effluents cannot be efficiently decolorized by conventional treatment methods, there is a growing interest to find economic and effective alternatives for the treatment of these effluents (Fernández-Fernández & Ricardo Pérez-Correa, 2007; Forgacs, Cserháti, & Oros, 2004; Grassi, Scodeller, Filiel, Carballo, & Levin, 2011).

Biosorption process has attracted interest in this context seems to be a good alternative to the traditional water decolorization methods. Different biological origin materials such as fungi, algae, yeast, bacteria and plant have been used as biomass source in order to remove dyes from colored effluents (Akar, Anilan, Gorgulu, & Tunali Akar, 2009; Akar, Anilan, Kaynak, Gorgulu, & Tunali Akar, 2009; Akar, Tosun, et al., 2009; Aravindhan, Rao, & Nair, 2007; Fernandez, Nunell, Bonelli, & Cukierman, 2012; Khambhaty, Mody, & Basha, 2012; Lin, He, Han, Tian, & Hu, 2011; Sajab et al., 2011; Sun et al., 2008; Tunali Akar, Gorgulu, Akar, & Celik, 2011; Tunali, Ozcan, Kaynak, Ozcan, & Akar, 2007). The main advantages of this process are simple operation, potential cost effectiveness, short equilibrium time, selectivity and reusability of some biosorbents, low quantity of sewage sludge disposed. Biosorbents are not affected by toxic wastes, they do not require nutrient supply, and they can be stored and used for extended period if dead biomass is used (Aksu & Balibek, 2010; Chojnacka, 2010).Plant fibers consisting mainly of cellulosic and lignin materials, carry many functional groups of alcohols, aldehydes, ketones, carboxyl, hydoxyl and ether, which can bind pollutant material such as metal ions. Hence the use of lignocellulosic biomaterials in bioremediation purpose has attracted interest (Ofomaja & Naidoo, 2010).

Recent progress in the biosorption technology has led to the development of more efficient biosorbent materials and researchers have tried the surface modification procedures by various kind of chemicals (Akar & Divriklioglu, 2010; Akar, Celik, & Tunali Akar, 2010; Fernandez et al., 2012; Mao, Won, Choi, Lee, & Yun, 2009; Vijayaraghavan, Won, Mao, & Yun, 2008). In this

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direction, citric acid modified *Thuja orientalis* (*T. orientalis*) cones were used as possible biosorbent for the treatment of Basic Blue 9 (BB9) contaminated solutions. They are readily available and economical biomaterials and their mature cones basically contain cellulose, hemicellulose, lignin, rosin and tannins as the structural components (Nuhoglu & Oguz, 2003). Cellulose is the basic structural component of plant cell wall containing highly uniform β-(1→4)-linked polyglucan. Hemicelluloses are a family of heteropolymers comprising various sugar units such as glucose, galactose, mannose, xylose, arabinose, fucose, glucuronic acid, and galacturonic acid, in various amounts or traces depending upon the plant species. Lignins are complex heteropolymers of plant cell wall. They are produced from dehydrogenative polymerization of cynnamyl alcohols (Boudet, Lapierre, & Grima-Pettenati, 1995; Ebringerova & Heinze, 2000; Peng, Peng, Xu, & Sun, 2012).

Cone biomass of *T. orientalis* was chosen as model sorbent because of its known biosorption ability toward dye molecules (Akar, Ozcan, Tunali, & Ozcan, 2008; Akar, Anilan, Gorgulu, et al., 2009; Akar, Anilan, Kaynak, et al., 2009; Akar, Tosun, et al., 2009; Tunali Akar, Gorgulu, Kaynak, Anilan, & Akar, 2009; Vijayaraghavan & Yun, 2008). High decolorization yields were obtained by using a small amount of modified biosorbent when compared with that of unmodified one. The suggested biosorbent was successfully used in batch and dynamic mode decolorization studies. Isotherm and kinetic parameters of the process were predicted. Applicability of this sorbent material in real conditions was tested. Its regeneration potential was also investigated in addition to the dye–biosorbent interaction mechanisms evaluated by SEM, EDX, IR and zeta potential analysis.

2. Experimental

2.1. Preparation of modified biosorbent

T. orientalis cones were collected from a number of plants in nature. In order to remove the adhering dirt and soluble impurities, they were thoroughly rinsed with deionized water. The samples were dried at 80 °C for 24 h, ground using a laboratory mill (IKA A11) and then sieved to select particle size of less than 100 mesh by using ASTM Standard sieve. The powdered biosorbent was stored in a glass bottle prior to use for the modification with citric acid (CA).

The similar modification procedure reported by Gong, Jin, Chen, Chen, and Liu (2006) was applied to *T. orientalis* in this study. 0.5 M CA was added to powdered biosorbent at a ratio of 12:1 (acid:biosorbent) and the mixture was stirred for 30 min. After drying at 50 °C for 24 h, the oven temperature was increased to 120 °C in order to complete the thermochemical reaction of CA with biosorbent. Then the CA-modified *T. orientalis* was cooled, washed with deionized water and filtered. Modified biosorbent was treated with 0.1 M NaOH for 60 min and excess NaOH was removed by washing several times with distilled water. Final modified biosorbent was dried at 50 °C and used as biosorbent for removal of basic dye.

2.2. Dye solution

By dissolving appropriate amount of BB9 in deionized water, a stock solution at a concentration of 1000 mg L^{-1} was prepared. The other required concentrations were obtained by the dilution of this solution. Fresh dilutions were used for each experiment. The pH of the working solutions was adjusted to desired values by adding 0.1 M HCl or 0.1 M NaOH solutions before addition of the biosorbent. pH of the solutions was measured by WTW Inolab 720 Model pH-meter.

2.3. Biosorption procedure

2.3.1. Batch experiments

In order to investigate the effect of important experimental parameters on the dye biosorption by CA-modified biosorbent, batch biosorption experiments were carried out. For each experimental run, a known mass of CA-modified biosorbent was added into beaker including 25 mL of 25 mg L^{-1} BB9 solution. The samples were agitated on a magnetic stirrer at a rate of 200 rpm. At the end of the biosorption trials, the dye solutions were separated from the biosorbent by centrifugation at 3500 rpm for 3 min.

The initial pH of the dye solutions was changed from 2.0 to 10.0 in order to study the effect of pH on BB9 biosorption. Biosorbent amount was varied from 0.01 to 0.05 g at pH 6.60. Biosorption kinetics was determined by analyzing the biosorption of BB9 from aqueous solutions at different time intervals and at various temperatures (15, 30 and 45 °C). For the isothermal evaluation of data, dye solutions at different concentrations were mixed with CA-modified *T. orientalis* till the equilibrium was attained. BB9 concentrations in the supernatant were determined by using UV-visible spectrophotometer (Shimadzu UV-2550) at maximum wavelength of dye.

2.3.2. Column experiments

A fixed-bed glass column with 9 mm internal diameter was used in continuous biosorption studies. Biosorption performance of CA-modified *T. orientalis* was studied by varying the flow rate (from 0.5 to 4.0 mL min^{-1}) and bed height (biosorbent amount: from 0.01 to 0.07 g). The dye solutions were pumped into the column using a peristaltic pump (Heidolph PD 5201). The effluent solutions were collected from the bottom of the column and analyzed for dye concentration. Temperature and initial pH of the dye solutions were kept at 25 °C and 6.60, respectively. In order to examine desorption ability of BB9 from CA-modified *T. orientalis*, the biosorbent in the column was first loaded with dye. BB9-loaded biosorbent was regenerated using 0.01 M HNO_3 for the investigation of reusability potential of the modified biosorbent. Acid solution was pumped into the column at the same conditions in the biosorption cycle. The bed was washed with deionized water and used for the next biosorption cycle. The biosorption and desorption cycles were repeated for 10 times. The eluted dye concentrations were determined as described before.

2.4. Data treatment

The equilibrium biosorption capacity (q_e) and desorption yield of the biosorbent were calculated from the following Eqs.

$$q_e = \frac{V(C_i - C_e)}{m} \tag{1}$$

$$\text{Desorption yield (\%)} = \frac{\text{desorbed dye concentration}}{\text{biosorbed dye concentration}} \times 100 \tag{2}$$

where C_i and C_e represent the initial and the equilibrium BB9 concentrations (mg L^{-1}), respectively, V is the volume of dye solution (L) and m is the amount of biosorbent used (g).

Each experiment in this study was repeated at least three times and the arithmetical average values from these independent experiments were used to give results. In figures, error bars show the standard error of the mean and the standard deviations are also given wherever necessary. Statistical treatment of data was performed using SPSS 15.0 for Windows. The significant difference between means of samples was determined by ANOVA followed by posthoc testing using Tukey's test and defined at 95% confidence level.

2.5. Biosorbent characterization

In order to determine the surface charge of the biosorbent as a function of pH, zeta potential measurements were carried out using a zeta potential analyzer (Malvern zeta sizer). The main functional groups on the biosorbent were investigated by FTIR spectrophotometer (Bruker Tensor 27). Samples were prepared as KBr disks and the spectra were recorded in the wavenumber range of 4000–400 cm^{-1}. The electron micrographs were obtained from a scanning electron microscope coupled with energy dispersive X-ray analysis (JEOL 560 LV SEM), at 20 kV and 3000× magnification.

3. Results and discussion

3.1. Effect of biosorbent amount

BB9 biosorption yields of unmodified and CA-modified *T. orientalis* at different biosorbent dosages are presented in Fig. 1a. This figure indicates that the biosorption yields of both biosorbent increased with increasing amount of biosorbents ($p < 0.05$). This was due to the greater availability of biosorptive sites for dye molecules with higher dosage of the biosorbent (Al-Anber & Al-Anber, 2008). The biosorption yields of BB9 were found as 92.25% and 97.87% with 0.03 and 0.015 g of natural and CA-modified *T. orientalis*, respectively. The biosorption performances of both biosorbent did not significantly change with further increase in the biosorbent dosage ($p > 0.05$). This may be attributed to the saturation of active sites on the biosorbent by dye molecules. These results also showed that the modification of *T. orientalis* with citric acid significantly enhanced the biosorption performance of the natural biosorbent.

3.2. Effect of pH

The variation of the biosorption yields of unmodified and CA-modified *T. orientalis* was investigated as a function of initial pH since it is an important factor affects the dye and biosorbent chemistry in solution (Saeed, Sharif, & Iqbal, 2010). The effect of pH on the BB9 biosorption yield of *T. orientalis* before and after CA treatment was studied in the range of pH 2.0–10.0. The results are given in Fig. 1b. As expected, BB9 biosorption capacity of both biosorbent increased with increasing pH values ($p < 0.05$). This could be probably due to the competition between hydronium (H_3O^+) ions and cationic dye molecules for binding sites on the biosorbent surface at acidic conditions (Altundogan, Arslan, & Tumen, 2007). An increase in the initial pH of the medium from 2 to 5 causes an increase in the biosorption yields of both biosorbent. After this pH value the biosorption performance of both biosorbent stayed almost constant ($p > 0.05$). Therefore, BB9 solutions were used without pH adjustment for further biosorption trials (original pH of the dye solution is 6.60). The biosorption capacity of CA-modified biosorbent was higher than that of unmodified biosorbent at all studied pH range. This may be explained by the addition of carboxyl groups (COOH) onto the biosorbent surface (Sajab et al., 2011).

The surface charge of the natural biomass varied from +14.10 to −33.85 mV when the pH was changed from 1.0 to 10.0 and its isoelectric point (IEP) was observed at about pH 2.0 (Tunali Akar et al., 2009). It is apparent from Fig. 1c zeta potential values of the same biomass varied from +0.27 to −41.27 mV after the modification process. The more negative surface charge values were recorded for the modified *T. orientalis* in the pH range of 2.0–10.0 when compared with the natural biomass. This finding also confirmed the enhanced biosorption potential of modified biomass.

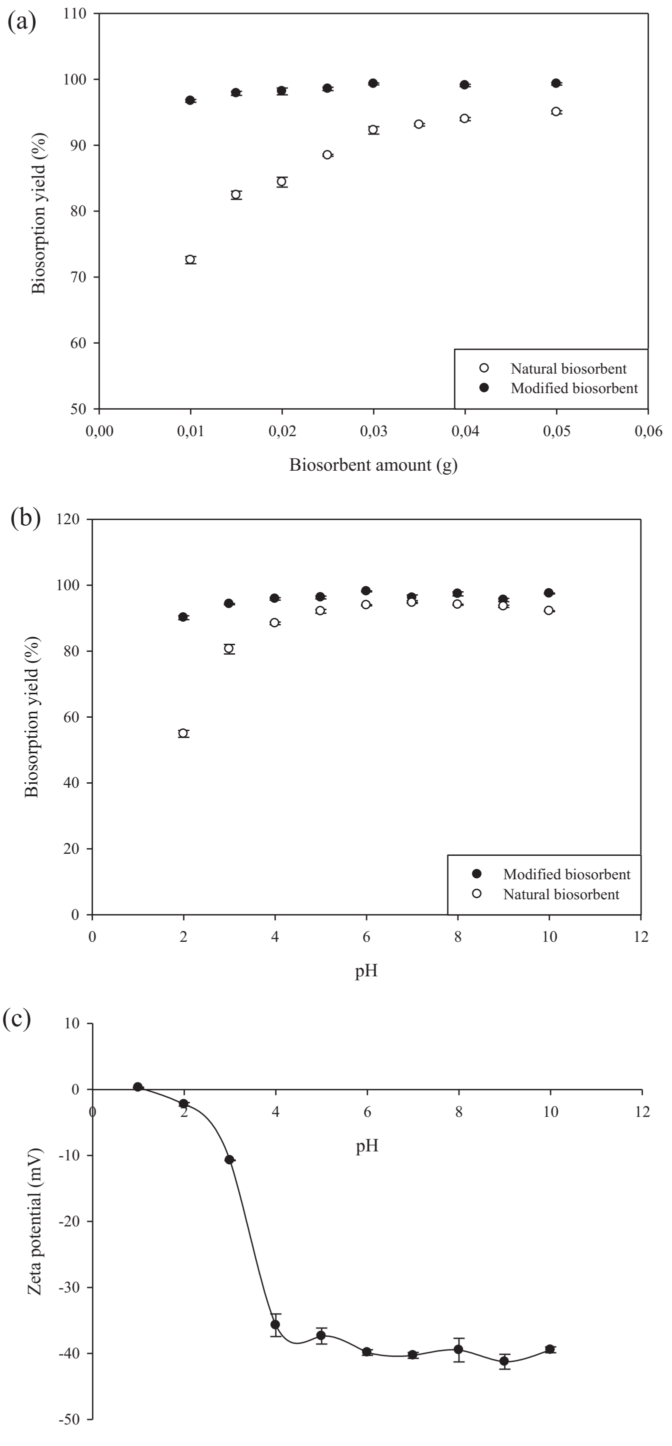

Fig. 1. Effect of biosorbent dosage (C_i: 25 mg L^{-1}; pH: 6.60; V: 25 mL; t: 60 min) (a) and pH (C_i: 25 mg L^{-1}; m: 0.015 g for modified and 0.03 g for natural biosorbent; V: 25 mL; t: 60 min) (b) on the biosorption of BB9 onto natural and CA-modified *T. orientalis* and zeta potentials of CA-modified *T. orientalis* at different pH values (c).

Fig. 1c indicates that the IEP of the modified biomaterial is at about pH 1.0. The high negative surface charge of the modified biomass above the IEP makes it useful for cationic dye removal because of the attraction forces between dye and biosorbent surface. The high negative zeta potential values recorded in the pH range of 5.0–10 for modified biomass also support the selected pH value (pH 6.60) for decolorization process.

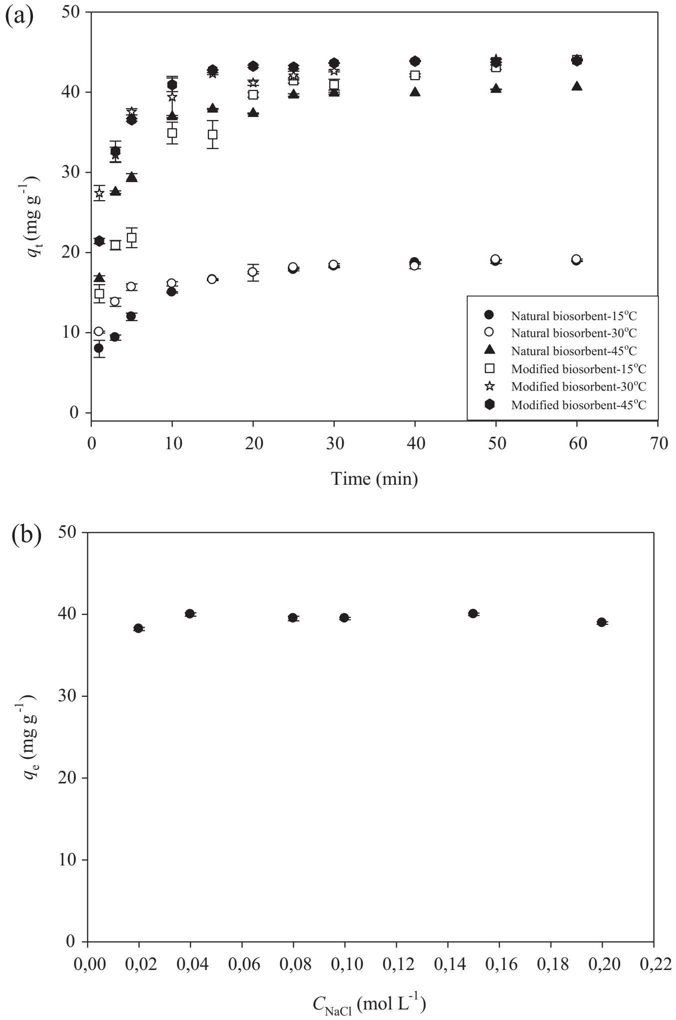

Fig. 2. Effect of contact time on the biosorption of BB9 onto natural and CA-modified *T. orientalis* at different temperatures (C_i: 25 mg L^{-1}; pH: 6.60; V: 25 mL; m: 0.015 g for modified and 0.03 g for natural biosorbent) (a) effect of ionic strength on the biosorption of BB9 onto CA-modified *T. orientalis* (C_i: 25 mg L^{-1}; pH: 6.60; V: 25 mL; m: 0.015 g; t: 25 min) (b).

3.3. Effect of temperature

Fig. 2a indicates the effect of temperature at different time intervals on the biosorption of BB9 onto unmodified and CA-modified *T. orientalis* biosorbents. An increase in the temperature from 15 to 45 °C did not cause an important change in the biosorption capacity of both biosorbent ($p > 0.05$). This may be an advantage for large temperature scale applications of these biosorbents.

3.4. Effect of ionic strength

The presence of some metal ions in dye-bearing wastewaters significantly affects the performance of a biosorption process since they cause high ionic strength (Maurya, Mittal, Cornel, & Rother, 2006). Therefore, the effect of ionic strength on BB9 biosorption by CA-modified *T. orientalis* was studied by varying ionic strength from 0.02 M to 0.2 M NaCl at pH 6.60. The results are presented in Fig. 2b. From this figure, it was observed that the biosorption performance of modified biosorbent slightly decreased with an increase in ionic strength. This may be explained by two mechanisms.

(i) The competition between positively charged BB9 species and sodium ions (Na^+) for the same active biosorption sites on the modified biosorbent. Thus, ion exchange mechanism could be responsible for BB9 biosorption.
(ii) Another way to explain the adverse effect of ionic strength may be changed activity coefficient of dye ions and thus limited their transfer to solid phase. If electrostatic attraction is included mechanism in the biosorption process, active sites on the biosorbent will be surrounded by counter ions and this weakens the binding force (Aksu & Balibek, 2010; Maurya et al., 2006; Vilar, Botelho, & Boaventura, 2005).

3.5. Kinetic studies

Time-dependent experiments were carried out in order to determine the equilibrium time and to evaluate the kinetics of BB9 biosorption onto both unmodified and CA-modified *T. orientalis*. The results in Fig. 2a indicated the rapid biosorption of BB9 in the initial stage of process at three different temperatures (15, 30 and 45 °C). This was followed by a longer period of much slower dye uptake. So, the biosorption reaction reached an equilibrium. The maximum equilibrium time was 25 min for both biosorbent. Then, the biosorption capacity of two biosorbents did not significantly change with contact time ($p > 0.05$).

In order to investigate the mechanism of BB9 biosorption the pseudo-first-order and the pseudo-second-order kinetic models have been used.

The linearized pseudo-first-order rate equation (Lagergren, 1898) is expressed as:

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

The most used form of linear pseudo-second-order rate equation (Ho & McKay, 1998) is represented by:

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

where q_e and q_t are the amounts of dye biosorbed in the equilibrium (mg g^{-1}) and on the sorbent surface at any time t (mg g^{-1}), respectively, k_1 (min^{-1}) and k_2 (g mg^{-1} min^{-1}) are the equilibrium rate constants of biosorption for the pseudo-first-order and the pseudo-second-order model, respectively. The initial biosorption rate, h (mg g^{-1} min^{-1}) at $t = 0$ is defined as $h = k_2 q_e^2$.

The linear plots (figures not shown) of the kinetic models for the biosorption of BB9 onto both unmodified and CA-modified *T. orientalis* were obtained and the calculated kinetic parameters are presented in Table 1. These results indicated that the pseudo-second-order is the best fit model with R^2 value of 0.999 at all studied temperatures. This model implies the chemisorption mechanism for BB9 biosorption. All of calculated q_e values obtained from this model are also close to the experimental values. R^2 values of the pseudo-first-order model were very low and predicted q_e values do not agree with experimental ones. These findings suggested the insufficiency of the pseudo-first-order model to explain the kinetics of BB9 biosorption onto both unmodified and CA-modified biosorbent.

3.6. Biosorption isotherms

In the present work Freundlich, Langmuir and Dubinin–Radushkevich (D–R) isotherm models were used to describe the equilibrium between BB9 biosorbed onto the biosorbent and in the solution. The general isotherm plots for the biosorption of BB onto unmodified and modified biosorbents are included in Fig. 3.

Table 1
Kinetic model parameters for the biosorption of BB9 onto natural and CA-modified biosorbent at different temperatures.

	Pseudo-first-order				Pseudo-second-order			
	T (°C)	k_1 (min^{-1})	q_e (mg g^{-1})	R^2	k_2 (g mg^{-1} min^{-1})	q_e (mg g^{-1})	h (mg g^{-1} min^{-1})	R^2
Natural biosorbent	15	3.19×10^{-2}	3.71	0.514	1.82×10^{-2}	19.84	7.18	0.999
	30	2.69×10^{-2}	2.98	0.484	2.99×10^{-2}	19.48	11.35	0.999
	45	2.08×10^{-2}	2.23	0.296	4.80×10^{-2}	20.11	19.43	0.999
CA-modified biosorbent	15	6.16×10^{-2}	13.87	0.689	5.61×10^{-3}	46.54	12.15	0.998
	30	3.97×10^{-2}	4.53	0.418	1.88×10^{-2}	44.90	37.90	0.999
	45	4.08×10^{-2}	5.32	0.503	2.38×10^{-2}	44.72	47.69	0.999

Table 2
Isotherm model parameters for the biosorption of BB9 onto natural and CA-modified biosorbent at 30 °C.

	Langmuir				Freundlich			Dubinin–Radushkevich (D–R)			
	q_{max} (mg g^{-1})	K_L (L mol^{-1})	R^2	R_L	n	K_F (L g^{-1})	R^2	q_m (mg g^{-1})	β (mol^2 kJ^{-2})	R^2	E (kJ mol^{-1})
Natural biosorbent	91.03	6.46×10^4	0.999	6.45×10^{-3}	2.56	5.18×10^{-3}	0.910	216.65	1.56×10^{-3}	0.803	17.88
CA-modified biosorbent	203.21	6.66×10^4	0.998	6.91×10^{-3}	3.13	7.23×10^{-3}	0.823	587.81	1.66×10^{-3}	0.891	17.34

According to Freundlich model (Freundlich, 1906) biosorption takes place at specific heterogeneous surfaces and the linear form of this model is represented as;

$$\ln q_e = \ln K_F + \ln C_e \tag{5}$$

where K_F (L g^{-1}) and n (dimensionless) are Freundlich isotherm constants. It was reported that n values in the range of 1–10 suggest favorable biosorption (Basha & Murthy, 2007). Table 2 shows the Freundlich model does not fit the experimental data in this study well ($R^2 < 0.911$). Therefore, Freundlich isotherm was not the suitable model for describing the biosorption of BB9 onto both unmodified and CA-modified *T. orientalis*.

The Langmuir isotherm model (Langmuir, 1918) can be written in linear form;

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \left(\frac{1}{q_{max}K_L}\right)\frac{1}{C_e} \tag{6}$$

where q_{max} (mol g^{-1}) is the monolayer biosorption capacity of the biosorbent and K_L (L mol^{-1}) is the Langmuir constant and related to the free energy of biosorption. As can be seen from Table 2 the Langmuir model has high R^2 values for both biosorbent and this indicates the BB9 biosorption data follow this model. The monolayer biosorption capacity values were obtained as 91.03 and 203.21 mg g^{-1} for unmodified and CA-modified *T. orientalis*, respectively. These values are in good accordance with experimentally obtained values and also approved the highest affinity for BB9 with CA-modified biosorbent. On the other hand, Table 3 indicates the important potential of CA-modified biosorbent for the removal of BB9 when compared with the various biosorbents reported in the literature (Banat, Al-Asheh, Al-Ahmad, & Bni-Khalid, 2007; Ferrero, 2007; Gong, Jin, Chen, Hu, & Sun, 2007; Hameed & Ahmad, 2009; Hameed & El-Khaiary, 2008a, 2008b; Hameed, Mahmoud, & Ahmad, 2008; Hameed, Krishni, & Sata, 2009; Hameed, 2009; Low & Lee, 1990; McKay, Ramprasad, & Pratapamowli, 1986; McKay, Porter, & Prasad, 1999; Nasuha & Hameed, 2011; Ponnusami, Vikram, & Srivastava, 2008; Sajab et al., 2011).

'R_L', a dimensionless constant (Hall separation factor) is used to determine the suitability of the biosorbent for the biosorbate and defined in the following equation (Hall, Eagleton, Acrivos, & Vermeulen, 1966; Yang et al., 2011).

$$R_L = \frac{1}{1 + K_L C_o} \tag{7}$$

where C_o is the highest initial dye concentration (mol L^{-1}). R_L values in this study (6.45×10^{-3} for natural and 6.91×10^{-3} for modified biosorbent) are between 0 and 1 and indicate the favorable biosorption process for BB9 removal onto both biosorbent.

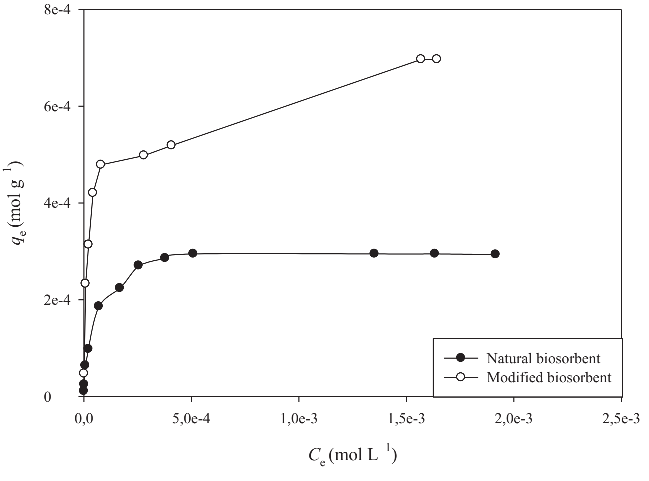

Fig. 3. General isotherm plots for the biosorption of BB9 onto natural and CA-modified *T. orientalis* (*V*: 25 mL; pH: 6.60; *m*: 0.015 g for modified and 0.03 g for natural biosorbent; *t*: 25 min).

Table 3
Biosorption results of BB9 onto different biosorbents from the literature.

Biosorbent material	Biosorption capacity (mg g^{-1})	References
Spent tea leaves	300.05	Hameed (2009)
Untreated guava leaves	295.00	Ponnusami et al. (2008)
Cotton waste	277.77	McKay et al. (1999)
Banana stalk waste	243.90	Hameed et al. (2008)
NaOH-modified rejected tea	242.11	Nasuha and Hameed (2011)
Modified rice straw	208.33	Gong et al. (2007)
Broad bean peels	192.72	Hameed and El-Khaiary (2008a)
Pumpkin seed hull	141.92	Hameed and El-Khaiary (2008b)
CA-treated kenaf core fibers	131.60	Sajab et al. (2011)
Pineapple stem	119.05	Hameed et al. (2009)
Coconut husk	99.00	Low and Lee (1990)
Teak wood bark	84.00	McKay et al. (1986)
Garlic peel	82.64	Hameed and Ahmad (2009)
Ground hazelnut shells	76.90	Ferrero (2007)
Olive pomace	42.30	Banat et al. (2007)
CA-modified *T. orientalis*	203.21	This study

D–R isotherm model (Dubinin & Radushkevich, 1947) is used to distinguish the nature of biosorption as physical and chemical and linearized as following equation;

$$\ln q_{\mathrm{e}} = \ln q_{\mathrm{m}} - \beta \varepsilon^2$$

where β is a constant related to the biosorption energy (mol^2 kJ^{-2}), q_{m} is D–R monolayer capacity, and ε is the Polanyi potential, which is equal to $RT \ln(1 + 1/C_{\mathrm{e}})$, where R (J mol^{-1} K^{-1}) is the gas constant, and T (K) is the absolute temperature. A plot of $\ln q_{\mathrm{e}}$ versus ε^2 (figure not shown) gives q_{m} and E values (Table 2) from the slope and intercept, respectively. The values of E (17.88 for unmodified and 17.34 for CA-modified) showed the chemical biosorption mechanism for the removal of BB9.

3.7. Dynamic flow mode parameters

The quantity of biosorbed dye is largely dependent on the flow rate and biosorbent amount inside the column. Therefore, BB9 biosorption studies were carried out at flow rates of 0.5, 1.0, 2.0, 3.0 and 4.0 mL min^{-1} for a fixed biosorbent amount. The results are presented in Fig. 4a. The biosorption yields of CA-modified biosorbent were found as 96.93 ± 0.65% and 97.51 ± 2.74% ($p > 0.05$) at flow rates of 0.5 and 1.0 mL min^{-1}, respectively. The biosorption yield of modified biosorbent decreased to 79.79 ± 2.36% when the flow rate was increased to 4.0 mL min^{-1} ($p < 0.05$). This observation could be explained by the lower contact time between dye solution and biosorbent filled into the column. Thus, 1.0 mL min^{-1} was chosen to make the process time and biosorbent efficient.

The effect of biosorbent amount on the column biosorption of BB9 was studied by varying amount of biosorbent from 0.01 to 0.07 g. The results (Fig. 4b) indicated the biosorption yield of the biosorbent increased from 74.85% to 97.67% when the amount of biosorbent was increased from 0.01 to 0.035 g ($p < 0.05$). Then, no further increase in the biosorption yield of CA-modified biosorbent was observed with increasing biosorbent amount ($p > 0.05$). These findings can be explained by the fact that the higher the bed depth the longer the contact time between biosorbate and biosorbent in the column (Low, Lee, & Ng, 1999).

Desorption studies were conducted to explore the reusability of the modified biosorbent to make the biosorption process economical. For this aim, biosorption/desorption cycles were repeated for 10 times. The results are presented in Fig. 4c. It was found that near complete desorption of biosorbed BB9 could be achieved at the end of 10th cycle. Furthermore, 35% decrease was observed in the biosorption yield of modified biosorbent at 10th cycle. This may be attributed to the degeneration of the active sites on the biosorbent surface after HNO_3 treatment during the desorption procedure. According to our literature survey, BB9 dye has been recovered only up to 5–6 cycles using various eluents from different sorbent materials (Mak & Chen, 2004; Vijayaraghavan & Yun, 2008). Thus, CA-modified biosorbent may be reused for 10 cycles in order to reduce the cost of biosorption process.

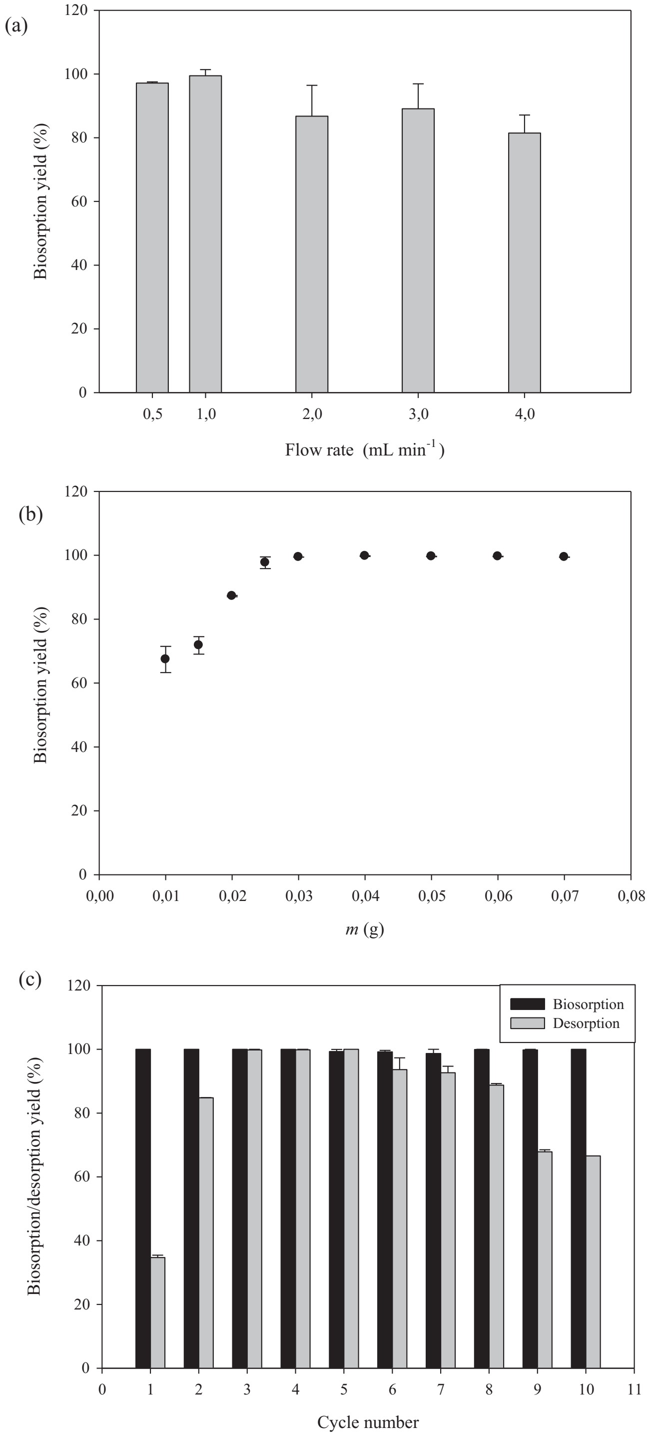

Fig. 4. The continuous mode parameters of BB9 biosorption onto CA-modified *T. orientalis*: effect of flow rate (*V*: 25 mL; pH: 6.60; *m*: 0.025 g; column id.: 9 mm) (a), effect of biosorbent amount (*V*: 25 mL; pH: 6.60; column id.: 9 mm; flow rate: 1 mL min^{-1}) (b) and biosorption/desorption cycles (*V*: 25 mL; pH: 6.60; *m*: 0.025 g; column id.: 9 mm; flow rate: 1 mL min^{-1}) (c).

3.8. Characterization of biosorbent and biosorption mechanism

IR spectroscopy was used to characterize the possible sorbent–sorbate interactions. The spectra of natural (A), modified (B) and dye loaded modified (C) biomasses in the range of 4000–400 cm^{-1} are presented in Fig. 5a. The broad absorption band in the spectrum of natural biomass at 3420 cm^{-1} corresponds to —OH and —NH stretching vibrations. The peaks observed at 2924 and 2856 cm^{-1} represent C—H vibrations of —CH_2 and —CH_3 groups. Their bending vibrations were observed at 1448 and 1381 cm^{-1}, respectively. The peaks at 1732, 1626 and 1517 cm^{-1} can be attributed to C═O stretching vibrations of carboxyl, amid I and amid II bands, respectively. Absorption bands around 1245, 1147 and 1105 cm^{-1} possibly represent C—N stretching vibrations. The peaks at 1057 and 891 cm^{-1} belong to P—OH stretching and aromatic C—H bending vibrations, respectively (Malkoc, 2006; Tunali Akar et al., 2009). After the chemical modification, the broad band at 3419 cm^{-1} shifted to 3422 cm^{-1} in addition to an intensity decrease. This finding may be attributed to esterification reaction between hydroxyl groups on the biomass and citric acid. The

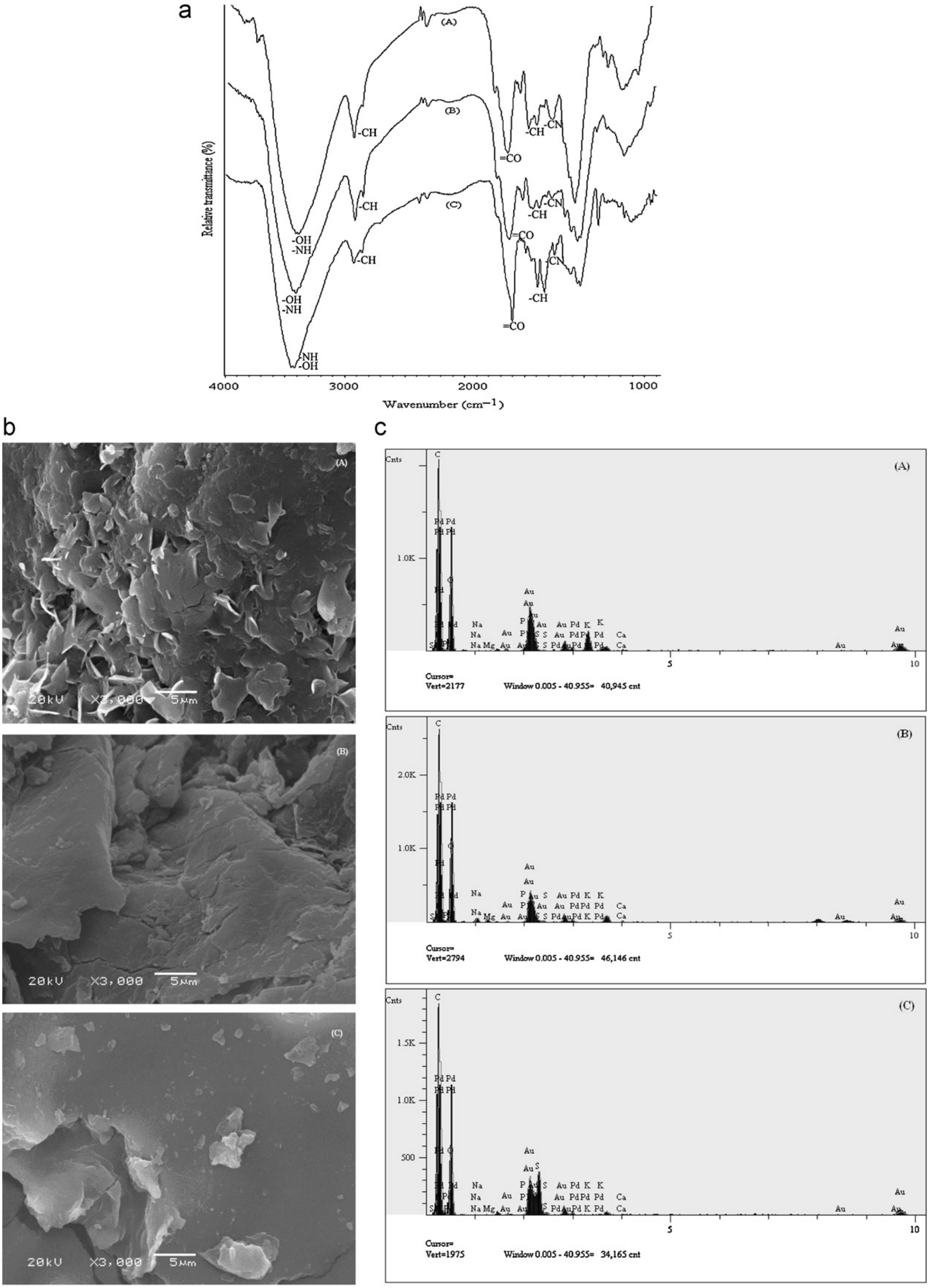

Fig. 5. IR (a), SEM (b) and EDX (c) spectra of natural (A) CA-modified (B) and BB9 loaded CA-modified (C) *T. orientalis*.

introduced free carboxyl groups of citric acid increased the net negative charges on the biomass. This leads to an increase in the binding capacity of biomass for cationic pollutants (Mao et al., 2009). The spectra of the modified biomass displayed some peak shifts from 1626 to 1630 cm^{-1}, 1148 to 1163 cm^{-1} and 1105 to 1110 cm^{-1}. The peak intensities at 1057 and 1245 cm^{-1} also decreased after the modification and the last band shifted to 1271 cm^{-1}. After contacting with dye, absorption bands at 1630 and 1163 cm^{-1} in the spectrum of modified biomass shifted to 1600 and 1141 cm^{-1}, respectively with an intensity change in these bands. Also some shifts from 1516 to 1489 cm^{-1}, 1450 to 1441 cm^{-1}, 1379 to 1390 cm^{-1} and 1271 to 1250 cm^{-1} were noticed in the spectra of dye-loaded modified biomass. These observations showed that the possibly involvement of the functional groups on the modified biosorbent surface in biosorption process. The appearance of a new peak at about 1332 cm^{-1} after dye biosorption may be attributed to C—N group of dye. Finally, a shift and an intensity increase of the aromatic C—H peaks at 895 cm^{-1} in the IR spectrum of modified biomass also indicated the sorbent–sorbate interaction.

SEM micrographs of the natural, modified and dye loaded modified biomaterials at 3000 times of magnification are presented in Fig. 5b. The micrographs showed that rough, porous and irregular surface structure of natural biomaterial (A). This structure clearly changed after the modification process and a layered structure looking like sponge became apparent (B). After the biosorption process, the modified biomaterial has smoother surface (C) than that of modified one. This finding revealed the coverage of the modified biomaterial surface with molecular cloud of dye.

The EDX profile (Fig. 5c) of the natural biomass (A) showed the presence of C, O, S, P, Ca, K, Na and Mg in the biosorbent structure. An intensity increase in these peaks (especially C and O) confirmed the modification of biosorbent with CA (B). Furthermore, the biosorption of dye onto modified biomass was also evidenced by an increase of the C, O and S signals in the EDX spectrum of dye-loaded modified biosorbent (C) since these elements were also present in the dye structure. It was also noted that the intensities of the Ca, Mg and Na peaks in the EDX spectrum of modified biomass decreased after the dye biosorption. Hence, the biosorption of BB9 dye on the modified biomass may be regarded as ion exchange mechanism in addition to other possible interactions.

4. Conclusion

Modification with CA significantly enhanced the biosorption potential of the natural biomass. The relatively short equilibrium time was observed for modified biosorbent and kinetic studies indicated that the biosorption process preferably obeyed the pseudo-second-order model. Langmuir model fit well to the data than Freundlich and D–R isotherms. Desorption experiments showed that BB9 can be successfully recovered and regenerated biosorbent can be reused in 10 consecutive cycles. The results emphasized that modified *T. orientalis* biomass can be used as an effective biosorbent for the decolorization of BB9 containing solutions and the good biosorption yields were recorded with the small amounts of biosorbent.

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