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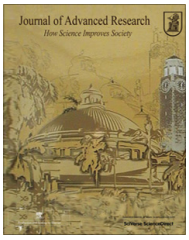

ORIGINAL ARTICLE

Adsorption of Methylene Blue, Bromophenol Blue, and Coomassie Brilliant Blue by α-chitin nanoparticles

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ABSTRACT

Expelling of dyestuff into water resource system causes major thread to the environment. Adsorption is the cost effective and potential method to remove the dyes from the effluents. Therefore, an attempt was made to study the adsorption of dyestuff (Methylene Blue (MB), Bromophenol Blue (BPB) and Coomassie Brilliant Blue (CBB)) by α-chitin nanoparticles (CNP) prepared from *Penaeus monodon* (Fabricius, 1798) shell waste. On contrary to the most recognizable adsorption studies using chitin, this is the first study using unique nanoparticles of ⩽50 nm used for the dye adsorption process. The results showed that the adsorption process increased with increase in the concentration of CNP, contact time and temperature with the dyestuff, whereas the adsorption process decreased with increase in the initial dye concentration and strong acidic pH. The results from Fourier transform infrared (FTIR) spectroscopy confirmed that the interaction between dyestuff and CNP involved physical adsorption. The adsorption process obeys Langmuir isotherm (R^2 values were 0.992, 0.999 and 0.992 for MB, BPB and CBB, and R_L value lies between 0 and 1 for all the three dyes) and pseudo second order kinetics (R^2 values were 0.996, 0.999 and 0.996 for MB, BPB and CBB) more effectively. The isotherm and kinetic models confirmed that CNP can be used as a suitable adsorbent material for the removal of dyestuff from effluents.

Introduction

Effluents from various industries contain harmful coloring agents, which have to be removed to maintain the quality of the environment. Paper, fabric, leather and dyestuff production are some of the industries that release harmful effluents [1]. Dyes used in various industries have harmful effects on living organisms within short exposure periods. The disposal of dyes in wastewater is an environmental problem that causes ill effects

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to the ecosystem [2]. Conventional wastewater treatments such as chemical coagulation, activated sludge, trickling filter, carbon adsorption and photo-degradation were used for the removal of dyes [3]. Recently adsorption processes have been demonstrated as a potential technique for the removal of dyes from wastewater. Dye adsorption is a process of transfer of dye molecules from bulk solution phase to the surface of the adsorbent. Screening of biological adsorbents is an eventual task for environmental scientists and engineers, with its due merits. The most common biological adsorbents, or material from which they are produced, used in the process of adsorption include activated carbon (coconut shell), tree bark, lignin, shellfish shells, cotton, zeolites, fern, and compounds contained in a number of minerals and microorganisms (bacteria, fungi and yeast) [4]. Ease of access, cheap rate, reliability and ability to compete favorably with the conventional adsorbents make the biological adsorbents on demand than the synthetic ones [5].

Chitin is a biopolymer of 2-deoxy-β-D-glucose (N-acetylglucosamine), which is linked by β(1–4) glycosidic bonds found in nature [6]. Chitin is a rigid scaffold found in arthropod cuticle. Arthropods, include the crustaceans (e.g. crabs, lobsters, and other isopods), insects (e.g. wasps, bees, ants, beetles), arachnids (e.g. spiders, scorpions, ticks, mites), centipedes, millipedes and several lesser groups, account for approximately 80% of all known animal species [7]. Distribution of chitin is a widespread trait among both unicellular organisms (yeast, protists and diatoms) and invertebrates, from the first Metazoans (sponges) through the invertebrate (chordates) and up to fish [8]. In fungi chitin is the characteristic component of the taxonomical groups Zygo-, Asco-, Basidio- and Deuteromycetes [9]. Chitin can be directly drawn out in large quantities from crab, prawn shells and seafood wastes. *Penaeus monodon* (Fabricius, 1798) is a crustacean found in all coastal areas worldwide. The waste produced from shrimps is an emerging problem in countries such as India, where the food industry is based mainly on seafood [10]. In India, more than 1,00,000 tons of shrimp bio-waste is generated annually and only an insignificant amount of that bio-waste is utilized for the extraction of chitin while the rest is discarded or underutilized [11–14]. Therefore, extraction of economically important chitin from the shells of *P. monodon* (Fabricius, 1798) and its utilization in wastewater treatment are an additional source of income, which also reduces the problems created by shrimp waste. The application potential of chitin is multidimensional, such as in food and nutrition, material science, biotechnology, pharmaceuticals, agriculture and environmental protection [15]. The stability of chitin opens the way for the use of chitin as a template molecule for hydrothermal reactions and ultimately leads to the synthesis of advanced materials [16]. Synthesizing nanoparticles from chitin and chitosan enhances its application due to its larger surface area [17]. The aim of the present study was to investigate the CNP adsorption capability on three major industrial dyes, namely Methylene Blue (MB), Bromophenol Blue (BPB) and Coomassie Brilliant Blue (CBB). Efficacy of CNP over dye retention has been investigated at varied operating conditions such as pH, CNP dosage, contact time and initial dye concentration. The adsorption capability of CNP toward these dyes has been evaluated using Langmuir and Freundlich isotherms and their adsorption kinetics has been analyzed using pseudo first order and pseudo second order kinetic models. The chemical structure experimental dyes are presented in Fig. 1(a)–(c).

Material and methods

Materials

P. monodon (Fabricius, 1798) shells were collected from the Estuary of Southeast coast of Mandapam, Tamil Nadu, India. Sodium hydroxide, Acetone, Ethanol and Hydrochloric acid used were purchased from Sisco Research Laboratories Pvt. Ltd., Mumbai, India, and Dialysis membrane was purchased from HiMedia Laboratories, Mumbai, India. Methylene Blue, Bromophenol Blue and Coomassie Brilliant Blue were purchased from Sigma–Aldrich, USA.

Chitin nanoparticles isolation and characterization

Shells of *P. monodon* (Fabricius, 1798) were collected from the east coastal regions of (Mandapam) southern Tamil Nadu, India. The shells were washed in running tap water to remove the soluble organics, adherent proteins and other impurities. Washed shells were air dried at 25 ± 1 °C for 2 weeks. Dried shells were soaked in 0.5 M NaOH at 25 ± 1 °C for 24 h for the removal of proteins and lipids existing with shells. The NaOH was drained and the shells were washed with distilled water until the pH reaches neutral. The shells were again dried at 50 °C in a hot air oven for 48 h. Dried shells were ground as fine powder using a domestic blender and subjected to acid hydrolysis. The shells were soaked in 0.25 M HCl for 45 min and rinsed with distilled water until the pH reaches neutral. Again the sample was soaked in 2.5 M NaOH for 6 h at 80 °C and washed with distilled water until the pH reaches neutral. The alkali treatment was repeated twice and the remaining organic soluble compounds from the sample were removed by washing with acetone and ethanol thrice. The sample was dried for 10–15 days in hot air oven at 40 °C and white colored chitin was obtained.

CNP were isolated from the purified chitin by repeated acid hydrolysis [17]. Chitin powder was soaked in 3 M HCl for 1.5 h at 90 °C in a water bath. The sample was centrifuged at 6000 rpm for 10 min and the pellets were collected. The acid hydrolysis step was repeated thrice and the pellets were suspended in distilled water to dilute the acid concentration. The suspension was dialyzed against distilled water until it reaches pH 6 and was homogenized using a tissue homogenizer. The homogenized sample was collected and lyophilized at −60 °C to get the powder form of CNP. Mechanical disruption and ultrasonication were carried out to cut down the size of nanoparticles.

UV–Visible spectrophotometer was used to study the covalent and noncovalent interactions of a compound [18]. UV–Visible spectra of chitin were recorded in aqueous acid solution (0.1 M HCl) in a 1.0 cm Quartz cell at 25 ± 1 °C. The absorbance was measured using Shimadzu UV-2401 PC double beam spectrophotometer at the range between 190 and 500 nm range and 0.1 M HCl solution was used as control.