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Development of novel chitosan–lignin composites for adsorption of dyes and metal ions from wastewater

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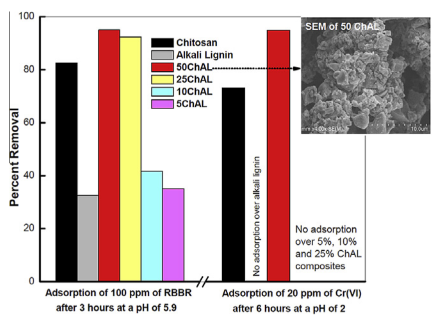
HIGHLIGHTS

- Chitosan–lignin composites with enhanced surface and chemical properties were developed.
- Weak hydrogen bonding interactions between chitosan and lignin were established via FTIR.
- Chitosan–lignin (50:50) composite exhibited high rates of removal of dyes and Cr(VI).
- Adsorption of Remazol Brilliant Blue R and Cr(VI) followed second order kinetics.
- The active sites and the mechanism of adsorption on the composite are unravelled.

GRAPHICAL ABSTRACT



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ABSTRACT

It is important to devise new strategies to derive value from lignin, which is a potential waste by-product from paper industries and present day biorefineries. In this research, we report, for the first time, a facile preparation and characterization of a range of chitosan–alkali lignin composites for the removal of harmful effluents present in wastewater. The composites were characterized by the presence of weak bonding between β-1,4-glycosidic linkage, amide and hydroxyl groups of chitosan, and ether and hydroxyl groups of alkali lignin. Various reaction parameters like chitosan content in the composite, initial pH and adsorbent dosage were optimized. Batch adsorption studies showed that chitosan–alkali lignin (50:50) composite exhibited maximum percentage removal of anthraquinonic dye, Remazol Brilliant Blue R (RBBR), and Cr(VI) compared to other composites, chitosan and alkali lignin. Adsorption of RBBR on the composite followed Langmuir isotherm, and the adsorption of both RBBR and Cr(VI) followed pseudo second order kinetics. A mechanism of adsorption that involves (i) electrostatic interaction of protonated amino and hydroxyl groups of the composite with anionic SO_3^- and $HCrO_4^-$ groups of dye and Cr(VI), respectively, and (ii) chemical interaction between amino and hydroxyl groups of the composite, and carbonyl moiety of the dye, was proposed.

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1. Introduction

Lignin, an amorphous, crosslinked and aromatic polymer, is naturally found in biomasses, and is also a major non-sugar component of wood [1]. Lignin is well known as a waste by-product from pulp and paper industries. However, it is also a major reject from the present day biorefineries that produce cellulosic ethanol after the separation of cellulose and hemicellulose in the pretreatment step. Lignin is composed of propyl-phenolic subunits containing phenolic, hydroxyl, carbonyl, methoxy and aldehyde groups that serve as potential active sites for adsorption of dyes and metal ions [2–4]. The composition and structural units of lignin differ depending on the source of biomass from which lignin is extracted. In paper industries, depending upon the pulping process, different types of lignins are obtained as waste by-products. The waste alkali lignin produced from kraft pulping process is inert and is usually burnt for power [1,5], eventhough its rich chemical functionality can be utilized in a better way to produce composites and value added chemicals. Reuse of lignin will not only reduce the amount of the biowaste, but also provide additional revenue to the industries [1]. Recently, lignin has found applications in the form of adhesives, tanning agents and as a precursor for producing activated carbon, which is a well known adsorbent [6]. This work aims at modifying lignin for use as an adsorbent for waste water decontamination.

Wastewater discharge from dye, paint, paper, textile and electroplating industries contain harmful chemicals like dyes and metal ions, which pollute the water bodies. The presence of very low concentrations of even 10 ppm of dyes in water imparts a color, making it undesirable for use [7]. The reactive dyes that are discharged into the water bodies are not biodegradable, and hence, are toxic to aquatic life. Remazol Brilliant Blue R (RBBR) is an anthraquinonic dye used widely in paints, inks, chemical indicators, dyeing of cottons, silk and as a starting material in the production of polymeric dyes [8]. Similarly, hexavalent chromium, Cr(VI), is mostly generated by chemical processes like electroplating, leather tanning, pigment manufacturing and mining [9]. Chromium metal ion exists in two valence states, viz., Cr(III) and Cr(VI), of which the latter is highly toxic and carcinogenic [10].

Adsorption is one of the superior physicochemical methods for wastewater detoxification compared to other methods like coagulation, ion exchange, oxidation, chemical precipitation, electrodeposition and membrane separation, owing to high removal efficiency for different types of effluents, ease of operation, availability of a variety of cheap adsorbents, and the absence of sludge and harmful by-product formation [11]. Recent investigations on the removal of effluents by adsorption are focused on utilizing readily available and cheap bio-based materials like maize [12], agricultural waste [13], jute fiber [14], rice husk [15] and mango seed [16]. Table 1 [4,13,15,17–22] presents a summary of adsorption capacities of various bio-based materials for the removal of dyes and metal ions. Researchers have utilized lignins extracted by organosolv and kraft pulping processes for adsorption of dyes and metal ions [4,17,18,23]. Typically, non-sulphonated lignins like alkali lignin can be used as adsorbents owing to their insolubility in water and high resistance to chemical reactions. However, the structure of lignin varies based on the type of biomass (e.g. softwood, hardwood, grassy), and hence, it is imperative that surface modified lignins and lignin-based composites are developed as potential adsorbent materials.

Chitosan, a copolymer obtained by deacetylation of chitin [24], is a well known biosorbent used for the removal of various types of pollutants like fluorides, dyes, heavy metal ions and organic compounds found in waste water [19,25]. Chitosan is a copolymer of 2-glucosamine and N-acetyl-2-glucosamine units, wherein the former constitutes a major fraction of the biopolymer chain. The adsorption characteristics of chitosan are due to the large number of hydroxyl (–OH) and primary amine (–NH_2) groups that act as highly active adsorption sites [26]. In acidic condition, the amine groups are protonated and thereby aids in the adsorption of dye/metal ion by electrostatic attraction. However, chitosan, as an adsorbent, has some disadvantages such as dissolution in highly acidic solution, low surface area, high cost, poor thermal and mechanical properties [27]. Physical or chemical modification of chitosan using different materials has been studied to improve its properties and adsorption capacity. Chitosan composites such as chitosan–cellulose [22], chitosan–zeolite [28], chitosan–polyaniline [29], and graphite oxide–magnetic chitosan [30] have been developed that exhibit better adsorption together with enhancement in other physical and chemical properties. The development of chitosan-based biocomposites will bring down the overall cost of the adsorbent owing to decrease in the use of expensive chitosan, and provide an opportunity for utilizing the renewable by-products produced in industries.

Table 1
List of different biosorbents and their sorption capacity for adsorption of dyes and metal ions as reported in literature.

Biosorbent	Dye/metal ion	Biosorption capacity (mg g^{-1})	References
Lignin	Cr(III)	17.97	[4]
Palm shell powder	Reactive Blue 21	24.86	[13]
Peroxide treated rice husk	Malachite Green	26.6	[15]
Tunisian activated lignin	Methylene Blue	147	[17]
Lignin from sugarcane bagasse	Methylene Blue	34.20	[18]
Chitosan	Cr(VI)	7.94	[19]
Immobilized green algae *Scenedesmus quadricauda*	RBBR	68	[20]
Garden Grass	Cu(II)	58.34	[21]
Cellulose–chitosan composite	Cu(II)	75.82	[22]
Chitosan–alkali lignin composite	RBBR	111.11	This work

Development of biodegradable chitosan–alkali lignin composites for dye and metal ion adsorption is a new area of application of alkali lignin. To the best of our knowledge, this is the first work to report the removal of effluents from wastewater using chitosan–alkali lignin composites with enhanced physicochemical properties. In this work, novel chitosan–alkali lignin composites were prepared, and characterized using various techniques like Fourier transform infrared spectroscopy (FT-IR), thermogravimetric analysis (TGA), scanning electron microscopy (SEM) and porosimetry to establish the molecular structure, thermal stability, surface morphology and specific surface area of the composites, respectively. The adsorption of RBBR and Cr(VI) ion on chitosan, alkali lignin and chitosan–alkali lignin composites was evaluated. Adsorption conditions such as chitosan content in the composite, solution pH and adsorbent concentration were optimized. Equilibrium adsorption isotherms and adsorption kinetics were evaluated. The dye and metal ion adsorbed composites were characterized and the mechanism of adsorption of RBBR and Cr(VI) on the composite active sites was proposed.

2. Experimental section

2.1. Materials

Chitosan (95% deacetylated) and Remazol Brilliant Blue R (C.I. 61200; $C_{22}H_{16}N_2Na_2O_{11}S_3$; MW 626.54 g mol^{-1}) were purchased