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Application of fluidized bed reactor containing GOx/$MnFe_2O_4$/calcium alginate nano-composite in degradation of a model pollutant

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ABSTRACT

In this study, heterogeneous GOx/$MnFe_2O_4$/Calcium alginate nano-composite catalysts were prepared for removal of Methylene Blue (MB) dye from artificial wastewater. In order to optimize decolorization efficiency of prepared catalysts, different flow patterns were investigated and Response Surface Methodology (RSM) were applied. RSM methodology employed to determine the effects of three main independent parameters ($MnFe_2O_4$ dose, glucose concentration, and initial pH value of the dye solution). The optimum value of $MnFe_2O_4$ dose, glucose concentration, and initial pH for decolorization of MB were found to be 0.23 g per 16 g of catalysts, 11.59 mM, and 10.68, respectively. Results demonstrated that decolorization efficiency in the fluidized bed reactor is significantly higher than packed bed operation and Erlenmeyer flask. At optimum point of operation obtained by RSM methodology, MB removal using GOx/$MnFe_2O_4$/Calcium alginate with fluidized bed reactor, packed bed reactor and Erlenmeyer flask after 2 h of operation was found to be 73.68, 62.86 and 66.33%, respectively.

1. Introduction

In the recent years, the rapid growth of world's population and industrial development has resulted in increased demand for new products, and consequently, large amounts of wastewaters containing organic pollutants such as pharmaceuticals, pesticides and dyes generated by different industries [1,2]. Due to the high solubility of dyes, discharge of industrial wastewaters containing these materials into natural streams leads to serious problems and affects human health [3,4]. There are numerous methods currently available to deal with these pollutants, including absorption, coagulation, membranes, biological methods, photocatalytic methods and Advanced Oxidation Processes (AOP), with every method having its own pros and cons [5–7].

Adsorption of pollutants is superior to other methods of wastewater treatment in terms of low cost of raw materials, simplicity of design, and ease of operation [8], while its only able remove pollutants from wastewater and additional steps are needed to eliminate them. Therefore, absorption method may incorporate with AOP methods to eliminate organic pollutants using a combined method [9]. AOPs, with Fenton process leading the line, are promising methods for complete mineralization of organic pollutants, Based on the generation of Hydroxyl radical ($OH^{\cdot}$) [10]. However, Fenton process needs the addition of H_2O_2 and large amounts of Fe (II) salts that cause corrosion and formation of large amount of chemical sludge, which needs further treatment of wastewater [11]. To overcome these shortcomings of Fenton process, heterogeneous Fenton process with in-situ generation of H_2O_2 considered as an alternative [12–14].

In heterogeneous Fenton process, the reaction rate is limited by mass transfer phenomena. In order to increase mass transfer between wastewater and solid catalyst, application of a reactor to obtain a better mixing is recommended [15]. Fluidized Bed Reactors (FBR), are a combination of Packed Bed Reactor (PBR) and Continuous Stirred Tank Reactor (CSTR), consisting of a vertical cylinder with a distributer located at the bottom part, which solid catalysts loaded on it. Fluid enters the reactor from the bottom of the cylinder and passes through distributer. If fluid's velocity is greater than minimum fluidization velocity (Umf), solid particles become suspended in the liquid phase and Fluidization phenomena occur. Due to high mass transfer rates, excellent mixing and relatively low operation cost, FBR recently attracted attention for water treatment processes [16–19].

Cationic dye Methylene Blue mostly utilized for dyeing cotton, wool, and silk. It causes eye irritation, methemoglobinemia, cyanosis, convulsions, dyspnea, skin sensitivity, and tachycardia in humans [20]. In this paper, GOx/$MnFe_2O_4$/Calcium alginate nano-composite was

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prepared for elimination of Methylene Blue (MB) dye as a model pollutant. Glucose oxidase (GOx) is one of the widely used available enzymes. Known as an oxidoreductase, it produces H_2O_2 during electron transfer reaction from the substrate (glucose) to oxygen. Calcium alginate absorbs MB and glucose molecules, while immobilized GOx enzyme provides $MnFe_2O_4$ nanoparticles with in-situ generated H_2O_2 to produce Hydroxyl radicals through Fenton process that eliminates the absorbed MB molecules [21].

The aim of this study is modeling and optimization of the methylene blue decolorization by GOx/$MnFe_2O_4$/Calcium alginate in a fluidized bed reactor using Response Surface Methodology (RSM). RSM is an efficient and widely used statistical-based method for prediction of multivariable processes and optimization. It provides rapid interpretation and reduction of experiments compared to a full experimental design [22]. Through the model, effects of three main independent parameters on the methylene blue decolorization by GOx/$MnFe_2O_4$/Calcium alginate in a fluidized bed reactor were determined. Additionally, to study the effects of flow pattern on decolorization process, the decolorization of artificial dye wastewater of methylene blue was compared with packed bed reactor and well-mixed erlenmeyer flask.

2. Materials and methods

2.1. Materials

GOx (EC.1.1.3.4 *Aspergillusniger*), glucose, NaOH (99%), HCl, $FeCl_3.6H_2O$, $MnCl_2.4H_2O$ and $CaCl_2$ were obtained from Merck. Alginic acid sodium salt from Sigma-Aldrich and MB were purchased from BuyakhSazan Company.

2.2. Preparation and characterization of $MnFe_2O_4$ nanoparticles

Co-precipitation phase inversion method was employed for the synthesis of $MnFe_2O_4$ nanoparticles from $FeCl_3.6H_2O$ and $MnCl_2.4H_2O$ with a molar ratio of 2:1. 100 mL of solution containing Mn^{2+} and Fe^{3+} with concentrations of 0.1 M and 0.2 M, respectively, were added drop wise to 100 mL of 3 M NaOH solution on the magnetic stirrer and was stirred for 2 h at 95 °C. The prepared $MnFe_2O_4$ powder was washed for several times using distilled water and dried for 12 h at 60 °C [23]. The catalysts were characterized by energy dispersive X-ray (EDX), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR), Braunauer-Emmett-Teller (BET) and transmission electron microscopy (TEM) measurements. The characterization results of $MnFe_2O_4$ nanoparticles have been reported in our previous works [24].

2.3. Immobilization of GOx on $MnFe_2O_4$ and assay of the biocatalyst activity

10 mL of GOx solution with an activity value of 882 U/mL was prepared in acetate buffer at a pH value of 5.5. Then, a specific amount of prepared $MnFe_2O_4$ nanoparticles were added to the enzymatic solution and stirred for 60 min at a rotation speed of 120 rpm [25].

According to Eq. (1), glucose is oxidized by GOx enzyme. The activity of GOx can be measured in presence of glucose by spectrophotometry analyzer, where the produced H_2O_2 is measured by Eqs. (2) and (3): [26]

$$C_6H_{12}O_6+O_2+H_2O\xrightarrow{GOx}H_2O_2+C_6H_{12}O_7 \quad (1)$$

$$H_2O_2+ 2H^{+}+ 2I^{-}\xrightarrow{MO(VI)}I_2+ 2H_2O \quad (2)$$

$$I_2+I^{-} \rightarrow I_3^{-} \quad (3)$$

According to the method described in our previous work, the amount of immobilized GOx in prepared GOx/$MnFe_2O_4$/calcium alginate nano-composite was calculated to be 5850 U/$g_{MnFe2O4}$ [27].

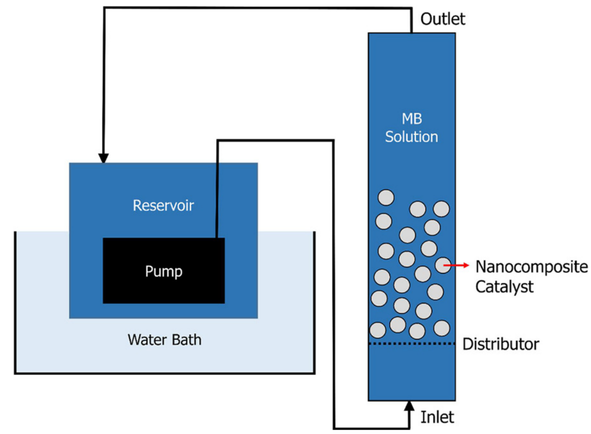

Fig. 1. Schematic of experimental fluidized bed reactor setup.

Table 1
Specifications of fluidized bed reactor.

Variable	Value
Column height	20 cm
Column diameter	2.54 cm
Total volume	101.34 mL
Pump power	5 w
Packed bed height	3.3 cm
Fluidized bed height	9 cm
Flow rate	250 $mL.min^{-1}$
Fluid velocity	0.82 $cm.s^{-1}$
Minimum fluidization velocity	0.64 $cm.s^{-1}$
Average diameter of catalysts	0.4 cm
Catalyst loading	16 g

Table 2
Levels of parameters and their variation limits.

Design Variable	Levels and Values				
	−1.68	−1	0	1	1.68
$MnFe_2O_4$ (g)	0.06	0.1	0.15	0.2	0.234
Glucose (mM)	11.59	15	20	25	28.4
pH	7.31	8	9	10	10.68

2.4. Preparation of GOx/$MnFe_2O_4$/calcium alginate nano-composite

In order to prepare GOx/$MnFe_2O_4$/Calcium alginate nano-composite, a specific amount of GOx-immobilized $MnFe_2O_4$ nanoparticles was mixed with 20 mL of 2% sodium alginate solution. Drops of prepared solution were added to 2% solution of calcium chloride to obtain insoluble granular nano composites.

2.5. Decolorization process

The fluidized bed and packed bed reactor experiments were performed in a glass column, packed with 16 g of prepared GOx/$MnFe_2O_4$/Calcium alginate nano-composite. Fig. 1 demonstrates the schematic of experimental FBR setup. The other details of the reactor and catalysts are tabulated in Table 1. Prepared GOx/$MnFe_2O_4$/Calcium alginate catalysts had a density close to the density of water and a small increment of inlet velocity over minimum fluidization velocity results in a great bed expansion, making these catalysts an appropriate choice for water treatment process in fluidized bed reactors with relatively low pump power requirement. The feed contains 200 mL of MB solution with certain concentration and a specific amount of glucose added as the substrate. The temperature of the dye solution was kept at 30 °C using a water bath. Erlenmeyer experiments were carried out in a