Canna indica-chitin-alginate composite beads for the treatment of textile dye effluent containing Rose Bengal dye

Abstract

Aim: To study the adsorption of Rose Bengal dye used in textile industries by Canna indica-chitin-alginate beads.

Methodology: C. indica-chitin-alginate composite beads were prepared using root tubers of Canna indica, chitin from shrimp shells and sodium alginate. Batch adsorption of Rose Bengal dye was carried out with optimized parameters like pH, contact time, adsorbent dosage and dye concentrations. Characterization studies like SEM, FTIR and TGA and reusability of composite beads were also studied.

Results: The maximum adsorption of 97.9% was obtained at pH 6, 80 min contact time with the optimized ratio of 1:1:0.05 C. indica-chitin-alginate towards 100 mg l−1 dye concentration. The SEM analysis showed a porous surface morphology whereas FTIR results exhibited the functional groups of Rose Bengal dye and composite beads, proving successful adsorption. Thermogravimetric analysis revealed that the composite beads could withstand a maximum temperature of 300°C.

Interpretation: It is inferred from the study that a biosorbent prepared from a commonly available plant and shells of shrimp, which is considered as a waste, can be effectively used in the adsorption of harmful textile dyes from the effluent in an eco-friendly and cost-effective way.

Key words: Alginate, Canna indica, Chitin, Composite beads, Rose Bengal dye
Introduction

Textile industry is one of the core industries in India which consumes almost 80% dye stuffs produced. According to the annual report 2017-18 of Ministry of Textiles, around 28.89 lakh kg dyes are used by textile industries all over India. High concentrations of these dyes are discharged into the aquatic environment through effluents which are highly harmful to the aquatic community. It interferes with the photosynthetic activities of phytoplankton and respiration of biomass (Yaseen and Scho, 2018). One such harmful dye is Rose Bengal, synonym of Acid Red 94. It is a hydroxyxanthenes dye, which gives a fluorescent pink color particularly on polyacrylonitrile fibers (Thomas and Udo, 2012). It is a cheap dye commonly used in textile, paper, cosmetics and printing industry (Naushad et al., 2015). Since it is a very harmful dye causing damage to eyes, particularly cornea, and affects skin causing severe allergy, removal of this dye from the effluent is the need of the hour (Kumar and Thirumalesh, 2013; Nandhakumar et al., 2015). Physical, chemical and biological methods using bacteria are the most common textile effluent treatments in practice (Saratale et al., 2011).

Coagulation, chemical flocculation, filtration by activated carbon and membrane filters are some of the effective but toxic and expensive physio-chemical methods applied for effluent treatment (Rajasulochana and Preethy, 2016). Alternatively, adsorption is the most versatile and widely used technology which uses chemical adsorbents like alumina, silica, metal hydroxides and activated carbon (Raval et al., 2017); however they are not much preferred in recent times due to their production cost, toxic nature, low regeneration capacity and other properties. Chitin is a polysaccharide that occurs naturally in large quantity. It is found in the exoskeleton of crab, shrimp shells, lobster, fungus, yeast, cuticles of insects and arthropods (Chawla et al., 2014). It is biodegradable, highly porous, non-toxic, biocompatible and eco-friendly. Shrimp shells are considered as large scale waste worldwide and are dumped directly into the sea in many developing countries (Roberto, 2017). Chitin can be directly obtained in large quantities from these shells by a simple and cost effective process. Chitin flakes of shrimp shells and sodium alginate were procured from Hi-Media. One percent sodium alginate solution was prepared using distilled water and heating it at 50°C continuously for the alginate to get dissolve completely. This was followed by addition of 2g of chitin powder and 2g of C. indica powder to 100 ml of 1% alginate with continuous stirring. The chitin-alginate mixture was then added as droplets in 5% calcium chloride solution using a sterile dropper for bead formation.

Optimization of Canna indica-chitin-alginate composite beads: A stock solution of 100 mg l⁻¹ Rose Bengal dye was prepared, and the stock was used for standardization process and for further optimization experiments. UV-Visible spectrophotometer (Perkin Elmer, Lambda 25, USA) was used to measure the Rose Bengal dye concentration before and after adsorption. Optimization of process parameters were carried out in a glass column as a batch process. The stock solution of Rose Bengal dye was fed into the column and the system was kept undisturbed. The sample was eluted and absorbance of treated sample was measured at 550 nm. The optimization of pH was carried out with pH of Rose Bengal dye varying from pH 2 to 8. The contact time was optimized by varying the contact time of adsorption process from 10 min to 120 min. Different ratios of C. indica: Chitin: Alginate starting from 1:1.02 to 1:1.09 were taken for the optimization of adsorbent dose. Finally, Rose Bengal dye concentration was optimized by varying the dye concentration from 0.02 g l⁻¹ to 0.1 g l⁻¹. With the optimized parameters, final adsorption of Rose Bengal dye was carried out and the amount of rose bengal dye adsorbed per unit mass (Qₑ) was calculated as:

\[ Qₑ = \frac{(C - Cₑ)V}{m} \]

Where, C and Cₑ are the concentration (mg l⁻¹) of Rose Bengal dye initially and after reaching equilibrium; m is the mass of C. indica-chitin-alginate beads (g) and V is the volume of Rose Bengal dye solution in ml.

Characterization of C. indica-chitin-alginate beads: Characterization of C. indica-chitin-alginate beads before and after adsorption was done by Scanning Electron Microscope (SEM) to study the surface morphology using S-3400 microscope with vacuum condition of 5kV and magnification varying from X 30 to 1.00K. Fourier Transform Infrared Spectroscopy (FTIR) study was also done to identify the functional groups. KBr disks of only C. indica-chitin-alginate beads and dye adsorbed C.indica-chitin-alginate beads were prepared. The functional groups present were graphically identified using ASCII PEDS 1.60 FTIR spectroscopy in the range of 4000 to 400 cm⁻¹. Finally, Thermogravimetric Analysis was carried out to find the changes in the physical and chemical properties of C. indica-chitin-alginate beads with respect to temperature. It was carried out using C. indica-chitin-alginate beads alone and along with adsorbed dye in TGA 050 V20.13 Build 39 instrument in the temperature range of 50°C to 800°C.

Recovery and reuse of C. indica-chitin-alginate beads: The reusability of C. indica-chitin-alginate beads was analyzed using
HCl (0.1N), NaOH (0.1N), acetic acid (98%), water and ethanol (97%). Further, optimization was done using various concentrations of HCl from 0.1% to 0.5% and after HCl treatment; the beads were washed twice with distilled water.

Results and Discussion

The maximum adsorption of Rose Bengal dye was found at pH 6 which was considered as the optimum level (Fig. 1A). The pH plays a major role in the adsorption as it affects the solubility of dye, the chemistry existing in the dye solution and the adsorption ability of the adsorbent (Intidhar et al., 2017). Since it is an anionic dye, the adsorption increased from pH 2 to 6 and started decreasing as the pH turned neutral and basic. This pattern of adsorption can be attributed to the surface charge of C. indica-chitin-alginate beads and dye solution. At low pH, protonation occurs making the surface available for the dye to adsorb through electrostatic interaction than at higher pH (Gholamhasan et al., 2017; Banerjee and Chattopadhyaya, 2017). Furthermore, a competition always exists between OH ions in the dye solution for the adsorption site, hence a decrease in the adsorption was observed at higher pH due to lack of available sites (Sarkar et al., 2012).

Initially at 10 min, there was a rapid adsorption which declined slowly around 80 min until saturation was reached at 100 min. The dye concentration did not vary significantly after 80 min (Fig. 1B). The rapid adsorption was initially due to availability of active sites on the exterior surface of the beads. Once saturation of active sites reaches the outer layer, the dyes move to the interior core of the beads by pore diffusion which takes a longer time as diffusion process occurs slowly (Yixi et al., 2016). Similar diffusion pattern was reported for various anionic dyes by different biological sorbents proving that diffusion time and adsorption time plays a major role in influencing the adsorption process (Yatin and

![Graphs of pH vs. Percentage of Adsorption, Contact time vs. Percentage of Adsorption, C.indica: Chitin: Alginate ratio vs. Percentage of Adsorption, Concentration of Rose Bengal vs. Percentage of Adsorption]

Fig. 1: Effect of (A) varying pH, (B) different contact time, (C) various ratios of C. indica-chitin-alginate beads and (D) varying Rose Bengal dye concentration on the percentage of adsorption of Rose Bengal dye.
Manish, 2012; Akazdam et al., 2017; Mirzaie et al., 2017). The final adsorbent dosage was optimized at 1:1:0.05 ratio for C. indica-chitin-alginate beads at which the maximum adsorption was obtained (Fig. 1C). An agglomeration of adsorbent particles occur when the concentration of adsorbent increases, further reducing the active sites available for adsorption (Singh et al., 2017). In a similar work reported by Maria et al. (2016) and Lunhong et al. (2011) alginate-cellulose composite beads and activated carbon/cobalt ferrite/alginate composite beads were used in different ratios for adsorption of dyes wherein an increase in the concentration of composite beads after reaching saturation point had negligible or no effect on the adsorption process.

From the dye concentration ranging from 20 mg l\(^{-1}\) to 100 mg l\(^{-1}\), the maximum adsorption was obtained at 100 mg l\(^{-1}\) (Fig. 1D) beyond which the adsorption remained static. The driving force for the dye to transfer from aqueous phase to solid phase of the adsorbent is provided by the initial dye concentration (Roopavathi and Shankakumar, 2016). Increase in dye concentration increases the concentration gradient, and the driving force generated by this concentration gradient creates empty sites for adsorption (Sundararaman and Muthuramu, 2016; Vinuth et al., 2016). As the concentration of solute in the solution increases, the availability of these empty sites decreases, thereby adsorption decreases (Aseel et al., 2012). Zhao et al. (2017) in a related study on the adsorption of anionic dye by peanut husk stated that increase in ionic strength also results in the saturation of available sites and reduces adsorption. With all the optimized parameters, 97.9% adsorption of Rose Bengal was successfully obtained in this batch column study. SEM analysis showed uneven surface morphology for the composite beads at X 250 magnification. The surface was also highly porous and fibrous in nature, similar to cellulose (Fig. 2). The beads were spherical in shape and the average bead size was 0.22 cm at X 1.0K magnification. A similar surface morphology was observed by Shaofang et al. (2012) and Mei et al. (2017) for chitin and chitosan which was also obtained from shrimp. Chitin was clearly arranged in a microfibrillar crystalline structure and chitosan had an irregular and broad cellular structure.

In the spectra for Rose Bengal dye adsorption on C. indica-chitin-alginate composite, the peaks at 1566.88 cm\(^{-1}\) and 1372.1 cm\(^{-1}\) represent the stretching vibrations of C=C bonds, while peak at 1623.77 cm\(^{-1}\) for Rose Bengal dye could be associated with the stretching vibrations of carbonyl (=C=O) groups. The peak at 2153.13 cm\(^{-1}\) indicated the stretching vibrations of carboxylic (COO-) group, while peaks at 2969.87 cm\(^{-1}\) and 2834.85 cm\(^{-1}\) could be correlated with the stretching vibrations of =C-H bonds for the Rose Bengal dye (Fig. 3). The peak at 1120.44 cm\(^{-1}\) indicated chitin with–NH group and 2884.02 cm\(^{-1}\) peak indicated vibration for–CH stretching. Previous reports by Hankare et al. (2012) and Premkumar et al. (2013) also showed a similar carbonyl stretching of Rose Bengal dye at 1608 cm\(^{-1}\) and =C-H stretching and vibrations at 2919 cm\(^{-1}\) and 2848 cm\(^{-1}\).

Thermogravimetric analysis showed that C. indica-chitin-alginate composite beads with Rose Bengal dye could withstand high temperatures. It starts degrading at 200.24°C due to water evaporation, retaining 86.79% of the beads followed by dehydration, depolymerization and decomposition around 301.08°C at which only 69.91% exists. A drastic change in stability was noted after this temperature till 650°C and ash content of 23.40% was obtained at 800°C (Fig. 4). A similar trend was reported by Jia-Xing et al. (2013) and Estevao et al. (2015) for Rose Bengal dye conjugated with polymers, and silica...
Fig. 3: FTIR of C. indica-chitin-alginate composite beads and Rose Bengal dye showing peaks at 1566.88 cm\(^{-1}\) (13), 1372.1 cm\(^{-1}\) (14), 1623.77 cm\(^{-1}\) (12), 2153.13 cm\(^{-1}\) (10), 2969.87 cm\(^{-1}\) (4) and 2834.85 cm\(^{-1}\) (5) which represents stretching vibrations of C=C bonds, carbonyl (=C-O) groups, carboxylic (COO–) group and =C-H bonds. The peaks at 1120.44 cm\(^{-1}\) (20) and 2884.02 cm\(^{-1}\) (6) indicate chitin with –NH group and vibration for –CH stretching.

Fig. 4: Thermogravimetric analysis of C. indica-chitin-alginate composite beads with Rose Bengal dye showing degradation at 200.24°C retaining 86.79% of the beads followed by dehydration, depolymerization and decomposition around 301.08°C, 650°C and 800°C with a final ash content of 23.40%.

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nanoparticles which had a thermal stability up to 300°C.

Although, the source for producing the composite beads is cheap and easily available, reusability of beads plays a major role from the industrial economy point of view (Setiabudi et al., 2016). Out of the five solvents used 0.1 N HCl best suited for the reuse of the beads and optimized percentage of 0.1 N HCl wash was found to be 0.5% for 10 min. Five cycles of adsorption was carried out with the same composite beads after washing with 0.1N HCl at the end of each cycle. The adsorption rate reduced to 55% after fifth cycle. Haichao et al. (2017) similarly used 1M HCl/methanol for washing and reused metal organic framework (PCN 222) until 8 cycles for mixed dyes removal. In a study by Gholamhasan et al. (2017) adsorption was carried out for xanthene dyes using lemon citrus peel active carbon. 0.1M NaOH was used for regeneration of active carbon but only three cycles of adsorption was possible with the regenerated lemon citrus peel active carbon. In removal of Rose Bengal by bottom ash, 150 ml of dilute NaOH was found to be adequate for recovery and reuse till fourth cycle of adsorption (Gupta et al., 2012).

Based on the above findings, it has been demonstrated that the root tubers of C. indica, shrimp shells and sodium alginate composite beads can act as good adsorbent for anionic dyes like Rose Bengal from textile effluents. The source for production of the composite beads is also economic, eco-friendly, easily available along with reusable property might serve as the best alternative for the chemical treatment of effluent from the industries in a cost effective manner.

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