Potential Application of Calabrian Pine Cone Biomass as Non-Wood Forest Product for Colour Bioremediation

Fatih Deniz

Department of Environmental Engineering, Faculty of Engineering and Architecture, Sinop University, 57000 Sinop, Turkey

e-mail: f_deniz@windowslive.com

Abstract

In this study, Calabrian pine cone biomass as a cheap non-wood forest product was explored for colour bioremediation from aquatic medium. Biosorption studies were performed at the optimized environmental conditions previously. C.I. Basic Red 46 dye was selected as model synthetic dye to simulate a possible coloured wastewater for this research. The kinetic data were evaluated by the pseudo-first-order, pseudo-second-order, logistic and intra-particle diffusion models. The equilibrium data were analysed by Freundlich, Langmuir and Dubinin-Radushkevich isotherm models. The logistic model presented the best fit to the experimental kinetic results. Langmuir model fitted better to the biosorption isotherm data than Freundlich model. The maximum monolayer dye biosorption capacity for Calabrian pine cone biomass was calculated to be 89.76 mg/g. Dubinin-Radushkevich model presented that the predominant mechanism for dye biosorption was likely physical biosorption. All these findings proposed that the cone biomass of Calabrian pine as a cheap and abundant non-wood forest product could be interesting alternative to expensive materials in removal of such unsafe dyes from coloured liquid environments. Moreover, further biosorption experiments should be carried out at the pilot scale to examine the feasibility of biosorbent for industrial applications.

Keywords: Calabrian pine; Cone biomass; Colour; Bioremediation

Introduction

A negative consequence of the growth of mankind, society and technology has been environmental disorder as large amounts of xenobiotic compounds are being accumulated. On the other hand, limited water resources and increasing demand for safe water require efficient water treatment methods [1]. In particular, the release of various harmful dyes into the environment has attracted great attention worldwide in recent years because of their extensive use in many industrial applications including textile, leather, food processing, dyeing, cosmetics, paper and dye manufacturing industries [2]. Nowadays, more than one hundred thousand kinds of commercial dyes are used with a rough estimated production of one million tons annually [3]. Dyes usually have a synthetic origin and complex chemical structure that make them persistence to light, oxidation and biodegradable process. As well known, the presence of dyes in water sources can cause reduction of light penetration, photosynthetic activity and gas solubility in addition to visual pollution. Also many dyes and their degradation derivatives are toxic at even carcinogenic in nature [4]. Therefore, the removal of these pollutants from contaminated water is a big challenge and thus it is necessary to develop efficient methods for this purpose.

Currently, biosorption using biological materials is emerging as a highly effective, economical and widely used method for the treatment of dye contaminated wastewater. It is considered as a potential alternative over the traditional costly treatment technologies [5]. Among biological materials, agro-forest lingo-cellulosic residues have shown good biosorption capacities for some dyes [6]. In particular, cones from conifers have been recently applied for removal of dyes, mostly with no further treatment other than crushing and washing with water [7-10]. Though these biosorbents have shown reasonable dye removal capacities, after biosorption process, the water is seen to have high chemical oxygen demand and biological oxygen demand as well as total carbon due to release of soluble organic compounds contained in the plant materials [11]. Some authors have applied different activation techniques to reduce the leaching of organic components and enhance biosorption capacity [5, 12, 13]. However, no work has been reported on the use of chemically modified Calabrian pine cone shell as an effective biosorbent for certain dye removal from aqueous solution. Pretreatment with dilute sodium hydroxide solution has been the most popular method of improving surface properties and removing soluble organic components of plant residues [14].

Materials and methods

Modified biosorbent preparation

Calabrian pine cone shells were collected from a plantation in Gaziantep, Turkey. After washing with distilled water to eliminate dust and other residues, the shells were dried at 80 °C and then crushed, milled and sieved. The fractions of particle between 63 and 500 μm were selected for chemical modification. The pine cone shells were suspended in 100 mL of a 0.1 M NaOH solution at a suitable ratio and the mixture was stirred using a magnetic stirrer for 2 h at room temperature. Then, it was thoroughly washed with distilled water to remove residual NaOH. The final product was dried at 80 °C. The fractions of particles between 63 and 500 μm were used as modified biosorbents for biosorption experiments.

Preparation of dye solution

C.I. Basic Red 46 was obtained from a local source. It was of commercial quality and used without further purification. C.I. Basic Red 46 dye stock solution at a concentration of 500 mg/L was prepared by dissolving appropriate amount of the dye in distilled water. The experimental concentrations were obtained by the dilution of this solution. 0.1 M HCl or 0.1 M NaOH was used for pH adjustment of the working solutions.

Biosorption experiments

The batch biosorption experiments were carried out with 0.05 mg of the biosorbent with 50 mL of C.I. Basic Red 46 solutions of desired concentration at pH 8 in a series of 100 mL conical flasks. The samples were agitated at a constant speed in a temperature-controlled water bath at 25 °C for the required time periods. The flasks were withdrawn from the bath at prefixed time intervals and the residual dye concentrations in the solutions were analyzed by centrifuging the mixtures and then measuring the absorbance of supernatants using a UV-visible spectrophotometer at the maximum wavelength of dye. The concentration of dye was calculated by comparing absorbance to the dye calibration curve previously obtained.

Results and discussion

Kinetics of biosorption

The prediction of biosorption mechanism and potential rate-controlling step(s) is an important issue to be considered [15]. The biosorption dynamics of C.I. Basic Red 46 onto the pine cone shell were investigated at the optimized dye biosorption conditions with various kinetic models, namely, the pseudo-first-order, pseudo-second-order, logistic and intra-particle diffusion. The logistic model is mainly used for modeling of microbial growth and product formation [16, 17]. On the other hand, this model is slightly employed for explaining dye biosorption dynamics. As displayed in the table, the logistic model presented the best fit to the experimental results with the most suitable statistical outcomes. Thus, these results show that the logistic function can be applied effectively for characterizing the removal kinetics of C.I. Basic Red 46 by the pine cone shell.

The effect of intra-particle diffusion as a potential rate-controlling step in the biosorption was evaluated by Weber and Morris intra-particle diffusion. According to this model, if a linear line passing through the origin, the intra-particle diffusion is the sole rate-limiting step. But, if multi-linear plots are exhibited, two or more steps control the biosorption process [18]. The plot for C.I. Basic Red 46 biosorption by the pine cone shell has three distinct regions. The initial region of the curve relates the biosorption on the external surface. The second stage corresponds to the gradual uptake presenting the intra-particle diffusion as rate-controlling step. The final plateau region indicates the surface biosorption and the equilibrium stage [19]. Hereby, the intra-particle diffusion was not the only rate-limiting step for the dye biosorption by the cone shell and also the other mechanism(s) may control the rate of biosorption or all of which may be operating simultaneously.

### Equilibrium isotherms of dye biosorption

Biosorption isotherms reveal the specific relation between dye molecules and biosorbent surface and highlight the distribution of dye molecules between the liquid and solid phases, when a biosorption process reaches its equilibrium state [20]. The equilibrium biosorption isotherms are of importance in the design of biosorption systems [21]. Accordingly, it was evaluated the fitness of the equilibrium data obtained from the biosorption experiments at the optimized dye removal conditions with Freundlich, Langmuir and Dubinin-Radushkevich models. As can be seen in the table, with more suitable statistical results, Langmuir model fitted better to the biosorption data than Freundlich model. This shows the monolayer coverage of C.I. Basic Red 46 dye molecules on the pine cone shell surface. In addition, the RL value obtained between 0 and 1 reflects a favourable biosorption for C.I. Basic Red 46 removal by the cone shell [22]. Besides, when compared with the natural cone shell of Calabrian pine (66.02 mg/g), the chemically modified cone shell (89.76 mg/g) has a greater biosorption capacity for C.I. Basic Red 46. The base modification improved the biosorption ability of the biosorbent for the dye. This may be due to increases in the total pore volume and surface area of the biosorbent related to extraction of plant extractives with base treatment [11].

In order to have an idea about the potential of the modified cone shell for C.I. Basic Red 46 removal from aqueous solution, its maximum biosorption capacity obtained from this work was also compared with those of reported for other biosorbents in the table [1, 23-29]. As can be seen from the table, the modified pine cone shell has a higher dye biosorption capacity than those of most biosorbents. In this way, it can be considered as a promising biosorbent for the removal of this dye from contaminated water.

Dubinin-Radushkevich model [30] is generally applied to express the nature of biosorption as physical and chemical. In this model, the value of mean free energy shows the mechanism by which biosorption takes place. A value of mean free energy below 8 kJ/mol displays physical biosorption while a value between 8 and 16 kJ/mol indicates chemical biosorption [31]. As can be shown in the table, the mean free energy for C.I. Basic Red 46 biosorption by the pine cone shell was found to be 2.292 kJ/mol. This presents that the predominant mechanism of the biosorption of dye by the cone shell was likely physical biosorption.

Conclusions

The chemical modification with NaOH (0.1 M) significantly enhanced the dye biosorption potential of the pine cone shell by 35% as compared with the natural cone shell. The logistic model was found suitable in describing the biosorption kinetics. The intra-particle diffusion was not the only rate-limiting step in the biosorption. The biosorption equilibrium was properly represented by Langmuir isotherm model. Dubinin-Radushkevich supported the physical biosorption mechanism. Thus, the chemically modified Calabrian pine cone shell can be used as an effective and inexpensive biosorbent for contaminated water with C.I. Basic Red 46.
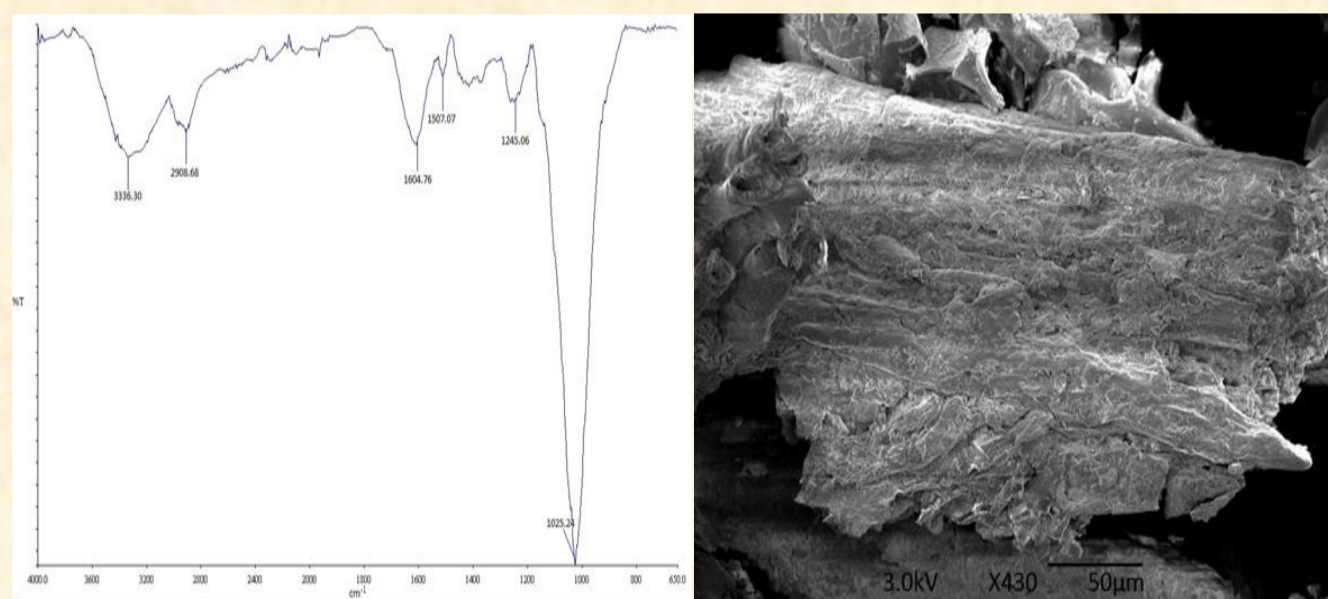
FTIR spectrum pattern and SEM image for Calabrian pine cone shell

Kinetic and isotherm parameters of biosorption system

Pseudo-first-order					Freundlich			
k_1 (min^{-1})	q_0 (mg g^{-1})	h_1 (mg g^{-1} min^{-1})	R^2	SD	K_f (mg g^{-1})(L mg^{-1})$^{1/n}$	n_f	R^2	SD
0.0677	86.67	5.863	0.824	8.058	33.01	3.712	0.684	10.781
Pseudo-second-order					Langmuir			
k_2 (g mg^{-1} min^{-1})	q_0 (mg g^{-1})	h_2 (mg g^{-1} min^{-1})	R^2	SD	q_0 (mg g^{-1})	R_L	R^2	SD
0.0009	93.70	7.918	0.987	2.375	89.76	0.654	0.980	2.941
Logistic					Dubinin-Radushkevich			
q_0 (mg g^{-1})	k (min^{-1})	R^2	SD		q_{DR} (mg g^{-1})	E (kJ mol^{-1})	R^2	SD
91.63	0.045	0.999	0.666		95.56	2.292	0.933	4.954
Intra-particle diffusion								
k_p (mg g^{-1} min$^{-1/2}$)	C (mg g^{-1})	R^2	SD					
5.928	32.35	0.954	4.126					

References

[1] A.R. Khataee, F. Vafaei, M. Jannatkhah, Int. Biodeterior. Biodegrad., 83 (2013) 33-40.
[2] E. Daneshvar, M. Kousha, N. Koutahzadeh, M.S. Sohrabi, A. Bhatnagar, Environ. Prog. Sustainable Energy, 32 (2013) 285-293.
[3] M. Ghaedi, S. Hajati, B. Barazesh, F. Karimi, G. Ghezelbash, J. Ind. Eng. Chem., 19 (2013) 227-233.
[4] T. Akar, A. Kulcu, S. Tunali Akar, Chem. Eng. J., 221 (2013) 461-468.
[5] S. Tunali Akar, Y. Yetimoglu Balk, O. Tuna, T. Akar, Carbohydr. Polym., 94 (2013) 400-408.
[6] M.E. Fernandez, G.V. Nunell, P.R. Bonelli, A.L. Cukierman, Bioresour. Technol., 106 (2012) 55-62.
[7] N.M. Mahmoodi, B. Hayati, M. Arami, C. Lan, Desalination, 268 (2011) 117-125.
[8] T. Sen, S. Afroze, H.M. Ang, Water Air Soil Pollut, 218 (2011) 499-515.
[9] F. Deniz, Desalin. Water Treat., 51 (2013) 4573-4581.
[10] F. Deniz, S. Karaman, S. Demirors Saygideger, Desalination, 270 (2011) 199-205.
[11] A.E. Ofomaja, E.B. Naidoo, Chem. Eng. J., 175 (2011) 260-270.
[12] A.E. Ofomaja, S.L. Ngema, E.B. Naidoo, Carbohydr. Polym., 90 (2012) 201-209.
[13] S. Dawood, T.K. Sen, Water Res., 46 (2012) 1933-1946.
[14] A.E. Ofomaja, E.B. Naidoo, S.J. Modise, J. Hazard. Mater., 168 (2009) 909-917.
[15] A. Roy, S. Chakraborty, S.P. Kundu, B. Adhikari, S.B. Majumder, J. Appl. Polym. Sci., 129 (2013) 15-27.
[16] M.M. Don, N.F. Shoparwe, Biochem. Eng. J., 49 (2010) 95-103.
[17] I. Eroglu, U. Gunduz, M. Yucel, I. Eroglu, Int. J. Hydrogen Energy, 35 (2010) 5293-5300.
[18] S. Chowdhury, P. Saha, Chem. Eng. J., 164 (2010) 168-177.
[19] P.D. Saha, S. Chakraborty, S. Chowdhury, Colloids Surf., B, 92 (2012) 262-270.
[20] K.Y. Foo, B.H. Hameed, Biomass Bioenergy, 35 (2011) 3257-3261.
[21] E. Errais, J. Duplay, F. Darragi, I. M'Rabet, A. Aubert, F. Huber, G. Morvan, Desalination, 275 (2011) 74-81.
[22] M.N. Sahmoune, N. Ouazene, Environ. Prog. Sustainable Energy, 31 (2012) 597-603.
[23] F. Deniz, Sci. World J., 2014 (2014) Article ID 138986.
[24] F. Deniz, Desalin. Water Treat., 52 (2013) 219-226.
[25] F. Deniz, S. Karaman, Chem. Eng. J., 170 (2011) 67-74.
[26] F. Deniz, S.D. Saygideger, Desalination, 268 (2011) 6-11.
[27] L. Laasri, M. Khalid Elamrani, O. Cherkaoui, Env Sci Poll Res Int, 14 (2007) 237-240.
[28] N.M. Mahmoodi, M. Arami, H. Bahrami, S. Khorramfar, Desalination, 264 (2010) 134-142.
[29] N. Yeddou Mezenner, A. Hamadi, S. Kaddour, Z. Bensaadi, A. Bensmaili, Journal of Chemistry, 2013 (2013) Article ID 965041.
[30] M.M. Dubinin, L.V. Radushkevich, Proc. Acad. Sci. Phys. Chem. Sect. USSR, 55 (1947) 331-333.
[31] G. Moussavi, R. Khosravi, Chem. Eng. Res. Des., 89 (2011) 2182-2189.