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ROLE OF FUNCTIONALIZED CHITIN-EDTA AS A PROMISING ADSORBENT FOR WATER PURIFICATION

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ABSTRACT

Reactive chemical dyes widely used in colouring fabrics are primarily responsible for contaminating water leading to rampant water pollution. In this paper, we report the synthesis of Chitin modified with EDTA nanoparticles and its efficacy as a dye adsorbent. Physicochemical techniques such as XRD, SEM, and FTIR have been used for characterizing the as-synthesized nanocomposite. The synthesized nanocomposite was examined to check its adsorption efficacy with respect to Rhodamine 6G dye as a function of various variables. The adsorption equilibrium for EDTA-CH nanocomposite was determined using various isotherm models. The thermodynamic parameters ΔG^0, ΔS^0, and ΔH^0 were also evaluated to check the dynamics of the dye adsorption process on EDTA-CH biopolymer. Our analysis showed that EDTA-CH can effectively adsorb cationic dyes and thus help in solving the problem of water pollution.

Keywords: Adsorption, Isotherms, EDTA, Chitin, Rhodamine 6G, Adsorption Capacity.

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INTRODUCTION

Water pollution, mainly by metal ions, dyes, and some other components, has attracted researchers' attention due to its important role in environmental degradation in our already fragile ecosystem.[1-4] With the advent of rampant industrialization and commercialization, in recent years, natural dyes which were relatively benign, have been superseded by cheaper but toxic artificial chemical dyes.[5-7] Rhodamine 6G (R6G) dye, a chemical dye, despite being highly poisonous, carcinogenic, and explosive in nature, is widely used in fabric and plastic manufacture for colouring, causing a serious threat to the ecology and environment.[8,9] Since most cationic dyes are characterized by an aromatic structure and xenobiotic qualities, they are difficult to break down and are linked to mutagenic and carcinogenic effects. The adsorption method especially is a popular technique used in the water purification industry owing to its cost-effectiveness, eco-friendly nature, and adaptability.[10-14] These adsorbents, however, separate with difficulty from the solution and require frequent regeneration. To compensate for these shortcomings, several attempts have been undertaken to create ecologically benign materials that exhibit selective dye adsorption and can be readily separated. For this purpose, Chitin (CH) which is a long-chain polymer of N-acetyl glucosamine, an amide derivative of glucose after being chemically modified was employed.[15] The present research work is focussed on the fabrication of a stable, cost-effective, and reusable nano adsorbent for R6G dye that can be used in practical applications towards water treatment. To this purpose, CH modified with Ethylenediaminetetraacetic acid (EDTA) nanoparticles were synthesized utilizing a one-pot co-precipitation approach as it is known to improve the aggregation of dye onto fabrics.[16] The dependence of the adsorption capacity of the EDTA- CH complex towards reactive dyes in aqueous solution on various factors was also investigated in detail. The data were then fitted into various adsorption isotherm models and the relevant parameters were calculated. It is pertinent to mention

that the synthesized material discussed here had never previously been examined for R6G adsorption to the best of our knowledge.

EXPERIMENTAL

Material and Methods

Analytical reagents were used throughout this work. Rhodamine 6G (λ_{max} = 526 nm in water), Chitin (99%), Hydrochloric acid (35%), Methanol, Sodium Hydroxide (97%), Acetic acid (35%), and Ethylenediaminetetraacetic acid (EDTA), were procured from Merck. The pH was adjusted by adding 0.5 M Sodium Hydroxide and 0.5 M Hydrochloric acid. Throughout the synthesis process, we used distilled water.

Synthesis of EDTA-CH

EDTA bis anhydride suspended in methanol was added to a Chitin solution in aqueous acetic acid (10%) and agitated for about 24 hours at room temperature.[17] Ethanol was mixed with the precipitate obtained and stirred for 12 hours after filtering. An effective pH value of 11 was obtained by adding 0.1 M NaOH solution to the precipitate. The functionalized EDTA-CH was then filtered and the precipitate was rinsed thoroughly with water. The precipitate was dried in the oven for a day at 40^0C to finally get a 42 % yield of a white solid.

Material Characterization

Analytical Techniques were used to characterize CH synthesized with EDTA samples. The morphological features of CH before and after alteration with EDTA molecules were determined using SEM (JEOL JSM 6610 at 20 kV). The crystallinity of the EDTA-CH material was determined by XRD (Bruker D8 Discover, Cu, 3 kW). FTIR spectroscopy (Thermo-Fisher NICOLET IS50, KBr pellets) was used to identify the surface functional groups of CH before and after EDTA treatment. A Perkin-Elmer PE-2400 micro elemental analyzer was used to determine the amounts of elements present.

Batch Adsorption Studies

The studies were performed to analyze the adsorption behavior of R6G dye as a function of various variables like temperature, time, etc. onto the functionalized EDTA-CH biopolymer. At the equilibrium stage, the adsorption capacity (q_e) of R6G onto functionalized EDTA-CH biopolymer was estimated.

RESULTS AND DISCUSSION

XRD Spectra Analysis

The XRD pattern shown in Fig.-1 was analysed for the parent compounds (EDTA and CH) and the resultant composite, to investigate the changes in the native lattice structure of the parent compounds due to the complex formation. The X-ray diffraction pattern of pure CH exhibits two characteristic broad peaks at 2θ = 10.1° and 2θ = 20.8°, followed by two smaller peaks between 2θ = 23.4° and 2θ = 26.2°.[18] The XRD pattern of EDTA shows the characteristic peaks of emission at 2θ = 28.5°, 2θ = 34.4° and 2θ = 56.5°.[19] The diffraction pattern of EDTA-CH reveals the characteristic diffraction peaks of both CH as well as EDTA nano particles confirming the successful synthesis of the desired nanocomposite.[20] While similarities between the XRD peaks of the parent compounds and the composite is observed, an exact correlation is not seen, hence it can be inferred that the lattice parameters of CH and EDTA have been altered due to their interaction and a primitive proof of the bonding of CH with EDTA is confirmed as desirable.

FTIR Spectra Analysis

The FTIR spectra of CH, EDTA, and the EDTA-CH complex in Fig.-2 indicates that the CH spectrum shows the characteristic stretching vibration bands occurring at various wave numbers. The spectra displayed an -OH group stretch at 3400 cm^{-1}, whereas the bands at 1659 and 1624 cm^{-1} in CH spectra correspond to Amide I stretching. The stretch bands at 1562 and 1320 cm^{-1} are a consequence of Amide II bending and Amide III stretching respectively, while the bands at 1077 cm^{-1} and 1035 cm^{-1} are brought about by both C-O-C and C-O stretching vibrations. A band at 1659 cm^{-1} is also evident due to C=O groups and N–H inside the same chain. An additional bond, responsible for enhanced thermal stability of CH, between the remaining C=O groups and the CH_2OH group of the side chain, results in the peak at

1624 cm^{-1}. In the EDTA spectrum, the band occurring at 1694 cm^{-1} is due to free C=O groups, whereas an amino band is seen at 1540 cm^{-1}.[21] Minor peaks at 3400-3500 cm^{-1} were also seen, indicating -NH_2 stretching vibrations. However, a substantial difference was noticed in the spectrum of the EDTA-CH complex with respect to the individual spectrums of CH and EDTA. It is observed that the peaks responsible for both C-O-C and C-O stretching vibrations in the CH spectrum at 1077 cm^{-1} and 1035 cm^{-1} are absent in the EDTA-CH spectra. Further, the broadband occurring at 3400-3500 cm^{-1} indicates a rise in -NH_2 and -OH groups stretching vibration due to the accumulation of -NH_2 and -OH functional groups of the biopolymer on the EDTA-CH complex.[22]

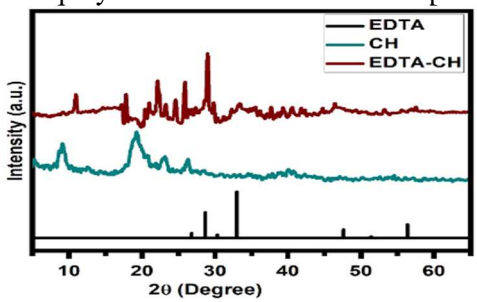

Fig.-1: XRD Curves of CH, EDTA, and EDTA-CH

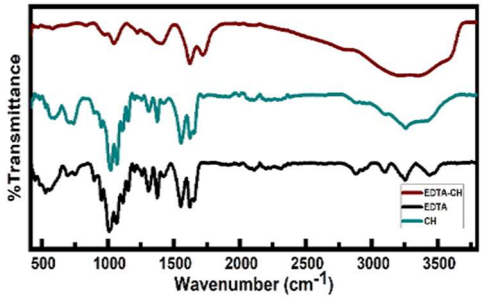

Fig.-2: FTIR Spectra of CH, EDTA, and EDTA-CH

SEM Analysis

The SEM images to check for surface irregularities before and after the interaction of the EDTA-CH with R6G dye are shown in Fig.-3. The SEM scan on the left shows the EDTA-CH nanocomposite surface before the dye was adsorbed, and the image on the right shows the EDTA-CH surface after the dye had been adsorbed. Before its interactions with the dye, the surface of the nanocomposite appears noticeably smoother in the image on the left (Scale 1µm). Finally, in the image on the right (Scale 50µm), a much rougher and more rugged surface is visible, serving as an indicator of the nanocomposite's ability to bind the dye indicating good adsorption capability.

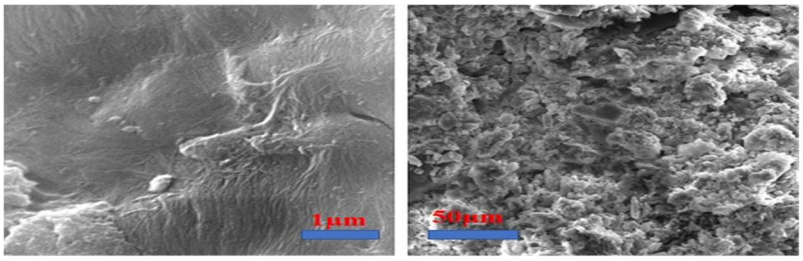

Fig.-3: SEM Images (L) Before Adsorption of Dye (R) After Adsorption of Dye

CHNS Analysis

Table-1 shows the carbon, hydrogen, and nitrogen contents of EDTA, CH, EDTA-CH, and R6G-EDTA-CH as ascertained by the elemental chemical analysis Technique (CHNS). It can be clearly seen that the proportion of carbon atoms (carboxyl group) in all four samples was consistently higher than that of the other elements. Although EDTA and CH contain relatively few nitrogen atoms (amine group) and hydrogen atoms (hydroxyl group) in their natural state, their percentage was found to increase as the EDTA-CH complexes and the adsorption process progresses. After dye adsorption, the R6G-EDTA-CH complex integrated 9.23% of nitrogen, 48.65% of carbon, and 6.54% of hydrogen, indicating that there was significant adsorption capacity.

Table-1: CHNS Analysis of EDTA, CH, EDTA-CH, and R6G-EDTA-CH

Sample	N%	C%	H%
EDTA	3.54	38.65	10.45
CH	3.23	51.23	3.22
EDTA-CH	8.42	41.69	4.95
R6G-EDTA-CH	9.23	48.65	6.54

Adsorption Parameters

We may observe the impact of a certain parameter on the adsorption behaviour of the adsorbent toward a particular pollutant by changing that parameter while maintaining the other factors constant for possible improved removal efficiency of pollutants.[23]

Effect of pH

The adsorption behaviour of functionalized EDTA-CH biopolymers was explored by changing pH from 1 to 12, while keeping the adsorbent dosage 0.005g and contact time 40 min. In comparison to acidic medium the functionalized EDTA-CH biopolymer shows superior adsorption capacity in the basic medium [Fig.-4(a)]. The adsorption capacity increases sharply at first as the pH increases and shows an improved sustained adsorption capacity when the medium becomes basic i.e., its pH exceeds 7, the reason being improved electrostatic interactions that exists amongst the dye and the adsorbent.

Effect of Temperature

As indicated in Fig.-4(b) adsorption capacity decreases as temperature rises to 350 K from 300 K. It was observed that there was a significant shift in adsorption capacity between 300-310 K and 340-350 K, with adsorption capacity 366-363 (mg/g) at 300-310 K and 351-348 (mg/g) at 340-350 K, indicating that temperature plays a significant part in determining adsorption capacity.

Effect of Time

From Fig.-4(c) we can see that with an increase in time up to 20 minutes the adsorption capacity shows a rapid increase initially, but progressively slows with further increase in time and gradually approaches equilibrium. Adsorption capacity peaked at 300-380 (mg/g) between 20 and 40 minutes, after which it became a constant, as seen by the line parallel to the x-axis.

Effect of Concentration of Dye

It is observed from Fig.-4(d) that the capacity of adsorption of EDTA-CH was markedly high when the dye concentration increased to 0.006 mg/L. After increasing the dye concentration, a slight growth in the adsorption capacity is observed which suggests saturation. The development of repulsive forces between the dye molecules that have been adsorbed may be responsible for the slowdown observed in the rate of adsorption.

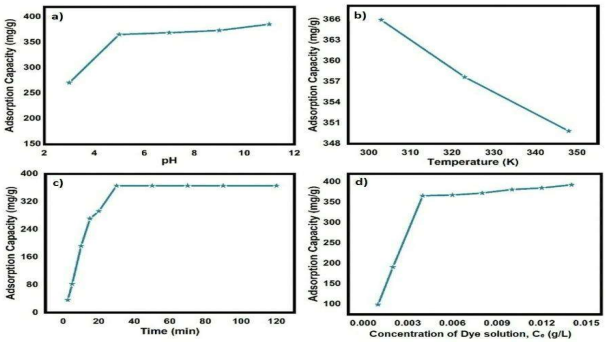

Fig.-4: Variation of Adsorption Capacity of EDTA-CH with (a) pH, (b) Temperature, (c) Contact Time, (d) Concentration of R6G Dye

Adsorption Isotherm Models

The adsorption equilibrium for EDTA-CH nanocomposite with various starting dye concentrations was investigated using four adsorption isotherms.[24-27] The experimentally recorded data was then fitted into four isotherm models. In Table-2, various parameters that have been evaluated pertaining to the four models considered are listed.[24-27] Graphs have been plotted using the linear equations representing the four isotherm models and are shown in Fig.-5. The relationship between dye and adsorbent has been investigated by analyzing the graphs. The Freundlich and Temkin isotherms are clearly more favourable than the other two isotherms (Langmuir and Dubinin Radushkevich), as seen in the graph. The regression coefficient (R^2) values were calculated for each adsorption model and are listed in Table-2. Since the regression coefficient (R^2) of Temkin was more than that of Freundlich and is showing the best fit, it is

surmised that it is the best-suited model suggesting multilayer adsorption. Figure-6 shows the combined linear data fit into all four isotherms models.

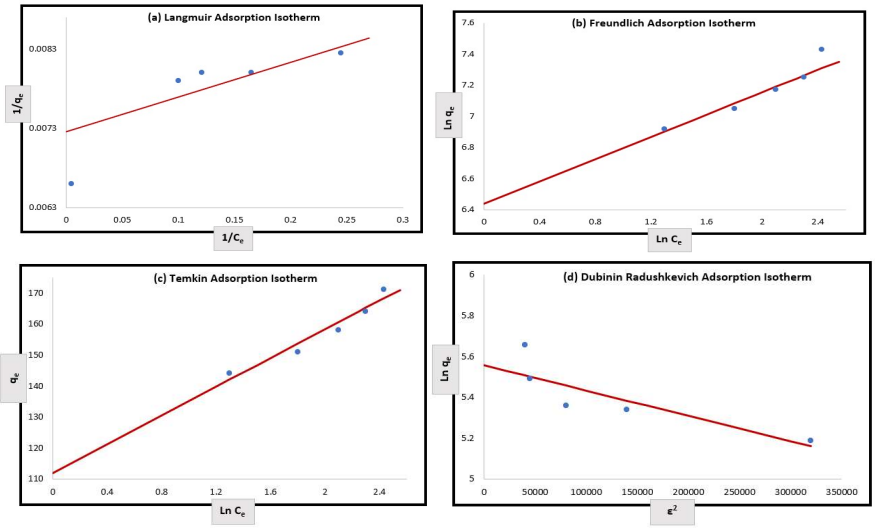

Fig.-5: Experimental Linear Data Fit into (a) Freundlich (b) Langmuir (c) Temkin (d) DR Isotherm

Table-2: Isotherm Parameters for Different Isotherm Models

Isotherm	Dyes	R6G
Langmuir	q_{max} (mg/g)	137.741
	K_L (L/mg)	1.66
	R^2	0.7608
Freundlich	K_F (L/mg)	625.192
	n	2.79236
	R^2	0.911
Temkin	B	23.15001
	K_T (L/mg)	125.9964
	R^2	0.94343
Dubinin–Radushkevich	β	1.24E-06
	q_s (mg/g)	259.039
	R^2	0.72249

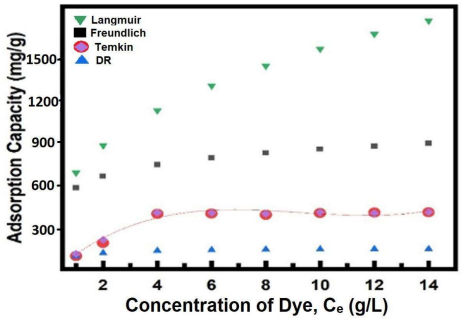

Fig.-6: Combined Linear Data Fit into Adsorption Models

Thermodynamic Study

The parameters ΔG^0 (Gibbs Free Energy Change), ΔS^0(Entropy Change), and ΔH^0(Enthalpy Change) are useful in determining the applicability of the adsorbent as decontaminant and were hence evaluated.[28] It is observed from Table-3 that the value of ΔG^0 for the R6G dye decreases when the temperature increases from 303 K to 348 K, indicating that for adsorption a low temperature is more favourable. The negative value of ΔG^0 suggests that the R6G dye adsorption on the EDTA-CH nanocomposite is spontaneous. It is also understood that the dye adsorption generates heat and is more orderly in view of ΔH^0 and ΔS^0 being negative respectively.

Table-3: Calculated Thermodynamic Parameters

Temp (K)	ΔG^0(KJmol^{-1})	ΔH^0 (KJmol^{-1})	ΔS^0 (KJmol^{-1})
303	-1.67	-10.76	-0.0300
323	-1.07		
348	-0.32		

CONCLUSION

In the current study, CH modified with EDTA nanoparticles were successfully synthesized and characterized by several techniques like SEM, XRD, and FTIR. The efficacy of the obtained nanocomposite as an adsorbent for R6G dye removal has been investigated by various techniques. EDTA-CH nanocomposite showed remarkable adsorption capacity for the R6G dye at room temperature for high pH values. The Temkin isotherm model best explained the equilibrium data experimentally obtained. It can also be inferred that the dye adsorption process analyzed in our work is exothermic, spontaneous and more orderly in view of ΔH^0, ΔG^0, and ΔS^0 being negative respectively. On the basis of our studies, we can say that EDTA-CH can be used as an efficient, cost effective and promising adsorbent for practical applications in elimination of cationic contaminants present in water.

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CONFLICT OF INTERESTS

The authors have no conflict of interest to declare.

AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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