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Biomass Waste Derived Sustainable Natural Biopolymer Chitosan for Wastewater Treatment

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Abstract

Discharge of untreated wastewater by textile industries causes environmental, health, and aquatic life problems which requires urgent development of cost-effective and sustainable materials that can be integrated with innovative treatment technologies to address water scarcity. Chitosan (CHT), an eco-friendly versatile biopolymer, extracted from shrimp and crab shells, has huge potential in sustainable wastewater treatment applications owing to its biodegradability, excellent adsorbing and film forming capability. In this study, we employed Monte Carlo (MC) simulation approach to investigate the adsorption of hazardous anionic, cationic and neutral dye pollutants comprised of reactive, basic, and disperse classes on CHT (110) surface material. The obtained adsorption energy in Kcal/mol against CHT was found in the order of anionic RR195 (-996.1) > anionic RO16 (-753.5), cationic BV10 (-635.5) > neutral DY3 (-627.7) dyes which indicated a spontaneous adsorption process with physisorption playing a dominant role through electrostatic and van der Waals interactions. Our research emphasized the utilization of CHT biopolymer which has excellent potential in coagulation, flocculation, adsorption, and membrane separation wastewater treatment processes. Our investigation also scrutinized challenges and future prospects of CHT-based materials, emphasizing the potential role of this natural biopolymer in promoting sustainable water pollution management practices.

Keywords: Adsorption Energy, Biopolymer Chitosan, Monte Carlo Simulations, Sustainable Wastewater Treatment.

1. INTRODUCTION

The textile industry is one of the major industries of Pakistan, contributing 8.5% of GDP and employing 40% of the workforce [1]. The industry also generates over 5.2 billion US dollars which accounts for 60% of the country's exports [2]. The sector contributes about 46% of the total industrial production and 9% of the Gross National Product (GNP) of the country [3]. On the contrary, it poses a serious threat to the environment such as water overconsumption and water pollution. Every year, water pollution is worsened by approximately 450,000 tons of dyes that are produced, as 40 liters of water is required to dye 1 kg of cloth, resulting in enormous quantities of wastewater [4, 5]. Even more alarming is the fact that only 1% of textile generated wastewater is treated, which is far below the sustainable development goal targets, *i.e.,* 50% [6]. The untreated textile effluents contain toxic organic water pollutants such as dyes which poses a great threat to human health [7]. Moreover, dye pollutants affect aquatic ecosystems leading to the loss of biodiversity, and harming fish and other wildlife [8]. It also affects soil quality which causes the reduction in agricultural productivity [9].

The development of sustainable, energy-efficient, cost-effective and easy to implement wastewater purification technologies becomes essential [10]. By harnessing the potential of innovative water treatment technologies, Pakistan can make significant progress in addressing its water crisis and achieving SDGs [11]. An efficient and sustainable wastewater treatment contributes to reducing water waste, lessening the strain on natural water resources, and fostering a route toward clean energy [12]. Wastewater treatment occurs through a series of steps, including coagulation, flocculation, sedimentation, filtration, and disinfection. Advanced wastewater treatment technologies such as adsorption and membrane separation can produce high-quality recycled water suitable for agriculture, industrial use, and irrigation which in turn conserves fresh water [13-15]. Out of different treatment methods available, physical treatment involving adsorption using abundant biomass waste outperforms over other methods [16].

Owing to the environmental toxicity and secondary pollution caused by graphene, activated carbon, and carbon nanotubes, water treatment research has been shifted towards the environmental friendly natural materials [17-21]. Natural bio-based materials (BBMs) produced from biomass (*e.g.,* cellulose, pectin, alginate and chitosan) are not only cost-effective but also possess valuable functional groups (*e.g.,* hydroxyl, carboxyl, amino) for effective contaminant adsorption. BBMs align with environmental conservation and sustainability goals because of their excellent physicochemical attributes, chemical stability, and significant specificity towards dyes, aromatic compounds and toxic metals [22]. Among BBMs, chitosan (CHT) outperforms in wastewater treatment due to its abundance, excellent adsorption capability and antimicrobial activity [23-25]. Despite its huge potential, few computational studies are found addressing the adsorption capability of chitosan against persistent wastewater pollutants. Present study aims to understand the adsorption behaviour of four different types of persistent wastewater dyes, *i.e.*, azo, reactive, basic and disperse (RR195, RO16, BV10, DY3) on chitosan (110) surface using Monte Carlo simulations.

2. MATERIALS AND METHODS

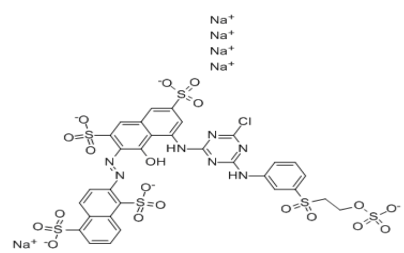
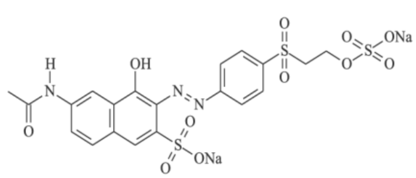
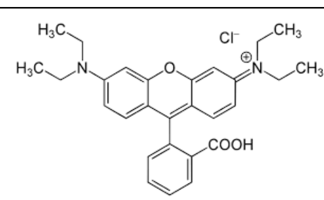
2.1. Selection of Dyes

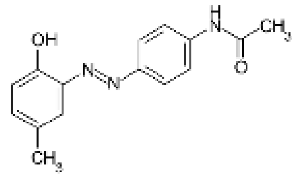
Four different dyes were selected by reviewing persistency in textile effluents collected from different cities of Pakistan [26-29]. Two anionic, reactive red 195 (RR195) and reactive orange 16 (RO16), one cationic, basic violet 10 (BV10), and one neutral, disperse yellow 3 (DY3), bearing molecular mass ranging from 1136.3 to 269.3 g/mol were shortlisted as displayed in Table 1.

2.2. Modeling of Pollutants and Material Surface

Four selected dye (RR195, RO16, BV10, DY3) structures were modeled in Materials Studio 2020 (Accelrys Inc., San Diego) and then converted into suitable format for subsequent geometry optimization. Chitin crystallographic information file (CIF) bearing entry 1501776 was fetched from the Crystallography Open Database (COD) and modified by deleting acetyl group to form deacetylated polymer chitosan [30, 31]. Chitosan crystal containing two monomers was cleaved in (110) surface. Cleaved chitosan (110) slab was extended with thickness value 3 and then repeated in 2 × 3 supercell dimensions having 20 Å vacuum in C direction. COMPASS II force field was used to assign charges and optimize dye pollutants and material surface with ultrafine quality and SMART algorithm [32]. Atom-based and Ewald procedures were employed to calculate the van der Walls with a cut off distance of 18.5 Å and electrostatic interaction energies with an accuracy of 2.0×10^{-5} kcal/mol, respectively [33, 34]. Figure 1 shows the pictorial presentation of optimized structures of four dyes and designing of chitosan surface from chitin crystal information.

Table 1: Selected dyes, their CAS-ID, 2D structures and their hazards.

S#	Dye Types / Names	2D Structure / Molecular Formula	CAS# / Molar Mass (g/mol)	Hazards
1	**Azo** Anionic Reactive Red 195 **(RR195)**	 $C_{31}H_{19}ClN_7O_{19}S_6.5Na$	93050-79-4 1136.3	Teratogenicity, carcinogenicity, nervous system diseases, neurotoxicity, and reproductive disorders
2	**Azo** Anionic Reactive Orange 16 **(RO16)**	 $C_{20}H_{17}N_3O_{11}S_3.2Na$	20262-58-2 617.5	Same as above
3	**Basic** Cationic Basic Violet 10 **(BV10)**	 $C_{28}H_{31}N_2O_3.Cl$	81-88-9 479	Neurotoxin, severe skin and eye allergies, and gastrointestinal disorders

4	**Disperse** Neutral Disperse Yellow 3 **(DY3)**	 $C_{15}H_{15}N_3O_2$	2832-40-8 269.3	Allergic contact dermatitis, carcinogenicity

2.3. Monte Carlo Simulations

The metropolis Monte Carlo simulation of each system (dye and chitosan) was performed with and without water using the Adsorption Locator module which simulates an adsorbent surface loaded with an adsorbate to find low energy adsorption sites [35]. Water and dyes were designated as adsorbate and chitosan (110) as adsorbent surface. Each system comprised one molecule of respective dye and one chitosan (110) slab. In case of aqueous medium, fifty water molecules were added additionally. Simulated annealing approach comprised of 5 successive heating-cooling cycles with 50000 steps per cycle covering automatic temperature control of 100 K to explore the adsorption energy (E_{ad}) of dyes onto chitosan (110) surface. Adsorption energy E_{ad} is defined as;

$$\mathbf{E_{ad} = E_{complex} - (E_{surface} + E_{dye})}$$

Where E_{dye}, $E_{surface}$, and $E_{complex}$ represent the potential energy of dye, chitosan slab (surface), and the complex of adsorbed dye on the slab, respectively.

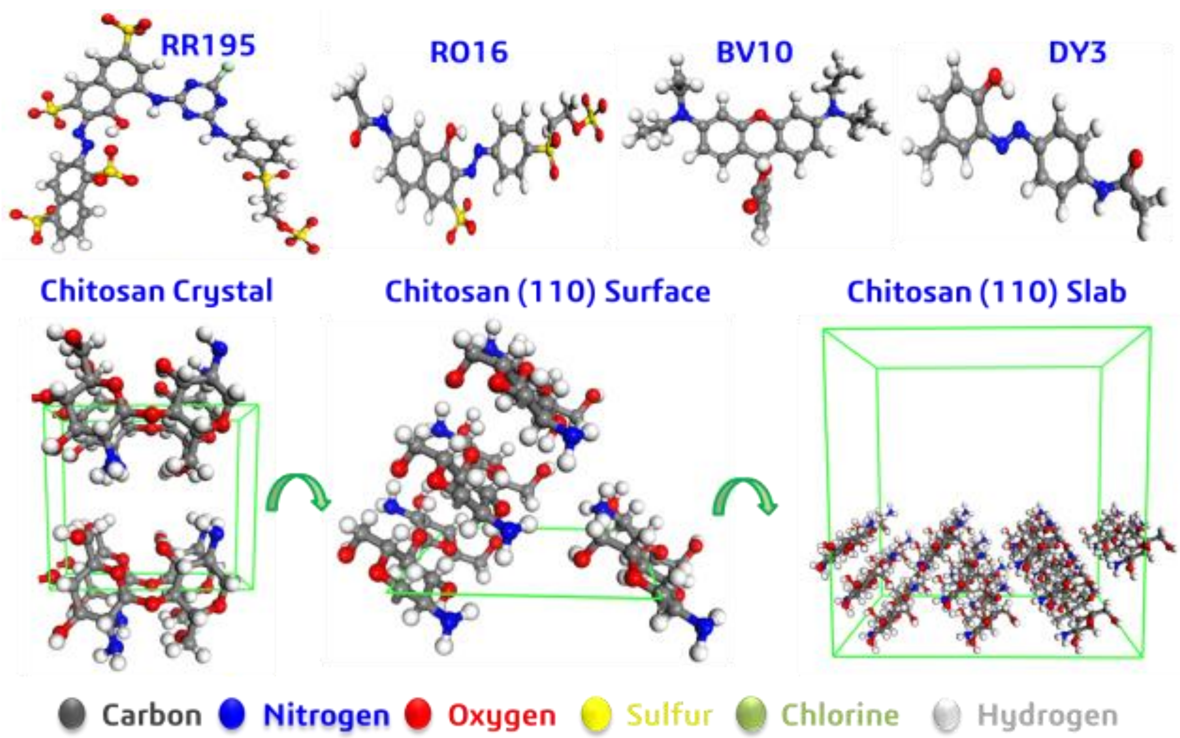


Figure 1: The optimized structures of four dyes (RR195, RO16, BV10, DY3) and designing stages of chitosan (110) surface.

3. RESULTS AND DISCUSSION

3.1. Monte Carlo Simulations

MC simulations assessed how different dyes bind to the adsorbent and facilitated a robust dye adsorption behaviour analysis in presence and absence of water. Adsorption energy will then be used to find a relationship between the reactivity of dye pollutants and their adsorption sites. Table 2 summarized different energy values obtained using the Adsorption Locator module for each chitosan (110)/dye complex in absence and presence of water. Descriptors obtained from MC simulations include the total energy (E_{Total}) of the dye-slab configurations, the rigid adsorption energy (RAE), the deformation energy (E_{Def}), the adsorption energy (E_{Ads} = E_{Def} + RAE). Further, additional energy descriptors were found where one of the adsorbate species (dye or water) has been removed (dE_{Ads}/dNi_{dye}) and (dE_{Ads}/dNi_{H2O}), respectively.

Table 2: Energy in kcal/mol obtained from adsorption locator for adsorption of RR195, RO16, DY3, and BV10 dyes on chitosan (110) surface in presence and absence of water.

Dye System	E_{Total}	E_{Ads}	**RAE**	E_{Def}	dE_{Ads}/dNi_{dye}	dE_{Ads}/dNi_{H2O}
RR195	-94.90	-291.1	-252.3	-38.79	-291.1	-
RR195/Water	-411.6	-996.1	-601.5	-394.6	-528.7	-31.57
RO16	-124.5	-88.34	-81.53	-6.817	-88.34	-
RO16/Water	-401.4	-753.5	-377.4	-376.2	-286.2	-30.02
BV10	-84.81	-36.34	-38.16	1.830	-36.34	-
BV10/Water	-295.6	-635.5	-255.7	-379.7	-50.98	-28.07
DY3	-95.53	-37.49	-39.35	1.850	-37.49	-
DY3/Water	-297.4	-627.7	-247.7	-380.0	-41.44	-29.38

The adsorption energy (E_{Ads}) is the most important descriptor to understand the strength of adsorption process and the nature of interaction. Negative values of the (E_{Ads}) show that all dyes could favourably interact with the chitosan slab. Moreover, all adsorption energy values in presence of water (-996.1 to -627.7) are very high than the values obtained in vacuum (-291.1 to -36.34) provided that adsorption process is more favourable in an aqueous phase. It is observed that the order of adsorption onto the chitosan slab is as follows; *i.e.,* RR195 (-996.1) > RO16 (-753.5) > BV10 (-635.5) ≈ DY3 (-627.7) which means dyes carrying negative charge adsorbed more strongly than cationic and neutral dyes. Furthermore, the high molecular weight of dye is responsible for more strong interactions than the dye carrying comparatively less molecular size, *i.e.;* (1136.3 > 617.5 > 479 ≈ 269.3 g/mol). Deformation energy refers to the energy due to relaxation of the dye onto the chitosan slab. High negative values in presence of water than lower values in vacuum suggested that the adsorption of dyes is more stable in aqueous phase. Comparison between differential energy descriptors for the removal of dye (dE_{Ads}/dNi_{dye}) or water (dE_{Ads}/dNi_{H2O}) clearly indicated that water removal is far easier than the removal of dye. We found almost similar values, *i.e.,* (-31.57, -30.02, -29.38, -28.07) for the removal of water due to the same charge, size and quantity of water molecules. However, ease for removal of each dye depends on their charge and molecular size. For instance, higher negative values were obtained for the removal of bigger size anionic RR195 (-528.7), RO16 (-286.2) dyes as compared to low molecular weight cationic BV10 (-50.98) and neutral DY3 (-41.44) dyes in an aqueous medium.

Figure 2A and 2B shows preferred adsorbed configurations of four dyes (RR195, RO16, BV10, DY3) onto chitosan (110) surface in absence and presence of water, respectively. In aqueous medium, solvation process further enhances the adsorption of dyes. It is because; the presence of water molecules increases the formation and stability of dye-chitosan interactions. Anionic dyes (RR195 and RO16) established strong hydrogen bonding interactions between their sulfonic acid group and chitosan hydroxyl (OH) and amidic (NH_2) groups. Whereas, cationic (BV10) and neutral (DY3) were able to create van der Waals interactions mostly.

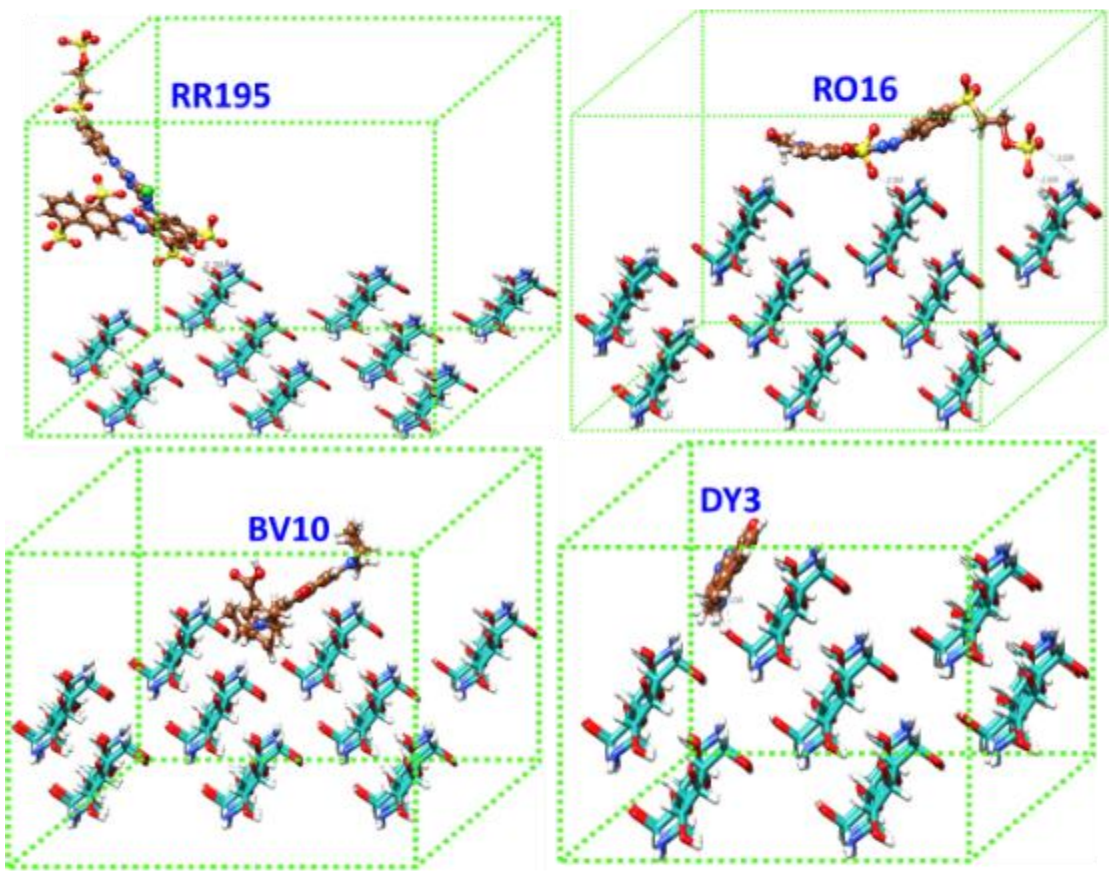


Figure 2A: The adsorbed configurations of four dyes (RR195, RO16, BV10, DY3) in absence of water onto chitosan (110) surface.

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From the comparison of Figure 2A and 2B, it is obvious that the role of surrounded water molecules is more pronounced in the stability of dye-chitosan interactions. Adsorption of all dyes seemed to be more stable and firmed in the presence of water which means selected dyes from wastewater streams could be strongly adsorbed and removed by the use of chitosan surface. A comprehensive 2D diagram illustrating the mechanism of dye-chitosan binding is shown in Figure 3.

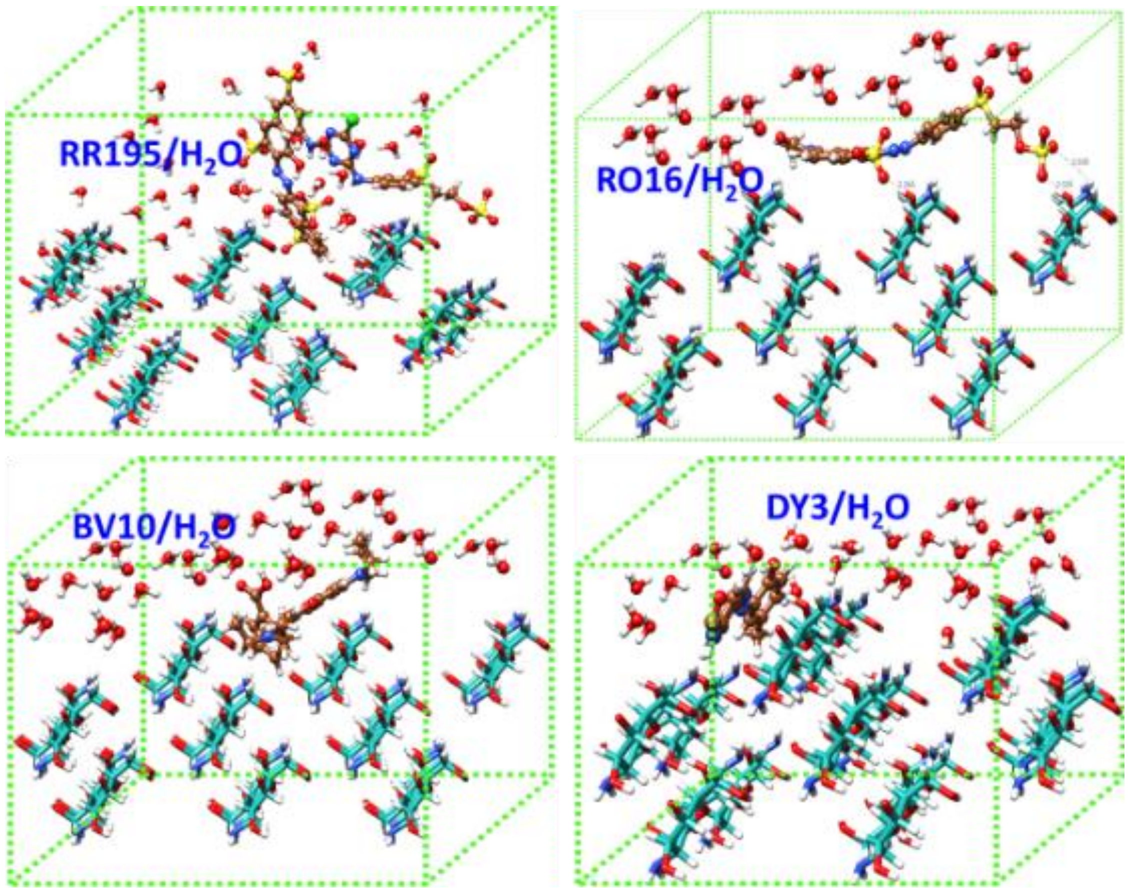

Figure 2B: The adsorbed configurations of four dyes (RR195, RO16, BV10, DY3) in presence of water onto chitosan (110) surface.

3.2. Comparison with Experimental and Computational Studies

Our results aligned with the previous experimental observations where mitigation of wastewater pollutants has been achieved by the use of chitosan in diverse material forms like beads [36], hydrogels [37], adsorbents and separation membranes [38]. Further, chitosan has the effect of chelate formation that can be combined with colloidal and suspended particles in water to form larger flocculates and their easy removal [39]. Chitosan based composite membranes can also be exploited in pressure driven separation processes such as ultrafiltration, nanofiltration, and reverse osmosis for effective and diversified wastewater treatment [40]. We further extend our discussion by the comprehensive comparison of our findings with the various experimental and computational studies on chitosan and its composites as adsorbent material. Reactive red 195 (RR195) removal using chitosan particles was studied by J. Perez-Calderon *et al.* showing favorable thermodynamics with maximum monolayer adsorption capacity (*Qm*) of 82.1 $mg.g^{-1}$ at pH=4 and 318 K which means 84.2% removal in 10 h at the 300 mg/L initial concentration [41]. Further, the study also indicated the successful utilization of chitosan particles in adsorption/desorption cycles emphasizing the regeneration and reusability of the adsorbent [41]. The author further improved their results by using cross linked chitosan/oxalic acid hydrogels by achieving 90.6% removal efficiency [42]. Reactive orange 16 (RO16) removal using chitosan-bentonite beads was studied by A. Benhouria *et al.* showing favorable thermodynamics and physical nature with maximum monolayer adsorption capacity (*Qm*) of 55.27 $mg.g^{-1}$ at pH=3-10, 328 K, and 300 mg/L initial concentration [43]. Rhodamine B (RhB or BV10) removal was studied by Pompeu *et al.* using nano-porous semi crystalline chitosan showing maximum adsorption capacity (*Qm*) of 505.131 $mg.g^{-1}$ [44]. Table 3 shows the comparison between adsorption energies of various anionic dyes obtained through adsorption locator using similar MC simulation parameters [45, 46]. By the careful analysis of adsorption energies obtained for anionic dyes shown in Table 3, it is obvious that chitosan (110) surface binds preferably anionic dyes with high adsorption energy followed by cationic and neutral dyes. In summary, use of sustainable natural biopolymer chitosan can play a crucial role in addressing wastewater treatment problems which will ultimately help in managing water crisis, particularly in the context of climate change, by reducing the strain on freshwater resources.

Table 3: Comparison of adsorption energy in kcal/mol cited from different studies on chitosan (110) surface for the adsorption of cationic and anionic dyes.

Dye/Water	**Type of Dye**	**E_{Ads}**	**Reference**
Eriochrome Black (EB^{3-}) / 400 H_2O	anionic	−1046.30	[45]
Eriochrome Black (HEB^{2-}) / 400 H_2O	anionic	−1052.49	[45]
Eriochrome Black (H_2EB^{-}) / 400 H_2O	anionic	−1042.53	[45]
Tartrazine (TRZ) /150 H_2O	anionic	-8459.71	[46]
Sunset Yellow (SSY) /150 H_2O	anionic	-5278.01	[46]
Brilliant Blue (BRB) /150 H_2O	anionic	-2486.50	[46]
Reactive Red 195 (RR195) / 20 H_2O	anionic	-996.1	this work
Reactive Orange 16 (RO16) / 20 H_2O	anionic	-753.5	this work
Basic Violet 10 (BV10) / 20 H_2O	cationic	-635.5	this work
Disperse Yellow 3 (DY3) / 20 H_2O	neutral	-627.7	this work

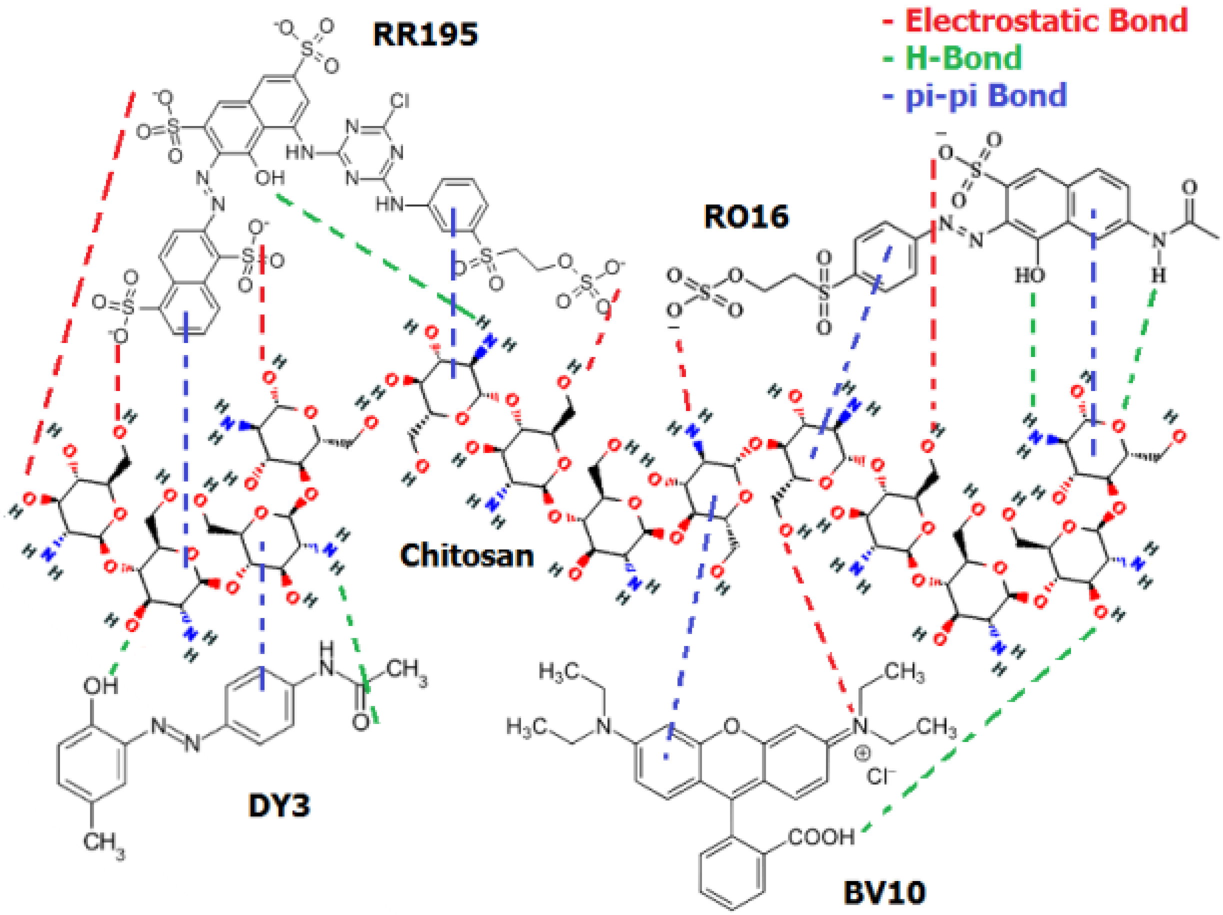

Figure 3: Schematic illustration of the adsorption mechanism of four dyes (RR195, RO16, BV10, DY3) on chitosan.

4. CONCLUSION

As climate change exacerbates water scarcity, adopting sustainable natural biomass derived materials for wastewater treatment can enhance water recycling and ensure a more resilient water management system. Our study summarized the use of chitosan (110) surface as case study using Monte Carlo simulations for the effective adsorption and removal of four hazardous dyes comprising reactive, basic and disperse classes. RR195 and RO16 are bigger in size and anionic in nature which contributes their strong and stable interactions with chitosan slab. While, being cationic BV10 and neutral DY3, were able to create van der Waals interactions on the chitosan surface. Future research opportunities include chitosan composites which would be able to mitigate broad range of contaminants using computational guided modeling. For the implication of chitosan in the real-world wastewater scenarios, associated challenges such as limited durability, stability under varying conditions, reduced efficiency for certain complex contaminants, and difficulties in ensuring reusability need to be addressed.

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