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Regular Article

Statistical optimization and artificial neural network modeling for acridine orange dye degradation using *in-situ* synthesized polymer capped ZnO nanoparticles

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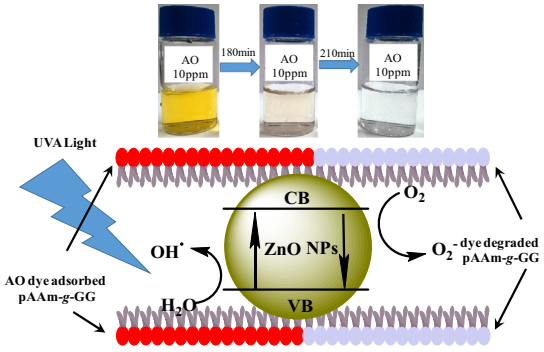
GRAPHICAL ABSTRACT



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ABSTRACT

ZnO NPs were synthesized by a prudent green chemistry approach in presence of polyacrylamide grafted guar gum polymer (pAAm-g-GG) to ensure uniform morphology, and functionality and appraised for their ability to degrade photocatalytically Acridine Orange (AO) dye. These ZnO@pAAm-g-GG NPs were thoroughly characterized by various spectroscopic, XRD and electron microscopic techniques. The relative quantity of ZnO NPs in polymeric matrix has been estimated by spectro-analytical procedure; AAS and TGA analysis. The impact of process parameters viz. NP's dose, contact time and AO dye concentration on percentage photocatalytic degradation of AO dyes were evaluated using multivariate optimizing tools, Response Surface Methodology (RSM) involving Box-Behnken Design (BBD) and Artificial Neural Network (ANN). Congruity of the BBD statistical model was implied by R^2 value 0.9786 and F-value 35.48. At RSM predicted optimal condition viz. ZnO@pAAm-g-GG NP's dose of 0.2 g/L, contact time of 210 min and AO dye concentration 10 mg/L, a maximum of 98% dye degradation was obtained. ANOVA indicated appropriateness of the model for dye degradation owing to "Prob. > F" less than 0.05 for

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variable parameters. We further, employed three layers feed forward ANN model for validating the BBD process parameters and suitability of our chosen model. The evaluation of Levenberg-Marquardt algorithm (ANN1) and Gradient Descent with adaptive learning rate (ANN2) model employed to scrutinize the best method and found experimental values of AO dye degradation were in close to those with predicated value of ANN 2 modeling with minimum error.

1. Introduction

Wastewater generation and disposal by indefinite sources in large volume is still one of the burning issues of the current era. Industrial as well as domestic effluents, which contain different class of components such as metals, pathogens, salts, pharmaceuticals, chemicals, and organic substances etc., when discharged unfettered to aquatic bodies, pose a grave threat to human health and environmental safety. Dyes and pigments are raw materials for many industries such as paper, plastic, leather, cosmetic, food, pharmaceuticals and textile industries, which not only pollute water stream but also their recalcitrant nature showed resistance towards biodegradation [1]. This in turn leads to eutrophication and an imbalance in aquatic food chain.

Along with various conventional approaches for wastewater treatment, semiconductor-assisted advanced oxidation processes (AOPs) is an emerging field towards detoxification of variety of toxic and hazardous pollutants in wastewater. The photo induced process acting on the semiconductor under UV or visible irradiation is capable to generate a number of free radicals species such as superoxide radical ($O^{2\cdot-}$), hydroperoxyl radical ($HO^{2\cdot}$), hydroxyl radical (OH) [2,3]. Among these various radicals, the ·OH is thought to play a central role in AOPs for wastewater treatment. Visible light induced dye degradation namely photosensitization leads injection of electron from excited dye molecules into conduction band (CB) of catalyst when redox potential of the acceptor dye is lower than the CB whereas, catalyst assisted photodegradation occur when irradiation intensity matches or exceeds the bond-gap energy of semiconductor which occur predominantly in UV irradiation [4]. In this context, Zinc oxide (ZnO) NPs (II-VI group semiconductor) having ~3.4 eV energy band gap and a large excitation energy of 60 meV have been widely used for its optoelectric, generating reactive oxygen species and photocatalytic properties [5,6]. A plethora of studies ensue the synthesis of ZnO NPs with various attracted morphologies and their effectiveness for degradation of various dyes in native or modified form. Hasnat et al. [7] reported anionic erythrosine dye degradation kinetics over ZnO NPs. To improve effectiveness with eco-affability of the ZnO NPs, surface modifications or composite formulations are essentially required. Guar gum (GG), a natural polymer extracted from guar beans (*Cyamopsistetragonoloba*) belonging to *Leguminosae* family is composed of galactose residue linked through α (1 → 6) to linear mannose units, which are attached to each other by β (1 → 4) linkages. Moreover, presence of hydroxyl groups in GG unit ensured their widespread applicability in industries as binder, thickener, suspending agents and moisture preserver. Its usefulness has also been exploited in sensors [8] as flocculants [9] and for therapeutic designs [10]. However, the flipside is it's speedy degradation with limited shelf lives [11]. Nonetheless, recent reports suggest this drawback can be overcome by copolymerizing with synthetic functional moieties [12,13] or modification in native structure [14]. Sharma et al. [15] and Gowrav et al. [16] reported methyl methacrylate and acrylamide monomer grafting onto GG surface which reinforce and/or impart a desirable properties to native GG. Gowrav et al. [16] and Toti and Aminabhavi [17] utilized polyacrylamide grafted GG (pAAm-*g*-GG) matrix for controlled release of diltiazem hydrochloride and glimepiride drug respectively.

In the present study, we employed a green chemistry approach for an *in-situ* ZnO@pAAm-*g*-GG NPs synthesis wherein the biopolymer matrix acts as stabilizing and capping agent to modulate NPs nucleation, concomitantly offering functionality for dye attachment. Furthermore, these capped ZnO@pAAm-*g*-GG NPs used aptly to examine AO dye degradation to assess their photocatalytic performance. AO is a cationic dye, having mutagenic potential and widely used in area of printing leather, printing ink and lithography. On the basis of prefatory analysis, statistical experimental design RSM was employed to optimize degradation process parameters such as ZnO@pAAm-*g*-GG NPs dose, contact time and initial AO dye concentration; collectively to achieve superior AO dye degradation. The aforementioned design is often preferred because relatively less experimental combination of the variables is required to estimate the complex response functions simultaneously [18]. Additionally, Artificial Neural Network (ANN) model was applied to predict the photodegradation of AO dye and to validate BBD methodology. A confirmatory experiment was carried out in order to test the reliability of both models.

2. Methodology and design of experiment

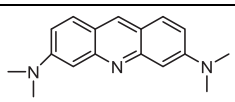
2.1. Chemical and reagents

Guar gum (GG), Zinc acetate dihydrate, Acrylamide and Acridine orange (AO), ZnO NPs (<50 nm) dye are obtained from Sigma Aldrich. All other chemicals used in this study were of analytical grade. Commercial GG was further purified using methanol. All working solutions were prepared in Milli-Q water. Molecular formula and structure of AO dye is given in Table 1.

2.2. Synthesis of ZnO@pAAm-g-GG NPs

ZnO@pAAm-*g*-GG NPs synthesized in a two-step reaction. Initially, pAAm-*g*-GG was synthesized with some modification using prior art [19]. In brief, 300 mg of purified GG and 99.5 mg (14 mmol) acrylamide monomer dissolved in 75 mL degassed Milli-Q water are stirred in inert atmosphere at 27 °C. Oxalic acid (3.7 mmol. 33.3 mg) and $KMnO_4$ (1.5 mmol, 23.7 mg) were then sequentially added to the above solution and the temperature of reaction mixture was allowed to rise to 37 °C for 2 h with constant stirring. With passage of time, the solution turns to a curdy mixture which was then poured to methanol/water (35/15, v/v)

Table 1
Chemical structure of AO dye.

Name	Dye structure	Molecular mass
Acridine Orange (AO) ($C_{17}H_{19}N_3$)		265.36 g/mol