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Research article

Sequestration of dyes from artificially prepared textile effluent using RSM-CCD optimized hybrid backbone based adsorbent-kinetic and equilibrium studies

Sukriti [a], Jitender Sharma [a, *], Amritpal Singh Chadha [a], Vaishali Pruthi [a], Prerna Anand [a], Jaspreet Bhatia [b], B.S. Kaith [a]

[a] Research and Development Laboratory, Department of Chemistry, Dr B.R. Ambedkar National Institute of Technology, Jalandhar, Punjab, India
[b] Department of Chemistry, D.A.V College, Jalandhar, Punjab, India

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ABSTRACT

Present work reports the synthesis of semi-Interpenetrating Network Polymer (semi-IPN) using Gelatin-Gum xanthan hybrid backbone and polyvinyl alcohol in presence of L-tartaric acid and ammonium persulphate as the crosslinker-initiator system. Reaction parameters were optimized with Response Surface Methodology (RSM) in order to maximize the percent gel fraction of the synthesized sample. Polyvinyl alcohol, L-Tartaric acid, ammonium persulphate, reaction temperature, time and pH of the reaction medium were found to make an impact on the percentage gel fraction obtained. Incorporation of polyvinyl alcohol chains onto hybrid backbone and crosslinking between the different polymer chains were confirmed through techniques like FTIR, SEM-EDX and XRD. Semi-IPN was found to be very efficient in the removal of cationic dyes rhodamine-B (70%) and auramine-O (63%) from a mixture with an adsorbent dose of 700 mg, initial concentration of rhodamine-B 6 mgL^{-1} and auramine-O 26 mgL^{-1}, at an time interval of 22–25 h and 30 °C temp. Further to determine the nature of adsorption Langmuir and Freundlich adsorption isotherm models were studied and it was found that Langmuir adsorption isotherm was the best fit model for the removal of mixture of dyes. Kinetic studies for the sorption of dyes favored the reaction mechanism to occur *via* a pseudo second order pathway with R^2 value about 0.99.

1. Introduction

Water contamination due to release of harmful toxic dyes in waste streams has become a major environmental hazard. Toxic dyes are released alongwith effluents by industrial units such as textile, leather, plastic, rubber and paper industries affecting the aquatic world. Such organic dyes further get *in-vitro* metabolized into many byproducts possessing carcinogenic, mutagenic and other harmful activities (Patricia et al., 2010; Rodrigo et al., 2007). Some of the dyes are non-biodegradable in nature and undergo a large amount of biomagnification processes through food chain. The annual production of dyes amount to about 7×10^5 tons, out of which 10–15% are discharged into water bodies (Anila et al., 2014). Moreover, dye effluents are also rich in suspended solids which reduce the photosynthetic ability of various aquatic plants thereby harming their vegetative and reproductive growth. Some of the toxic dyes that cause water pollution include rhodamine-B, auramine-O, methylene blue, congo red, crystal violet, alizarine, eriochrome black-T and safranin (Aguilar et al., 2014; Reddy and Lee, 2013).

Rhodamine-B is pink colored cationic dye and is a major constituent of textile processings. However, its consumption causes many side effects like tissue sarcoma, cancer, reproductive toxicity, neurotoxicity, burning sensation in eyes and chest pain (Jain et al., 2007). Complex aromatic character leads to non-biodegradability and its presence in environment for a long time. On the other hand, auramine-O is a yellow colored water soluble diarylmethane cationic dye and comes in the category of major water pollutants. It has neurotoxicity and hepatitis effects causing irreparable harm to

* Corresponding author. Department of Chemistry, Dr B.R. Ambedkar National Institute of Technology, Jalandhar, 144011 Punjab, India.
E-mail addresses: sukriti.chemistry@gmail.com (Sukriti), jitenders.14.cy@nitj.ac.in (J. Sharma), amrit.chem55@gmail.com (A.S. Chadha), vaishalipruthi@gmail.com (V. Pruthi), prerna.anand.15@gmail.com (P. Anand), jaspreetbhatia81@gmail.com (J. Bhatia), kaithbs@nitj.ac.in (B.S. Kaith).

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living organisms (Martelli et al., 1998). Thus, the treatment of dyes contaminated water sources is very important from environmental point of view.

These days various techniques like flocculation, coagulation, ion-exchange and chemical precipitation are used for the remediation of polluted water but these techniques are not cost effective and byproducts left behind cause other environmental problems (Raghu and Basha, 2007; Verma et al., 2012). Use of polymeric adsorbents in different forms like sheets, slabs and membranes for toxic dye removal has an edge over other treatment methods due to their simple processing abilities, easy regeneration and no harmful end products (Rafatullah et al., 2010).

IPNs with 3 D Interpenetrating network structure possess the potential to absorb and retain aqueous fluid thousand times their own weight. Because of such unique characteristics such materials are widely used in biomedical, tissue engineering, agricultural sector and removal of toxic metal ions and dye from contaminated water (Ahmed, 2015; Hoffman, 2012).

Earlier in order to obtain the superabsorbents with maximum fluid uptake efficacy traditional methods were used involving variation of one reaction parameter at a time and keeping other factors constant. However, this traditional approach was not economical and is time consuming. Moreover, the interaction between different reaction parameters and their impact on maximum gel fraction are not visible through the traditional techniques. Therefore, more accurate, quick and economical methodology based on statistical principles has been used by different workers all over the world. RSM is one of such technique which involves simultaneous variation of reaction parameters to generate data for the development of empirical models (Sukriti et al., 2016; Kaith et al., 2014a,b).

During last few decades use of IPNs as adsorbents for removal of toxic dyes from industrial effluents is encouraged because of their high efficiency and no adverse impact on the nature (Chensi et al., 2011; Wanngaha et al., 2011). Novelty of the present work lies in the preparation of superabsorbent semi-IPN using hybrid natural backbone and biocompatible L-tartaric acid as a crosslinker so as to give 3-D stability to the device synthesized. Moreover, RSM technique was used to get accuracy and impact of interaction between different reaction parameters while, optimizing the different reaction parameters parameters like solvent, temperature, time, pH, initiator, monomer and cross-linker concentration as a function of gel fraction so as to get efficient ecofriendly superabsorbent system. Moreover, perturbation plots along with desirability plots were used to understand the process optimization and modelling. Further the synthesized ecofriendly semi-IPN was used for the removal of carcinogenic and mutagenic dyes like rhodamine-B and auramine-O from industrial effluents. In order to study the behavior of the sorption of the mixture of dyes onto the semi-IPN Langmuir and Freundlich adsorption isotherm studies were carried out. These studies were further strengthened with pseudo-First order and pseudo Second-order kinetic models which were employed to study the adsorption kinetics of the mixture of dyes onto the semi-IPN. Thus, this work deals with the synthesis of the ecofriendly semi-IPN using RSM design which could be used for the treatment of the toxic dye contaminated water without any adverse impact on the surroundings.

2. Experimental

2.1. Materials and method

Gum xanthan and Gelatin as a backbone were procured from Sigma Aldrich and CDH Chemicals Ltd., India, respectively. Polyvinyl alcohol (PVA) and ammonium persulphate (APS) was obtained from S D fine chemicals Ltd. Cross linker L-tartaric acid was purchased from Merck.

2.2. Instrumentation

The characteristic functional groups of the hybrid backbone and the synthesized semi-IPN were studied using Agilent Technologies Carry 630 FTIR Spectrophotometer possessing diamond crystal, in the range of 400 cm^{-1} to 4000 cm^{-1}. Images of Scanning Electron Microscopy-Energy Dispersive X-Ray Spectroscopy (SEM-EDX) for determining the morphological changes and elemental constitution, were obtained using JEOL JSM-6490LV microscope at 10 kV with platinum coating. The absorbance spectra for dye uptake studies were obtained using Agilent Technologies Carry 631 UV–Vis Spectrophotometer. The weighings were performed on CPA225D Sartorius analytical balance.

2.3. Sequential experimental design

RSM is an efficient technique for process optimization in a minimal experimental runs and which is used to explain the combined effects of all the factors. Gel fraction depends upon number of variables like time, temperature, solvent amount, initiator concentration, monomer concentration, crosslinker concentration and pH of medium. The effect of different parameters along with the interactions between these parameters required full factorial design whereas use of full factorial requires $2^7 = 128$ runs. Thus, to screen important process variables, intelligent minimum run resolution V optimal design was used. The design was used to minimize the integral of the prediction variance across the design space. Seven process variables were varied at maximum and minimum levels. Gel fraction was selected as response. There are total 39 experimental runs. Significant process variables were selected by performing Annova modelling and using pareto chart. Model was selected based upon p-values and non-significant lack of fit. Three significant process variables, gelatin concentration, monomer concentration and crosslinker concentration were optimized using Central Composite Design (CCD). Numerical optimization was done to get conditions of process variables for maximum gel fraction.

2.4. Synthesis of semi-IPN

Synthesis of the adsorbent was carried out on the basis of optimized process variables obtained through RSM and CCD techniques used for the synthesis of adsorbent with maximum percentage gel fraction. Different reaction variables optimized through RSM and CCD were: PVA (2.0 g), L-tartaric acid (1.9×10^{-4} $molL^{-1}$), APS (0.05 mol L^{-1}), pH ($\cong$ 7.0), reaction time (3 h), temperature (70 °C) and amount of solvent (10.0 mL).

Synthesis of semi-IPN was carried out in a single step using aqueous medium. For each experiment, 1.0 g of Gum xanthan–Gelatin (1:1, w/w) hybrid backbone was added to about 10 mL of solvent in the reaction flask followed by slow addition of 2.0 g of polyvinyl alcohol and 0.416 mol L^{-1} of L-tartaric acid as a monomer and cross linker, respectively. Reaction mixture was stirred continuously for 5–10 min in order to attain the homogeneity. Further, to this resulting mixture 0.05 mol L^{-1} of ammonium persulphate was added and reaction was carried out for 3 h at 70 °C. Semi-IPN formed was washed thoroughly with distilled water to remove homopolymer and dried at 60 °C till constant weight was obtained.