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Article

Biocatalyst immobilized graphene oxide for effluent treatment: Sustainability, efficiency and cost effectiveness

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ABSTRACT

Increasing scarcity of potable water resources on a global scale has been recorded in recent times. This has made laws concerning water usage more stringent. These laws have made it imperative to develop novel, efficient, affordable and less time-consuming processes for effluent treatment and subsequent reuse. In the previous decades, processes like chemical oxidation, solvent extraction, coagulation, catalytic degradation, adsorption, biodegradation (aerobic, anaerobic and electrochemical) and membrane-based separation have been widely investigated for decontamination and reclamation of polluted wastewaters. However, most of these processes are unsuitable on their own for wide-scale application due to their huge operational cost, quantity of sludge produced and time consumed for efficient effluent treatment. Thus, contemporary investigations have reported integrated application of different wastewater treatment processes for efficient treatment of effluents bearing a mixture of emerging pollutants. The present study provides a comparative analysis of different integrated processes of wastewater reclamation in terms of their efficiency and cost effectiveness for identification of processes acceptable for sustainable commercial-scale applications. This study reports an integrated biodegradation- adsorption approach for achieving efficient removal of Metanil yellow with reduced treatment time and disposal hazards. In this study, graphene oxide was investigated as a support material for bacterial strain, *Dietzia sp*. Immobilized microorganisms were found to be more advantageous in comparison to the conventional suspension system as they offered a higher dye removal efficiency, increased biomass, enhanced degradation and strengthened resistance to hazardous pollutants. Besides, the proposed process is highly cost effective with efficient reusability potential. The experimental parameters were optimized using Central Composite Design of Response Surface Methodology. Results proved the efficiency and cost effectiveness of the integrated adsorption and biodegradation approach in removal of azo dyes indicating the possibility of its application for real time effluent treatments.

INTRODUCTION

In comparison to other effluents, textile effluent is considered as one of primary concern owing to it's toxic nature and volume of production (Banerjee et al. 2015). The industries that process and manufacture textiles use a staggering amount of water and produce an equally concerning amount of dye-rich effluents. Textile processing and manufacturing industries consume an enormous volume of water and result in generation of an equally alarming quantity of dye-rich effluents. Besides bearing different dissolved and suspended dyes and pigments, the extreme acidic or alkaline pH of these effluents also pose a strong concern. Every year, almost 7×10^5 t of different dyes and pigments are produced commercially (Gupta and Suhas 2009). Several of these enter natural water bodies through the untreated effluents discharged into the same and exert toxic impact on neighboring life (Khan et al. 2013).

The main objective of this study included remediation of azo dye bearing effluents with biocomposite prepared from immobilization of *Dietzia* sp. on graphene oxide (GO) nanosheets. The novelty aspect of this study is the simultaneous application of two processes (namely, biodegradation and adsorption) widely reported for treatment of dye-rich effluents. Both processes have respective limitations. Biodegradation based processes require a lot of time for complete disintegration of dyes present in effluents. On the other hand, application of adsorption often poses questions regarding the fate of the pollutants retrieved from the effluents. Simultaneous application of these two processes were found to overcome limitations of each process with higher performance efficiency. Similar results have been documented in earlier works as well (Banerjee et al., 2018; Roy et al., 2018).

The process of remediation reported herein was improved using response surface methodology (RSM). The best fit of the tested RSM models to experimental data was determined with analysis of variance (ANOVA). 99.88% removal of dye was recorded with the method reported herein.

METHODOLOGY

Materials and instruments

Metanil yellow (MY; $C_{16}H_{18}ClN_3S$; λ_{max} = 630 nm) and other reagents (analytical grade) were used as commercially procured. MY stock solutions (120 mg L^{-1}) were prepared with distilled water and diluted with distilled water (as required) to prepare working solutions of desired strength. The pH of the solution was altered using 0.1N HCl or 0.1M NaOH as per requirement. All experiments were conducted with Erlenmeyer flasks of 250 mL capacity. For the purpose of determining the remaining dye concentration in solution, samples were taken out of the flasks at prearranged time interval. Residual dye in solution was determined spectrophotometrically using a quartz cuvette (optical path = 1 cm).

Culture conditions of selected bacterial strain

Isolation and culture conditions of *Dietzia* sp. used herein has been reported previously by Das et al. (2016). Cultures were maintained in nutrient agar slants with a subculture every second month.

Preparation of bacteria immobilized GO

GO was prepared via Hummer's method with slight modifications as reported by Banerjee et al. (2015). *Dietzia* sp. immobilization on GO was carried out via 'adsorption- incubation' method (Banerjee et al. 2018).

Process optimization

MY remediation by GO-biocomposite was optimised using central composite design (CCD) feature of RSM, a mixed mathematical and statistical tool for modelling and optimization. In this study, a four factor (initial MY concentration, solution pH, temperature and GO-biocomposite dosage) model having three levels was developed using Design Expert (Version 7.0 Minneapolis, USA). The spectrum of the chosen experimental criteria along with their respective units have been illustrated in **Table 1**.

CALCULATIONS

Determination of residual dye concentrations

MY removal (%) was determined using the equation given as follows:

$$\text{Removal (\%)} = \frac{(C_i - C_e)V}{C_i} \text{X } 100$$

Whereby, C_i and C_e denote initial and equilibrium dye concentrations (mg L^{-1}) respectively. V (L) indicated the volume of test solution.

Process optimization

Process optimization was carried out on the basis of 50 experiments recommended by the RSM design matrix. Results obtained from RSM based process optimization suggested that the four independent variables selected for this study was guided by the quadratic polynomial equation given as follows:

$$Y = m_0 + \sum_{i=1}^{k=5} m_i x_i + \sum_{i=1}^{k=5}\sum_{j=1}^{k=5} m_{ij} x_i x_j + \sum_{i=1}^{k=5} m_{ii} x_i^2 + E$$

Where, Y = response (% MY removal), m_0 = constant coefficient, m_a (a = i, j, ij) = regression coefficients (of linear, quadratic and interaction correspondingly), x_b (b = i,j) = experimental parameters (independent variables) and E = error.

Statistical analysis

To lower handling error, every experimental technique

was carried out three times. All results were expressed as Mean ± SD. Statistical analysis of data for process optimization was also carried out using Design Expert.

RESULTS AND DISCUSSION

RSM based optimization

Results obtained for RSM analysis in terms of predicted and experimental %MY removal have been shown in **figure 1**. A large F-value (670.21) indicated that the quadratic model best fitted ($p < 0.0001$) the data obtained herein with only a 0.01% chance of this F-value occurring due to noise. This high F-value also indicated that each term included in the quadratic polynomial equation was significant at 95% level of confidence. The values of regression coefficient (R^2), adjusted R^2 and predicted R^2 were found to be 0.996, 0.994 and 0.990 respectively. Good accordance between these values also indicated best fit of the quadratic polynomial model to the data obtained herein.

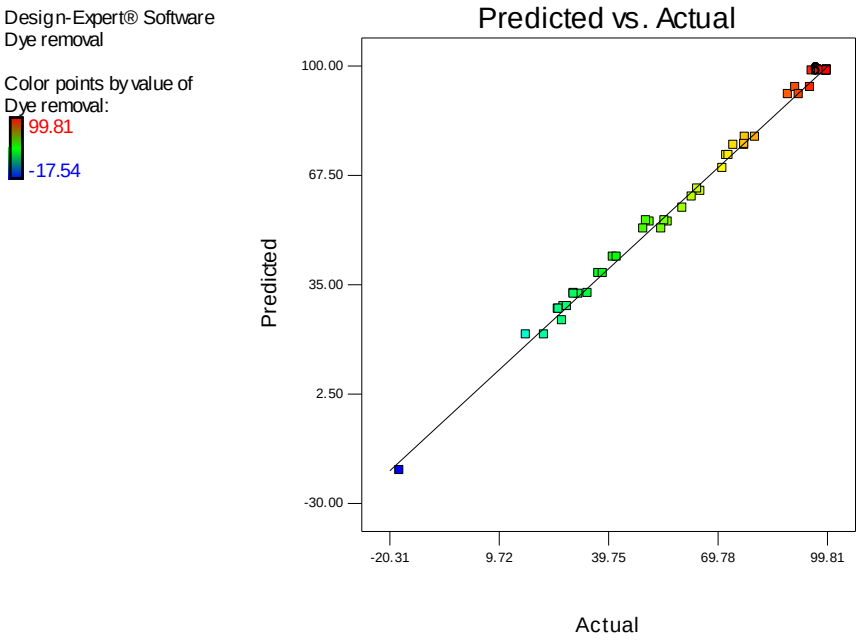

Figure 1. Predicted vs. experimental removal of MY as calculated from RSM analysis

Moreover, an A_{deq} Precision value as high as 101.14 indicated that the selected model guided the predicted % dye elimination in a semi-empirical equation given as follows:

% Dye Removal = -359.13314 +0.83874 * Initial dye conc. +25.68364 * pH +11.63334 * Temperature +167.54033 * Composite dose +0.035562 * Initial dye conc. * pH +2.21985E-003 * Initial dye conc. * Temperature -0.20895 * Initial dye conc. * Composite dose +0.14839 * pH * Temperature +9.18070* pH * Composite dose -1.95950 * Temperature * Composite dose -5.53964E-003 * Initial dye conc.^{2} -2.21383 * pH^2 -0.15089 * Temperature^2 -85.02719 * Composite dose^2

Figure 1 showed negligible (0.20%) deviation between %MY removal predicted theoretically and obtained experimentally. RSM analysis suggested an initial MY concentration of 124.34 mg L^{-1}, effluent pH of 8.96, adsorbent dosage of 0.70 g L^{-1} and temperature of 39 °C as optimum conditions for MY removal by GO biocomposite. A maximum MY removal of 99.88% was obtained under these optimized conditions. Inter-parameter interactions observed in this study has been described below.

Table 1: Experimental details of RSM optimization of Metanil Yellow removal by GO-biocomposite

Factors	Units	Levels			Star point α = 1.68	
		Low (-1)	Central (0)	High (+1)	-α	+α
A: Initial dye concentration	mg L^{-1}	56.87	90.345	123.82	10.64	170.65
B: Solution pH		4.78	8.03	11.28	0.54	14.64
C: Temperature	K	25.00	32.50	40.00	14.28	51.23
D: Biocomposite dosage	g L^{-1}	0.63	0.89	1.15	0.27	1.52

Effect of varying initial MY concentration and solution pH

% MY removal increased with a parallel increase in pH and initial MY concentration in solution. However, extreme basic pH conditions (10-12) resulted in lower dye removal for initial dye concentrations ranging between 35-60 mg L^{-1}. This decrease in dye removal rates under alkaline conditions could have had occurred due to deprotonation of dyes under the said condition and/or exhaustion of all available uptake sites of the GO biocomposite (Khan et al. 2013).

Effect of varying initial MY concentration and GO biocomposite dose

A increase in % MY elimination with a simultaneous rise in biocomposite dosage may have had occurred due to an expansion in composite surface area which in turn provided more active sites for MY uptake (Khan et al. 2013; Banerjee et al. 2015). However, % MY removal did not increase further with greater biocomposite dosage. Exhaustion of active uptake sites of biocomposite due to aggregation may be held responsible for stagnancy of dye uptake at higher biocomposite dosage (Banerjee et al. 2015).

Effect of varying temperature and initial MY concentration

A significant increase in % MY uptake was recorded with a corresponding rise in both temperature and initial MY concentration. Increase in temperature may cause an increase in porosity and total pore volume of biocomposite moieties in turn facilitating a faster rate of MY diffusion over both exterior and interior pores of biocomposite. Similar results were reported earlier by (Nguyen et al. 2009).

Effect of varying biocomposite dose and solution pH

Higher adsorbent surface area may be the cause of the increase in MY removal percentage that coincides with a rise in biocomposite dosage and solution pH (up to pH 8). A further decrease in %MY uptake with increase in alkalinity and biocomposite dosage may have occurred due to deprotonation of MY at basic pH (Saeed et al. 2010).

Effect of varying temperature and solution pH

Deprotonation of dyes may be held responsible for decrease in % MY removal under alkaline conditions and elevated temperatures (Khan et al. 2013).

Effect of varying temperature and biocomposite dose

% MY removal gradually increased with a corresponding rise in both parameters. Elevated temperatures may have led to an increase in porosity and total pore volume of biocomposite moieties in turn causing more rapid dye diffusion through GO surfaces.

Cost effectiveness of the proposed process

Cost efficiency of the concerned process was determined as per Liang et al. (2018). The graphite used as a precursor of GO cost around US$ 0.457×103 ton^{-1}. Other reagents (technical grade) used in this study were affordable for commercial scale applications. The expenses incurred for gelatin (powder) and PAA (liquid) were US$ 1.30×103 ton^{-1} and US$ 1.88×10^3 ton^{-1} respectively. The lyophilized culture of *Dietzia* sp. used in this study cost around US$ 21.49. The total cost of all major components of the GO nanocomposite is estimated to be around US$ 3.64×103 ton^{-1} (in addition to the one-time expense for procuring this microbial strain). The total cost of the process reported herein was lower in comparison to GO aerogel-based ones proposed by Liang et al. (2018). Other constant expenses insignificant on a long-term condition were not considered in this study (Bhattacharya et al. 2014). On the basis of the optimized conditions, the treatment cost ($ m^{-3}) without the labor and operational cost was estimated to be US$ 1.82 m^{-3} of effluent. The treated effluent was obtained by membrane filtration that cost around US$ 0.478 to 0.592 m^{-}

^{3} million^{-1} gallon of wastewater day^{-1} (inclusive of capital, maintenance and operation) (Liang et al. 2018). Cost incurred by the integrated process reported in this study was lower than Fenton's (US$ 3.50 m^{-3}), ozonation (US$ 4.94 m^{-3}) combined ozonation and H_2O_2 (US$ 5.02 m^{-3}) processes reported previously (Banerjee et al. 2018; Guo et al. 2014; Holkar et al. 2016). Therefore, the integrated process for treatment of azo dye bearing effluents reported herein were considered acceptable for industrial applications.

Comparison with contemporary literature

Processes reported in contemporary literature has been compared in Table 2. Analysis of results reported in similar studies indicated that the process reported in this study was more efficient in terms of both dye removal and time taken in comparison to contemporary studies.

Table 2: Comparison of findings of present study with contemporary literature

Dye (Concentration)	Process	% Dye Removal	Time taken	Reference
Metanil yellow (5 mg L^{-1})	Adsorption (polymeric natural carbohydrate of turmeric powder)	99.5	180 min	Kubra et al. (2021)
SY, MB, and EB (dye conc. 5–25 mg/L)	Adsorption (activated carbon (AC) and AC-nanocomposite)	96.63 (SY), 98.12 (MB), and 99.65 (EB)	38–442 s	Moosavi et al. (2020)
Methyl orange (10 mg L^{-1})	Adsorption (Adsorbents prepared using rice and graham flour)	>99	5h	Munjur et al. (2020)
Metanil yellow (124.34 mg L^{-1})	Integrated adsorption-biodegradation (GO-biocomposite)	99.88	12h	Present study
Congo red	Adsorption (ZnO nanoparticles)	>98	120 min	Singh et al. (2023)
Levafix Blue CA (100 mg L^{-1})	Adsorption/ Fenton oxidation (magnetite nanoparticles)	100	30 min	Thabet et al. (2021)
Rhodamine B and methylene blue (10 mg L^{-1})	Membrane filtration (Sm-MOF/GO nanocomposite membrane)	>91	-	Yang et al. (2020)

CONCLUSION

This work is the first report of MY uptake by GO-biocomposite under optimized conditions. RSM proved to be an excellent tool for achieving efficient process optimization. This optimization requires highly reduced number of experiments, in turn ensuring minimization of time and cost incurred. Under optimized conditions a maximum MY removal of 99.88% was obtained. Hence, it may be concluded that the efficiency of MY uptake by GO-biocomposite demonstrated in this study rendered the same suitable wide scale treatment of real effluents laden with azo dyes.

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