Removal of indigo carmine by bacterial biogenic Mn oxides

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Abstract. Indigo carmine (IC) is one of the oldest, most important and highly toxic dyes used and released in the effluents of many industries, such as textile, paper and plastics. Biogenic Mn oxides (BMO) were prepared by culturing *Marinobacter* sp. MnI7-9 in presence of Mn (II). The Point of Zero Charge (PZC) of the BMO is 7.5 by salt titration method. The surface area (BET) is 27.68 m^2 g^{-1} by the nitrogen adsorption-desorption method. The adsorption kinetics of low concentration IC (5 mg L^{-1}) on the BMO fit the pseudo-first order model, while the adsorption kinetics of higher concentration IC (20 mg L^{-1}) fit the pseudo-second order model. Intra-particle diffusion is an important rate-controlling step. The equilibrium adsorption data fit well in the Langmuir isotherm equation. The maximal adsorption capacity is 115.61 mg g^{-1} at 25℃. A larger IC removal amount can be obtained when the amount of the BMO is 2 g L^{-1} at pH 6.5. These results suggest that the BMO can be used as an efficient material for IC removal from aqueous solution.

Introduction

High Mn (II) concentration in soil will harm plant. Exposure to excess Mn may cause Parkinson-like symptoms and infertility in mammals and malfunction of the immune system. At the present day, serious Mn (II) pollution exists in many kinds of soil and water, especially some mineland soils [1]. A variety of microorganisms, including bacteria and fungi, can oxidize Mn (II) to insoluble biogenic Mn oxides (BMO) which play important roles in the biogeochemical cycle of Mn, control the distribution of metals and other trace elements in ocean and terrestrial environments and also remove toxic organic compound such as Diclofenac and 2-anilinophenylacetate [2-4].

Indigo carmine (disodium salt of 3,3-dioxobi-indolin-2,2-ylidine-5,5-disulfonate, IC) is one of the oldest, most important and highly toxic dyes used and released in the effluents of many industries, such as textile, paper and plastics. To the best of our knowledge, the successful use of a BMO for IC removal has not yet been reported. Our aim was to determine whether the BMO produced by culturing *Marinobacter* sp. MnI7-9 in waste containing Mn (II) is an efficient material to remove IC from aqueous solution.

Materials and methods

The BMO preparation, scanning electron microscopy (SEM) observation and X-ray diffraction (XRD) analysis were performed as described previously [4]. Specific surface area of the sample was determined by N$_2$ adsorption method (BET) with an AUTOSORB-1MP-CR surface analyzer instrument and its Point of Zero Charge (PZC) was determined by salt titration method [5].

The kinetics of IC removal by the BMO was performed as follows: a series of 150.00 mL of IC solution at varying concentrations (from 5 to 20 mg·L^{-1}) was added to 0.50 g the BMO in 250 mL Erlenmeyer flasks. The flasks were stoppered and shaken at 150 r min^{-1} at 28℃. 5 milliliters of the reacted solution was withdrawn at specific time intervals, separated by centrifugation at 12000 r min^{-1} and filtrated with 0.22 μm membrane. The IC concentration was determined spectrophotmetrically by measuring the absorbance at 610 nm. Blank test was conducted without the BMO to check for IC retention at the filter paper surface and other possible losses. The IC removal by the BMO was calculated according to the difference of IC concentration. All chemical analyses were replicated three times and the means were recorded.

The effect of the IC concentrations was investigated in the range of 20-200 mg L^{-1} in the above batch experiments with the addition of 1 g L^{-1} BMO and shook at 25℃ for 6 d.

The Effect of solution pH on IC removal was performed as follows: the batch experiments were followed as the above description using 20 mg L^{-1} IC and 1 g L^{-1} the BMO and shook at 28℃ for 48 h. The solution pH was varied from 4 to 10 by adding 0.1 mol L^{-1} NaOH or HCl solution.

Effect of the BMO on IC removal: batch experiments were carried out as above described using the different amount of the BMO with 20 mg L^{-1} IC at 28℃ for 48 h.

Results and Discussion

Characterization of the BMO adsorbent

The BMO produced by strain MnI7-9 were stick-shaped and adhered to the surface of strain MnI7-9 cells and the combination of the BMO and the cells were regular spindle-like particle had obvious crystalline peaks of δ-MnO$_2$ and γ-MnOOH on the CuKα XRD patterns as it was observed in our previous study using SEM [4]. The specific surface areas of the BMO is 27.68 m^2 g^{-1} by BET. Point of Zero Charge (PZC) of the BMO is determined by salt titration method and showed a PZC value of 7.42 (Fig. 1).
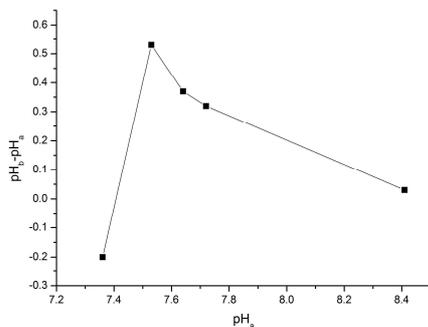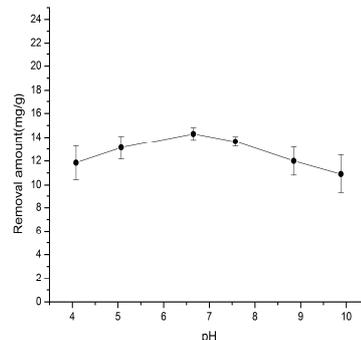

Fig. 1 PZC of the BMO

Fig. 3 Effect of pH on IC removal by the BMO
(20 mg L^{-1} IC, 1 g L^{-1} BMO, 28 ℃, 150 rpm, 48 h)

Indigo carmine removal kinetics by the BMO

The IC removal kinetics curves by the BMO are given in Fig. 2(A). It is observed that the removal rate is fast first, and then is very slow; less time is needed to reach IC maximal removal for lower concentration IC and the removal reaction equilibrium time is about 60 h. Once the easily available sites are occupied, the excess dye molecules in the solution find remote sites inside the pores of adsorbents with difficulty, which results in a decrease in adsorption rate with increase in contact time. This result is in agreement with previous studies [6-7]. The IC removal amount increases with IC concentration increase and the IC removal is 5.7 mg g^{-1} for 20 mg L^{-1} IC at 28℃ (Fig. 2(A)). These results indicate the BMO may be useful as a sorbent for IC.

The pseudo-first-order kinetic model of Lagergren [8] is expressed as follows:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{1}$$

where q$_t$, q$_e$ and k$_1$ represent the adsorption quantity (mg g^{-1}) at time t (h), the equilibrium adsorption quantity (mg g^{-1}) and Lagergren rate constant (h^{-1}), respectively. The rate constant of pseudo-first-order adsorption is determined from the slope of the plot of *t* vs. *ln(q$_e$-q$_t$)*. The second-order kinetic model [9] is expressed as follows:

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

where q$_t$, q$_e$ and k$_1$ represent the adsorption quantity (mg g^{-1}) at time t (h), the equilibrium adsorption quantity (mg g^{-1}) and the pseudo-second-order rate constant (g mg^{-1} h^{-1}), respectively. The constants of different models and correlation coefficient R^2 are shown in Table 1.The R ^{2} values for 5 mg L^{-1} IC

is 0.971 for the pseudo-first order model and 0.933 for the pseudo-second order model, while the R^2 values for 20 mg L^{-1} IC is 0.943 for the pseudo-first order model and 0.988 for the pseudo-second order model (Table 1). So the adsorption kinetics of lower concentration IC (5 mg L^{-1}) on the BMO fit the pseudo-first order model better than the pseudo-second order model due to the higher R^2 values, while the adsorption kinetics of higher concentration IC (20 mg L^{-1}) fit the pseudo-second order model better than the pseudo-first order model. Similar kinetics has been observed for IC adsorption by rice husk [10] and brazil nut shell [7].

   The adsorbate species are most probably transported from the bulk of the solution into the solid phase through an intraparticle diffusion process, which is often the rate-limiting step in many adsorption processes. The possibility of intraparticle diffusion was explored by using the model of Weber-Morris [10]:

$$q_t = k_i \sqrt{t} + c \tag{3}$$

where k_i and c are the constant of intraparticle diffusion rate and the constant related to liquid film thickness, respectively. It is essential for the q_t versus $t^{1/2}$ plots to go though the origin if the intraparticle diffusion is the sole rate-limiting step. The parameters and the fitting graphics are showed in Table 1 and Fig. 2(B). All correlation coefficients in Table 1 are higher than 0.92 indicates that intraparticle diffusion plays a significant role in the IC removal by the BMO. However, no plot passes through the origin in Fig. 2(B). This indicates that although intraparticle diffusion is involved in the adsorption process, it is not the sole rate-controlling step [11]. These results indicates that adsorption of IC on the BMO is a multi-step process, which involved adsorption on the external surface and diffusion into the interior [12]. Similar results were found for adsorption of methylene blue onto hazelnut shell [13] and adsorption of acid blue 193 onto natural sepiolite [14].

Table1. The kinetics parameters of IC removal by the BMO.

odels	Constants	Concentrations [mg/ L]		
		5	10	20
Pseudo-first-order model	k_1 [h^{-1}]	0.051	0.038	0.035
	r^2	0.971	0.973	0.943
Pseudo-second-order model	k_2 [g mg^{-1} h^{-1}]	0.011	0.006	0.002
	r^2	0.933	0.978	0.988
Weber-Morris model	k_i [g mg^{-1} $h^{-1/2}$]	0.153	0.308	2.000
	r^2	0.929	0.990	0.983

Fig.2 The removal kinetics (A) and Weber and Morris model (B) for IC removal by the BMO (3.3 mg L^{-1} the BMO, 28℃, 150 rpm).

Effect of pH on IC removeal by the BMO

Effect of pH on IC removeal by the BMO is shown in Fig. 3. It is clear from Fig. 3 that the IC removal amount by the BMO is first increased and then decreased with the initial pH increase, and maximum removal takes place at pH 6.5. A similar trend of pH effect was observed for the adsorption of Acid Orange 7 and Acid Orange 10 on the ethylenediamine-modified magnetic chitosan nanoparticles [15].

More protons will be available for the BMO at lower pH than the PZC of the BMO (7.6) and result an increase of removal of anionic dye species. However, a decrease of IC removal is found in Fig. 3 may be attributed to the decrease in IC dissociation which leads to a lower concentration of the anionic dye species available to interact with the BMO's active sites [15]. Above the PZC, the increase in negatively charged sites of the BMO does not favour the adsorption of anionic dye due to electrostatic repulsion. So the removal amount decreases.

Effect of the BMO amount on IC removal

The effect of the BMO amount on IC removal is shown in Fig. 4. It can be seen that the IC removal efficiency increased when the BMO amount is from 0.5 g L^{-1} to 2 g L^{-1} and the removal efficiency remained almost constant when it is the BMO amount higher than 2 g L^{-1}. Optimum BMO amount is found to be 2 g L^{-1}. This result is similar with the reference [10]. An increase in the IC removal with the BMO amount appeared to be attributed to large surface area and the availability of more adsorption sites. However, further increase in the BMO amount does not affect the uptake capacity due to unavailability of IC.
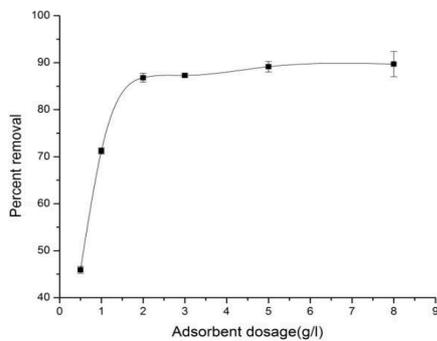

Fig.4. Effect of the BMO amount on IC removal (20 mg L^{-1} IC, 28℃, 150 rpm, 48 h)
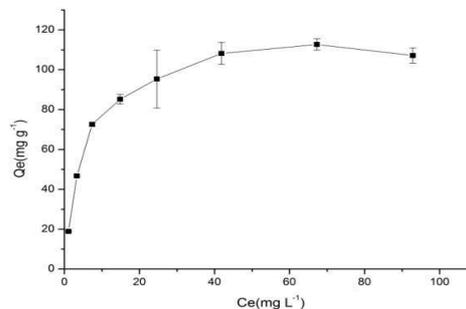
Fig. 5. The isotherms of IC on the BMO (25 ℃, 150 rpm, 144 h)

Effect of the IC concentrations on IC removal

The IC equilibrium adsorption by the BMO is shown in Fig. 5. The adsorption data were analyzed by Langmuir and Freundlich isotherms, two widely used models. The Langmuir isotherm applies to the adsorption on homogenous surfaces and is based on the assumption that maximum adsorption corresponds to a monolayer coverage on the adsorbent surface. The Langmuir equation is given by:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_{max}} + \frac{1}{KQ_{max}} \tag{3}$$

where Q_e is the adsorbed IC amount per mass of adsorbent (mg g^{-1}), Q_{max} is monolayer saturation at equilibrium (mg g^{-1}), C_e is equilibrium concentration (mg L^{-1}) and K indicates the affinity of IC to bind with the adsorbents. The isotherm constant K and monolayer capacity Q_{max} are shown in Table 2. The R^2 of 0.997 (Table 2) support the assumption that the adsorption date follows the Langmuir model. It is seen that the maximum adsorption of IC onto the BMO is 115.61 mg g^{-1}. This adsorption capacity of the BMO for IC is higher than 1.09 mg g^{-1} for Brazil nut shells at room temperature [7], 71.48 mg g^{-1} of chitosan [16] and 29.28 mg g^{-1} of rice husk ash [10].

Table 2 Langmuir and Freundlich isotherm parameters

Langmuir			Freundlich		
Q_{max}[mg g^{-1}]	K[L mg^{-1}]	R^2	K_F [L mg^{-1}]	n	R^2
115.61	0.2142	0.997	0.3058	2.7084	0.844

The Freundlich isotherm is an empirical equation widely employed to describe solid-liquid adsorption, encompassing the surface heterogeneity. The mathematical expression for the Freundlich isotherm is written as:

$$\ln Q_e = \frac{1}{K_F} + \frac{1}{n}\ln C_e \tag{4}$$

where Q_e is the adsorbed IC amount per mass of adsorbent (mg g^{-1}), C_e is equilibrium concentration (mg L^{-1}), K_F is the Freundlich constant and $1/n$ indicates the intensity of the adsorption. The values of K_F, n and R^2 are shown in table 2. The R^2 of 0.997 in the Freundlich isotherm is higher than the R^2 (0.844) in the Langmuir isotherm (Table 2). Therefore, the Langmuir equation is more appropriate model for these data.

Conclusion

The BMO prepared by culturing *Marinobacter* sp. MnI7-9 can be successfully used for the IC removal from solution. The IC removal effect is related with reaction time, pH of IC solution, the BMO amount and IC concentration. The removal reaction equilibrium time is about 60 h. The adsorption kinetics of lower concentration IC (5 mg L^{-1}) on the BMO fitted the pseudo-first order model, while the adsorption kinetics of higher concentration IC (20 mg L^{-1}) fit the pseudo-second order model. The intra-particle diffusion is an important rate-controlling step. A larger IC removal amount can be gotten when the BMO amount is 2 g L^{-1} at pH 6.5. The equilibrium adsorption data fit well in the Langmuir isotherm equation. The maximal adsorption capacity is 115.61 mg g^{-1} at 25℃. This study concludes that the BMO could be applied as an efficient material for the IC removal from aqueous solution.

References

[1] M.S. Li, Y.P. Luo and Z.Y. Su: Environ. Pollut. Vol.147 (2007), p.168

[2] W. Wang, Z. Shao, Y. Liu and G. Wang: Microbiology Vol.155(2009) , p.1989

[3] S. Liao, J. Zhou, H. Wang, X. Chen, H. Wang and G. Wang: Geomicrobiol J. Vol.30 (2013), p.150

[4] F. Meerburg, T. Hennebel, L. Vanhaecke, W. Verstraete and N. Boon: Microb. Biotechnol. Vol. 5(3) (2012), p. 388

[5] S. Liao, L. Ren, D. Zhu, W. Zhou, J. Cui and G. Liu: Commun. Soil. Sci. Plan. Vol.42(7) (2011), p. 768

[6] V.K. Gupta, R. Jain, S. Malathi and A. Nayak: J. Colloid Interface Sci. Vol. 348 (2010), p. 628

[7] S.M. de Oliveira Brito, H.M.C. Andrade, L.F. Soares and R.P. de Azevedo: J. Hazard. Mater. Vol. 174 (2010), p. *84*

[8] Y.S. Ho and C.C. Chiang: Adsorption. Vol. 7 (2001), p. 139

[9] Y.S. Ho and G. McKay: Process Safe. Environ. Protect. Vol.76B (1998), p. 183

[10] R. Uma, C. Vimal, D. Indra and H.Dilip: J. Environ Manage. Vol. 90 (2009), p. 710

[11] N. Kannan and M.M. Sundaram: Dyes Pigments. Vol.51 (2001), p. 25

[12] K.G. Bhattacharyya and A. Sharma: Dyes Pigments. Vol. 65(2005), p. 51

[13] M. Dogan, H. Abak and M. Alkan: J. Hazard. Mater. Vol.164 (2009), p. 172

[14] A. Ozcan, E. M. Oncu and A. S. Ozcan: Colloid Surface A. Vol.277 (2006), p. 90

[15] L. Zhou, J. Jin, Z. Liu, X. Liang and C. Shang: J. Hazard Mater. Vol.185 (2011) , p.1045–1052

[16] A.G. S. Prado, J. D. Torres, E. A. Faria and S. C. L. Dias: J. Colloid Interface Sci. Vol. 277 (2004), p. 43

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10.4028/www.scientific.net/AMR.864-867.1779

DOI References

[1] M.S. Li, Y.P. Luo and Z.Y. Su: Environ. Pollut. Vol. 147 (2007), p.168.

http://dx.doi.org/10.1016/j.envpol.2006.08.006

[3] S. Liao, J. Zhou, H. Wang, X. Chen, H. Wang and G. Wang: Geomicrobiol J. Vol. 30 (2013), p.150.

http://dx.doi.org/10.1080/01490451.2011.654379

[4] F. Meerburg, T. Hennebel, L. Vanhaecke, W. Verstraete and N. Boon: Microb. Biotechnol. Vol. 5(3) (2012), p.388.

http://dx.doi.org/10.1111/j.1751-7915.2011.00323.x

[5] S. Liao, L. Ren, D. Zhu, W. Zhou, J. Cui and G. Liu: Commun. Soil. Sci. Plan. Vol. 42(7) (2011), p.768.

http://dx.doi.org/10.1080/00103624.2011.552662

[6] V.K. Gupta, R. Jain, S. Malathi and A. Nayak: J. Colloid Interface Sci. Vol. 348 (2010), p.628.

http://dx.doi.org/10.1016/j.jcis.2010.04.085

[7] S.M. de Oliveira Brito, H.M.C. Andrade, L.F. Soares and R.P. de Azevedo: J. Hazard. Mater. Vol. 174 (2010), p.84.

http://dx.doi.org/10.1016/j.jhazmat.2009.09.020

[8] Y.S. Ho and C.C. Chiang: Adsorption. Vol. 7 (2001), p.139.

http://dx.doi.org/10.1023/A:1011652224816

[9] Y.S. Ho and G. McKay: Process Safe. Environ. Protect. Vol. 76B (1998), p.183.

http://dx.doi.org/10.1205/095758298529326

[10] R. Uma, C. Vimal, D. Indra and H. Dilip: J. Environ Manage. Vol. 90 (2009), p.710.

http://dx.doi.org/10.1016/j.jenvman.2008.01.002

[11] N. Kannan and M.M. Sundaram: Dyes Pigments. Vol. 51 (2001), p.25.

http://dx.doi.org/10.1016/S0143-7208(01)00056-0

[12] K.G. Bhattacharyya and A. Sharma: Dyes Pigments. Vol. 65(2005), p.51.

http://dx.doi.org/10.1016/j.dyepig.2004.06.016

[13] M. Dogan, H. Abak and M. Alkan: J. Hazard. Mater. Vol. 164 (2009), p.172.

http://dx.doi.org/10.1016/j.jhazmat.2008.07.155

[14] A. Ozcan, E. M. Oncu and A. S. Ozcan: Colloid Surface A. Vol. 277 (2006), p.90.

http://dx.doi.org/10.1016/j.colsurfa.2005.11.017

[16] A.G. S. Prado, J. D. Torres, E. A. Faria and S. C. L. Dias: J. Colloid Interface Sci. Vol. 277 (2004), p.43.

http://dx.doi.org/10.1016/j.jcis.2004.04.056