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***Quercus robur* acorn peel as a novel coagulating adsorbent for cationic dye removal from aquatic ecosystems**

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Graphical abstract

MB - Methylene blue; AO - Acridine orange; MG - Malachite green; WS1 - Lake water; WS2 - Sea water

Highlights

- Oak acorn peel (OP) effectively removed cationic dyes by biosorption
- Dye removal by OP was not influenced by temperature
- Pseudo-second-order kinetic, Langmuir and Freundlich isotherm models were fitted
- Mechanism of dye removal was by coagulation-coupled adsorption process
- OP rapidly removed the dyes from artificially spiked wastewater

Abstract

Oak acorn peel (OP) was used in natural form for the removal of cationic dyes, methylene blue (MB), acridine orange (AO) and malachite green (MG) from aqueous solutions. OP removed 60-97% of 600 mg L⁻¹ dyes at wide ranging pH (2-10). Adsorption equilibria were attained within 3 h. Sorbent (5 g L⁻¹) adsorption capacity was 109.43, 115.92 and 111.85 mg g⁻¹ for MB, AO and MG, respectively. Adsorption kinetics was described using pseudo-second-order model. Equilibrium adsorption data were interpreted by Langmuir and Freundlich isotherms. Dye removal was by coagulation-coupled adsorption. Coagulation was due to the formation of complexes between the dye molecules and OP polyphenols that led to the deposition of precipitated flocs.

Keywords: Biosorption; Coagulation; Oak acorn peel; Cationic dyes; Wastewater treatment

1. Introduction

Worldwide production and extensive use of dyes in industries of textile, tannery, food, paper, printing, carpet and mineral processing generate colored wastewaters (Gong et al., 2007). It is estimated that nearly 10,000 different types of dyes are produced globally per annum, of which 1-15% of the dyes are lost in the effluents during dyeing process from textile industries representing a serious problem all over the world (Barka et al., 2011). Being mutagenic and carcinogenic, most of the dyes are highly toxic to the aquatic biota. The presence of visible colored substances in natural streams that are perceptible even at a concentration as low as 1.0 mg L⁻¹ make the water undesirable for human consumption (Hamdaoui et al., 2008). In health point of view, allergy and skin irritation are caused by dyes (Royer et al., 2009). Therefore, industrial effluents containing dyes need to be treated before being released into the environment. Multiple technologies are employed to achieve

the regulatory standard for treated dye water discharge such as sorption, coagulation/flocculation, chemical oxidation, membrane separation, electrochemical, aerobic and anaerobic microbial degradation. Among all the methods, biosorption is highly preferred due to its cost-effectiveness (Kuppusamy et al., 2016a,b). Also, during biosorption, the dye species in water effluents are transformed to a solid phase diminishing the effluent volume to a minimum. Subsequently, the adsorbent can be regenerated or kept in a dry place without direct contact with the environment (Pavan et al., 2014). Many researchers demonstrated the feasibility of using low-cost and easily available adsorbents such as tomato peel (Mallampati and Valiyaveetil 2012), peanut hull (Gong et al., 2005), almond shell (Duran et al., 2011) and many other agro-industrial and municipal waste materials (Bhatnagar and Sillanpaa 2010) for the removal of dyes and various pollutants from water. Still the continuous search exists for alternative new, cost-effective and efficient biosorbents with unique traits that are abundantly available locally (Kuppusamy et al., 2016c,d,e) for cationic dye removal.

Extensive research has been done using oak acorn (Saka et al., 2012; Kuppusamy et al., 2016d). Often, the damaged oak acorns are considered as trash. The peel of the disposed oak acorns could be explored for its potential use, particularly as sorbents, for pollutant removal. We employed oak acorn peel (OP) for the first time in an effort to find its novel biosorbing property for removal of cationic dyes. Methylene blue (MB, $C_{16}H_{18}N_3SCl$), acridine orange (AO, $C_{17}H_{19}N_3$) and malachite green (MG, $C_{23}H_{25}ClN_2$), the most problematic cationic dyes in wastewaters and effluents often used as model compounds, were chosen in the present study. The OP used in this study was not subjected to any chemical modification. Biosorption studies were carried out under various parameters such as pH, temperature, adsorbent dosage, contact time and initial dye concentration. Kinetic data and sorption equilibrium isotherms obtained in batch process were analyzed using different models. The mechanism of decolorization mediated by OP has been established.

2. Materials and Methods

2.1. Preparation of adsorbent

Acorns, fallen off from oak (*Quercus robur*) trees, were collected from the Adelaide Botanical garden, South Australia during April 2012, washed with Milli-Q water ($18 \Omega \text{ cm}^{-1}$, Milli-Q, ELGA labwater, UK) to remove the adhering soil particles, and air-dried for 3 days. Peels were collected, powdered, passed through a sieve (0.5 mm), and stored in a desiccator with polythene sealing for use in experiments as needed. Characteristics of OP is given in Kuppusamy et al. (2016d) study.

2.2. Adsorbates

Analytical grade MB, AO and MG (Table 1) were purchased from Sigma Aldrich. Required concentrations of the dyes were obtained by appropriate dilution of the stock solutions prepared in MQ water. NaOH (0.1 mol L^{-1}) and HCl (0.1 mol L^{-1}) were used to adjust the pH.

2.3. Biosorption study

Batch biosorption experiments were carried out in a set of centrifuge tubes containing 20 mL of dye solution to investigate the effects of initial pH (2-10), contact time (0-550 min), biosorbent dosage ($1.25\text{-}5.0 \text{ g L}^{-1}$), initial dye concentration ($100\text{-}900 \text{ mg L}^{-1}$), and temperature (24 and 37 °C) in order to determine the optimum conditions. After incubation, samples were centrifuged and absorbance of the residual dye concentration was recorded (at 663 nm for MB, 490 nm for AO and 617 nm for MG) using SynergyTM HT Multi-Detection Microplate Reader (Bio-Tek^R Instruments, Inc., Vermont, USA). Biosorption kinetics was investigated using 600 mg L^{-1} initial dye concentration, 5 g L^{-1} biosorbent dose and at

solution pH of 7.0. Biosorption isotherms were examined by adding 5 g L⁻¹ adsorbent with dye solution at various initial concentrations (0-1000 mg L⁻¹) and pH 7.0. The dye removal efficiency is defined as:

$$\text{Removal (\%)} = \frac{C_o - C_e}{C_o} \times 100 \quad (1)$$

where, C_o and C_e (mg L⁻¹) are the initial and equilibrium dye concentrations. Also, the amount of dye adsorbed per unit mass of OP can be calculated using the following equation:

$$q_e (\text{mg g}^{-1}) = \frac{C_o - C_e}{M} \times V \quad (2)$$

where, q_e (mg g⁻¹) is the dye adsorption capacity, V (L) is the volume of the dye solution and M (g) is the mass of the adsorbent used.

2.4. Kinetic and equilibrium studies

Kinetic behaviour of adsorption in which chemical sorption is the rate limiting factor is more suitably described using pseudo-second-order model, and is defined as:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

where, K₂ (g mg⁻¹ min⁻¹) is the pseudo-second-order kinetic rate constant. Values of K₂ and q_e were calculated from the intercept and slope of plot t/q_t vs t .

The Langmuir isotherm model is applicable to monolayer adsorptions and is given by the relation:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad (4)$$

where, C_e (mg L⁻¹) is the equilibrium dye concentration and q_e (mg g⁻¹) is the amount of dye adsorbed at equilibrium. Also, q_m (mg g⁻¹) is the maximum dye adsorption capacity by the biomaterial and K_L (L g⁻¹) is the Langmuir adsorption constant related to the free energy of adsorption which are obtained from the slope and intercept of plot C_e vs C_e/q_e .

The Freundlich isotherm model proposes a monolayer sorption with heterogeneous energetic distribution of active sites accompanied by interaction between adsorbed molecules. The Freundlich expression can be written as:

$$\log q_e = \log K_f + \left(\frac{1}{n}\right) \log C_e \quad (5)$$

where, K_f ($\text{mg}^{1-1/n} \text{L}^{1/n} \text{g}^{-1}$) and n are the Freundlich adsorption constant and heterogeneity factor, respectively.

2.5. Coagulation study

In the present study, deposition of precipitated dye flocs coupled with adsorption was observed. Hence, a separate experiment was conducted to determine the potential of OP extract as a natural coagulant for dye removal. About 0.1 g biosorbent was mixed with 20 mL boiled water and kept overnight under shaking (120 rpm at 24 °C). Subsequently, the suspension was filtered (using 0.4 μm filter) and used within a day. Decolorization and coagulation of MB, AO and MG (600 mg L^{-1}) in OP water extract (20 mL) was monitored at different incubation times and compared with that of the control samples (boiled water containing only dye) through spectrophotometric scanning of the reaction mixtures at its maximum absorbance (λ_{max}). The extent of decolorization (%) was calculated (same as equation 1) and values given are the means of triplicates.

3. Results and discussion

3.1. Effect of acidity and contact time on dye removal

The effect of solution pH on adsorption capacity of MB, AO and MG on OP was investigated at initial pH values ranging from 2-10, and the results are shown in Fig. 1. Cationic dye removal was at least 60% at far acidic condition (pH 2) and was as high as 97% in rear alkaline (pH 10) medium. It is important to point out that, most of the studies reported

in the literature (Royer et al., 2009; Barka et al., 2011; Pavan et al., 2014) indicated that biosorption of cationic dyes was very weak ($< 20\%$ removal) or not present at acidic medium (pH 2-5). However, OP used in this study is much superior over the reported biosorbents owing to its fairly high cationic dye removal ($>60\%$) under wide ranging pH conditions (pH 2-10). This could be attributed to its negative surface charge. The best pH range for adsorption of cationic dyes on OP was from 7 to 10. The higher amount of cationic dye adsorption by OP at pH values at and/or above 7 can be explained, considering the electrostatic interactions between the surface charge of the adsorbent which was negative at pH 7 (-6.02 mV) and 10 (-9.99 mV) for the positively charged dyes. It should be stressed that the rate of removal significantly varied among the three dyes. The variation in per cent removal of MB (64-93%) and MG (78-90%) was lower compared to that of AO (91-97%) for pH values ranging from 2 to 10 (Fig. 1a, b and c). This implies the influence of structural complexity of the dye molecule over the sorption capacity of biomaterial, and also indicates that the selected biosorbent exhibits different rates of adsorption of the cationic dye species.

To evaluate the effect of contact time between dyes and biosorbent, the agitation time was extended up to 540 min (Fig. 1). Adsorption of dyes was found rapid during initial stages of the sorption process (within 30 min), and was followed by a gradual progression and achieved equilibrium within 180 min. This observation is expected because the dye molecule first encounters the boundary layer effect, then gets adsorbed from the surface, and finally diffuses into the porous structure of the adsorbent; the whole process takes longer time (Sreelatha et al., 2010).

3.2. Effect of adsorbent dosage on dye removal at varying temperatures

Data obtained from the experiments conducted at 24 and 37 °C with varying concentrations of OP showed a sharp escalation in the biosorption yield with increase in

biosorbent dosage (Fig. 2). When the biosorbent dosage was increased from 1.25 to 5 g L⁻¹, the biosorption capacity increased from 50 to 115 mg g⁻¹ for MB, 68 to 119 mg g⁻¹ for AO and 58 to 114 mg g⁻¹ for MG. The observed biosorption yield with enhanced sorbent dose can be attributed to the larger availability of surface area and increase in the number of active sites for adsorption of the same number of dye molecules (Royer et al., 2009; Sreelatha et al., 2010; Pavan et al., 2014). A further increase in biosorbent concentration above 5 g L⁻¹ did not significantly improve the sorption capacity (data not shown).

3.3. Determination of kinetic parameters

Pseudo-second-order kinetic model was found to be more suitable with a regression value close ($R^2 = 0.99$ for MB and MG) and equal to unity ($R^2 = 1$ for AO) (see Table 1, data of pseudo-first-order model is not shown as its regression co-efficient was far away from unity and did not fit to the current data). Data presented in Table 1 show that the calculated $q_{e, \text{pred.}}$ values of pseudo-second-order model is in good agreement with the experimental values $q_{e, \text{exp.}}$. Attainment of faster adsorption equilibrium by OP is shown by the calculated pseudo-second-order rate constant (K_2) which is higher for AO (0.026 g mg⁻¹ min⁻¹) followed by MG (0.0036 g mg⁻¹ min⁻¹) and MB (0.0014 g mg⁻¹ min⁻¹). Thus, the best fitness of the pseudo-second-order model shows that the biosorption of cationic dyes onto OP was most likely controlled by chemisorption (Ncibi et al., 2007).

3.4. Determination of equilibrium parameters

The values of the coefficient of determination ($R^2 = 0.99$ or 1) indicate that there is a strong positive evidence that the sorption of dyes by OP follows both the Langmuir and Freundlich isotherms. The applicability of both Langmuir and Freundlich isotherms to the studied system implies that both monolayer sorption and heterogeneous surface conditions

exist under the used experimental conditions as reported by Hamdaoui et al. (2008) for MG sorption by dead leaves of plane (*Platanus vulgaris*) tree. The Freundlich constants K_f ($\text{mg}^{1-1/n} \text{L}^{1/n} \text{g}^{-1}$) and n (g L^{-1}) were 94.73 and 25.32, 100.02 and 20.66, and 95.48 and 31.75 for MB, AO and MG, respectively. Furthermore, cationic dyes were favourably sorbed by OP due to n value obtained from Freundlich isotherm which was higher than 2 (Hamdaoui et al., 2008). From the Langmuir model, the maximum monolayer pollutant adsorption (q_m) values at 24 °C and pH 7 were 120.48, 131.58 and 116.28 mg g^{-1} for MB, AO and MG, respectively. The Langmuir constant K_L for MB, AO and MG was 2.71, 1.34 and 5.66 L g^{-1} , respectively. The q_m value for OP obtained in our study is comparable with that of *Salvadora persica* stems ash (22.78 mg g^{-1} for MB) (Bazrafshan et al., 2012), apricot waste-based activated carbon (102.04 and 116.27 mg g^{-1} for MB and MG, respectively) (Basar, 2006), *Parthenium hysterophorus* (88.49 mg g^{-1} for MB) (Lata et al., 2007), groundnut shell waste-based activated carbon (222.22 mg g^{-1} for MG) (Malik et al., 2007), magnetically-modified sawdust (24.1 mg g^{-1} for AO) (Safarik et al., 2005), *Opuntia ficus indica* cladodes (200.22 for MB) and *Scolymus hispanicus* L (263.92 mg g^{-1} for MB) (Barka et al., 2011).

3.5. Mechanism of dye removal – Coagulation-coupled adsorption

In the adsorption experiments, we witnessed the deposition of precipitated dye flocs coupled with the sorption of dyes by the biosorbent material. This might be because of the bridging and charge neutralization by affinity between the cationic dye molecules and some of the non-soluble negatively charged species which are released by the biosorbent material into the aqueous phase that acts as natural coagulants (Yan et al., 2008). Hence, we tested OP extract for its ability to induce fast decolorization and gradual flocculation of MB, AO and MG removal.

3.5.1. OP water extract as a natural coagulant

The per cent decolorization of reaction mixtures over time, as shown in Fig. 3, revealed the fast removal of dye colors, indicating the formation of soluble dye-coagulant complexes. The slope difference for the extent of dye decolorization and formation of insoluble flocs gradually increased with time and reached equilibrium within 180 min, resulting in 82, 86 and 66% decolorization of MB, AO and MG, respectively. This suggests that OP extract can induce coagulation and flocculation of cationic dyes by means of an initial supramolecular interaction between the dye particle and the extract.

Coupled with adsorption, yet another method for decolorization and removal of dyes is coagulation whereby soluble organic dyes can be separated from a dissolved state by the formation of flocs with coagulants. To date, very few evaluations of natural materials as organic coagulants for removal of cationic dyes have been reported (Jeon et al., 2009). As of utmost significance, along with adsorption, our selected material formed coagulated flocs and contributed to the decolorization of dye. The negatively charged or dipole containing natural polyphenols particularly tannins in OP would interact with the soluble cationic dyes (MB, AO and MG) via ion-ion and ion-dipole forces (Leopoldini et al., 2006) resulting in an initial fast colorization. Complex formation following the initial supramolecular interaction might neutralize the cationic dyes and finally would result in the development of colloidal flocs. Preformed colloidal flocs could act as bridging adsorbents for floc growth. Such growth with enmeshment of other soluble molecules might induce the final precipitation and deposition of the cationic-polyphenol complex. Thus, three different complex states, namely initial supramolecular interaction, colloidal floc and precipitate floc might be formed by natural polyphenols with the cationic dye molecules as briefed by Jeon et al. (2009).

4. Conclusions

This study being the preliminary confirmation of the potential of OP extract to act as a natural coagulant for cationic dye removal, further investigation, particularly the examination of precipitated flocs by GC-MS and identification of the specific hydroxyl-phenyl group that is reasonable for the coagulation factor will be necessary to permit a full understanding of the coagulation mechanism involving OP derived polyphenols in cationic dye removal. Thus, the mechanism of dye removal is a combined coagulation and adsorption onto OP. Adsorption is contributed by the surface charge of the biomaterial and coagulation is attributed by the release of some of the anionic functional groups particularly natural polyphenols (-OH group), which together enhance the dye removal process. The excellent option of coupled coagulation-adsorption mechanism by a biosorbent is not noticed extensively, and thus the results of this study are important emphasising deliberative wider use of OP on commercial basis. It is of particular interest that for the first time we explored the use of OP water extract as a natural organic coagulant for removal of toxic cationic dyes.

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Figure 1. Effect of pH and contact time on removal of (a) MB, (b) AO, and (c) MG by OP (Sorbent dose, 5 g L⁻¹; temperature, 24 °C; pH, 7.0; initial dye concentration, 600 mg L⁻¹).

Figure 2. Effect of adsorbent dosage on dye removal at (a) 24 and (b) 37 °C (pH, 7.0; initial dye concentration, 600 mg L⁻¹; incubation time, 3 h).

Figure 3. Decolorization and coagulation of (a) MB, (b) AO and (c) MG (600 mg L⁻¹ each) induced by OP water extract. Photographs were taken 'a' at the start and 'b' after 48 h incubation at 24 °C of the decolorized and coagulated extract.

Table 1. Pseudo-second-order, Langmuir and Freundlich isotherm model constants for dye removal

Constant	MB	AO	MG
Pseudo-second order kinetic model			
$q_{e, \text{exp}} (\text{mg g}^{-1})$	109.43	115.92	111.85
$K_2 (\text{gmg}^{-1} \text{min}^{-1})$	0.0014	0.026	0.0036
$q_{e, \text{pred}} (\text{mg g}^{-1})$	111.11	116.28	112.36
R^2	0.99	1	0.99
Langmuir isotherm			
$q_m (\text{mg g}^{-1})$	120.48	131.58	116.28
$K_L (\text{L g}^{-1})$	2.71	1.34	5.66
R^2	0.99	0.99	0.99
Freundlich isotherm			
$K_f (\text{Lg}^{-1})$	94.73	100.02	95.48
n	25.32	20.66	31.75
R^2	0.99	0.99	0.99