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Efficient removal of methylene yellow dye with activated carbon-chitosan composite beads

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ABSTRACT

Pakistan is facing severe water scarcity and dealing with major water pollution problems, this study seeks to address these environmental challenges. The focus of this research is the development and application of activated carbon-based composite beads for contaminant removal and water purification. To achieve this goal, biopolymer composite beads were synthesized with chitosan (Cs) as matrix and activated carbon as filler, resulting in two types of beads: Cs blank beads and Cs/AC beads. The surface morphology of these beads was investigated by scanning electron microscopy (SEM) and the structure was elucidated by FTIR spectroscopy. The presence of chitosan polymer was verified at characteristic wavenumbers such as 3298 cm-1 (N-H stretching), 2905 cm-1 (C-H stretching), 1570 cm-1 (NH bending), 1377 cm-1 (C-O-C), and 1033 cm-1 (C-OH). Furthermore, the study investigated the adsorption capacity of Cs/AC beads in the case of the extraction of methylene yellow pigment, a common pollutant in water The adsorption efficiency was tested by carefully measuring variables such as time of concentration, adsorbent concentration and pH. An optimization system was used to maximize extraction efficiency. Notably, the adsorption/removal of methylene yellow dye commenced upon exposure to Cs/AC, and after 150 minutes, a steady state was reached (92% removal), indicating no further removal. Consequently, this time point was identified as the optimal contact duration for subsequent investigations. Besides, a slightly acidic pH of 7 within the solution, coupled with higher concentrations of the adsorbent, was identified as the optimal condition. This research provides valuable insights into mitigating water pollution and improving water quality in Pakistan through the development and utilization of advanced composite materials.

Keywords Water Pollution Mitigation; Activated Carbon-Chitosan Composites; Methylene Yellow; Surface Morphology; Composite Beads

1. INTRODUCTION

The expanding global population is consistently exerting a detrimental effect on water resources, primarily by intensifying water consumption and contaminating it. There exist numerous well-recognized water pollutants of both organic and inorganic origins, such as azo dyes, hazardous metals, pesticides, and more. Dye contamination of water resources has become an alarming environmental concern in recent years due to the extensive use of dyes in various industries, particularly the textile and dyeing industry. The dyeing process in the textile industry produces 10–15% of the dyes released to the environment (Purnaningtyas et al. 2020). Annually, a vast quantity of these dyes is manufactured, with the industrial production of dye compounds reaching approximately 7 x 10^{-5} tons (Oladoye et al. 2022). Usually, dyes are very stable in variable temperature, light and water and from the environment they are difficult to reduce or remove from environment during typical processes of water treatment and other biodegradation methods (Cheng et al. 2020, Couto 2009). Due to their toxic effects like mutagenic and harmful effect, these dyes become threat to aquatic life and humans. It is therefore inevitable for the dyes to be removed from wastewater (Zhou et al. 2014). Methylene yellow dye (cationic dye) is one of them which is widely used in industries and has several adverse impacts on human health and environment. (Dutta et al. 2021). Methylene yellow dye can be toxic, carcinogenic, and mutagenic, making it essential to remove it from industrial effluents and wastewater. It is therefore essential to use treatment strategies, aiming to ensure the sustainability of the environment to future generations through physical, chemical and biological technologies or a combination of them (Putri et al. 2021).

The treatment of dye waste has been carried out by various methods such as biological processes, coagulation/flocculation, membrane filtration, ozonation, ion-exchange, advanced oxidation processes, activated sludge processes, and adsorption (Dutta et al. 2021). In this technology, drying is one of the most important and useful purification methods. It is fast, cost-effective, simple, non-fouling, efficient and/or selective, mechanical stability, and recycling (Zhou et al. 2019) drying, as an effective and environmentally friendly method, for the

solvent extraction of synthetic materials from water It is widely recognized as a promising method (Li et al. 2022). High soil to increase adsorption efficiency and exploitation site Absorbents are used for crucial. Activated carbon, known for its remarkable adsorption properties, and chitosan, a biocompatible, biodegradable, and non-toxic polymer, have become prominent as potential attractants for synthetic solvents.

This manuscript examines the development of activated carbon-chitosan composites as effective adsorbents for the removal of methylene yellow dye from aqueous solutions The porous structure of activated carbon and synergistic combination of functional groups of chitosan are expected to provide a platform good for improved dye adsorption. The specific objectives of this study are (i) to synthesize activated carbon-chitosan composite beads and (ii) to investigate the adsorption of methylene yellow using these synthesized beads.

The research presented herein contributes to the growing knowledge on eco-friendly and cost-effective solutions for wastewater treatment and pollutant removal, addressing both environmental concerns and potential health hazards associated with dye contamination.

2. MATERIALS AND METHOD

2.1 Materials

Activated Carbon, Chitosan C-342, formic acid, methanol, ethanol, sodium hydroxide (NaOH), ethyl acetate, distilled water and acetone were purchased from Sigma Aldrich. For this study, methylene yellow of commercial grade was used.

2.2 Chitosan Beads Synthesis

To form the beads, approximately one gram of chitosan was placed in a 40 mL solution of 2% formic acid and stirred continuously at a uniform magnetic agitation speed of 30 rpm for a duration of 24 hours. This process yielded a homogenous chitosan solution. Simultaneously, a 10% NaOH gelation bath was prepared. The solution of chitosan was dissolved in NaOH bath using syringe pipette to form beads as shown in figure 1A The beads were subsequently rinsed multiple times to achieve a neutral pH level. The synthesized beads were then placed in a desiccator for further use.

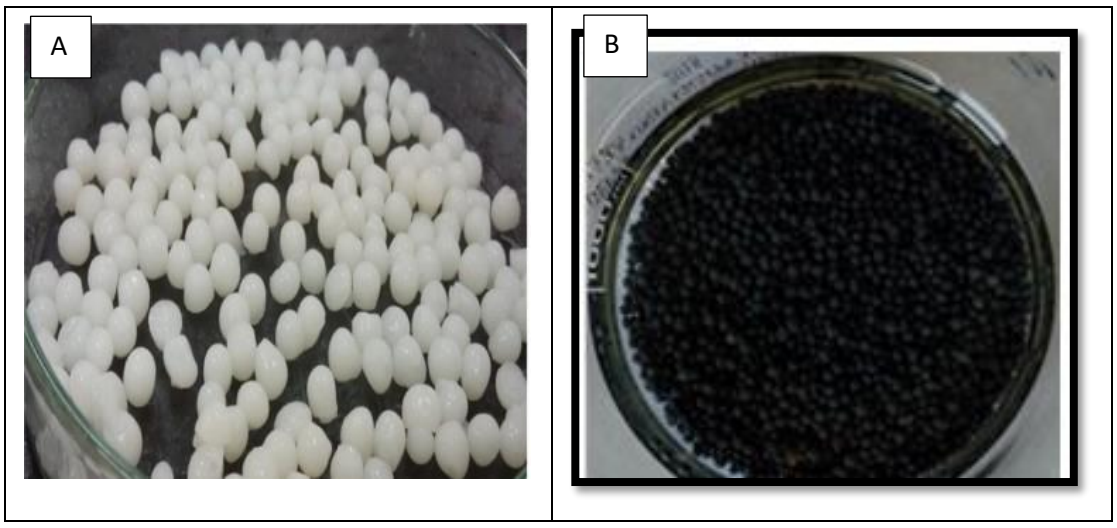

Figure 1. Chitosan Blank Beads, (A) and Chitosan/Activated Carbon Composite Beads (B).

2.3 Activated Carbon-based Chitosan Beads Synthesis

To prepare chitosan/activated carbon (Cs/AC) composite beads, one gram of chitosan was dissolved in a 40 mL solution of 2% formic acid and stirred continuously at a constant magnetic agitation speed of 300 rpm for 24 hours. This process resulted in the formation of a homogeneous chitosan solution. Simultaneously, 0.2 g of activated carbon was dispersed in water through sonication and added drop by drop into the chitosan solution, giving it a honey-like consistency.

The chitosan/activated carbon mixture was then carefully transferred using a syringe pipette into a bath containing 10% NaOH to create spherical beads (Fig. 1B). to achieve neutral pH beads were washed thoroughly several times and were stored in desicator for further use.

2.4 Characterization

The synthesized samples were characterized using advanced instrumentation techniques. Fourier Transmission

Infrared Spectroscopy (FTIR) measurements were made at 25ºC with spectrometer having spectrum 100, PerkinElmer spectrum version 10.4.00. The functional groups of the beads were detected b in the range of 4000–500 cm^{-1} at the resolution of 8.0 cm^{-1}.

The surface morphology and the dispersion of activated carbon in the developed beads was examined by using JEOL SEM-6480LV scanning electron microscope (SEM) operating at 120.0kV. SEM was used to observe the porous nature of Cs/AC beads.

2.5 Swelling Response

To evaluate the swelling response of the beads in distilled water for 120 minutes. i.e. composite beads (1g) were submerged in distilled water.

$$\boldsymbol{Swelling}\ \left(\frac{g}{g}\right) = \frac{(Ws-Wd)}{Ws} \quad (1)$$

where, Ws = swollen weight and Wd = dry weight

2.6 Batch Adsorption Reaction

2.6.1 Adsorption of Methylene Yellow Dye

The adsorption efficiency of the Activated Carbon-based Chitosan beads was assessed for the removal of methylene yellow dye using UV spectroscopy. Initially, a stock solution of methylene yellow of 100 mg/L was prepared and then further diluted to various working concentrations. The adsorption experiment was conducted at room temperature up to 150 minutes with 30 minutes interval. To establish adsorption-desorption equilibrium, the samples were kept in the dark for 60 minutes before the adsorption process was initiated. The adsorption studies were carried out using different parameters including adsorbent dosage (ranging from 1 to 1.5 g), dye concentration (5 ppm), and pH (1-14). The degradation (removal) of methylene yellow dye (%) was calculated using Equation (2).

$$\%\boldsymbol{degradation} = \frac{(A_0-A)}{A_0} \quad (2)$$

where ''A_0'' is the initial absorbance, and ''A'' is the absorbance of dye after light irradiation. The rate of degradation was evaluated by using Pseudo-first-order kinetic equation as Eq. (3)

$$\boldsymbol{ln\frac{C}{C_0} = kt} \quad (3)$$

k is the rate constant, ''C_0'' is absorbance before irradiation, and ''C'' represents the absorbance of the dye solution at time t.

2.6.2 Beer's Lambert Law

The concentration of a solution is calculated according to the Beer-Lambert law by measuring the absorbance of the solution, using the following equation

$$\boldsymbol{A = \varepsilon Cl} \quad (4)$$

where, A = absorbance; C = Concentration, ε = molar absorption coefficient; and l = path length.

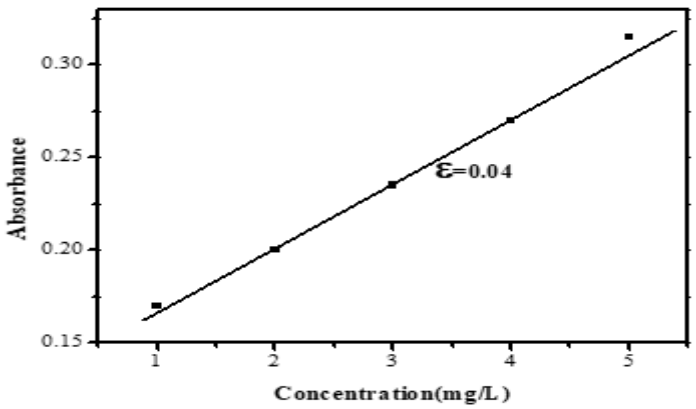

Figure 2. The calibration curve for absorption of methylene yellow dye.

The adsorption efficiency of the Cs/AC was assessed using different concentrations (1-5 ppm) of the dye as indicated in figure 2.

3. RESULTS & DISCUSSION

Biopolymer composite beads were created using chitosan (Cs) as the matrix material, with activated carbon serving as the filler for the synthesis of nanocomposite beads. Both Cs blank beads and Cs/AC beads were successfully synthesized. Comprehensive characterization of the prepared samples was performed, employing techniques such as SEM and FTIR, among others.

Furthermore, the sorption capabilities of these beads were evaluated, specifically focusing on their adsorption efficiency in the context of methylene yellow dye removal. UV spectroscopy was used in this study to evaluate the performance of Cs/AC beads in the dye adsorption process.

3.1 Surface Morphology of Composite Beads

The surface morphology of composite beads was examined by SEM, and micrographs are illustrated in Fig. 3 A & B. Figure 3A shows SEM micrographs of blank chitosan beads, which exhibit perfectly smooth surfaces due to chitosan's inherent property of being easily soluble in acidic solutions (Worthen et al. 2019). Pure chitosan (Cs) is not pore free and has a uniform and smooth surface (Kandil and Ali 2023).

On the other hand, figure 3B presents SEM micrographs of chitosan/activated carbon-based composite beads. Importantly, the surface morphology of the Cs/AC bead revealed better diffusion of the activated carbon filler in the chitosan matrix, which increased the porosity of the bead compared to the Cs-empty bead (Worthen et al. 2019). AC was found to be well dispersed in the Cs matrix as shown in figure 3B. The addition of activated carbon (AC) to chitosan (Cs) resulted in improved adhesion due to the compatibility and interaction between the hydroxyl (OH) groups on the AC surface and the OH and/or amino (NH_2) groups on Cs. Thus, the surface roughness of Cs beads increases with the addition of AC and this uneven texture of Cs/AC -based composite confirmed through SEM analysis suggests that the silicate palettes have been well-dispersed and tends to increase surface area (Anouar et al. 2019). This increased surface area of the Cs/AC- composite can enhance its ability to adsorb dyes, (Kandil and Ali 2023). The micrographs were taken at magnification levels of 1µm and 500 nm.

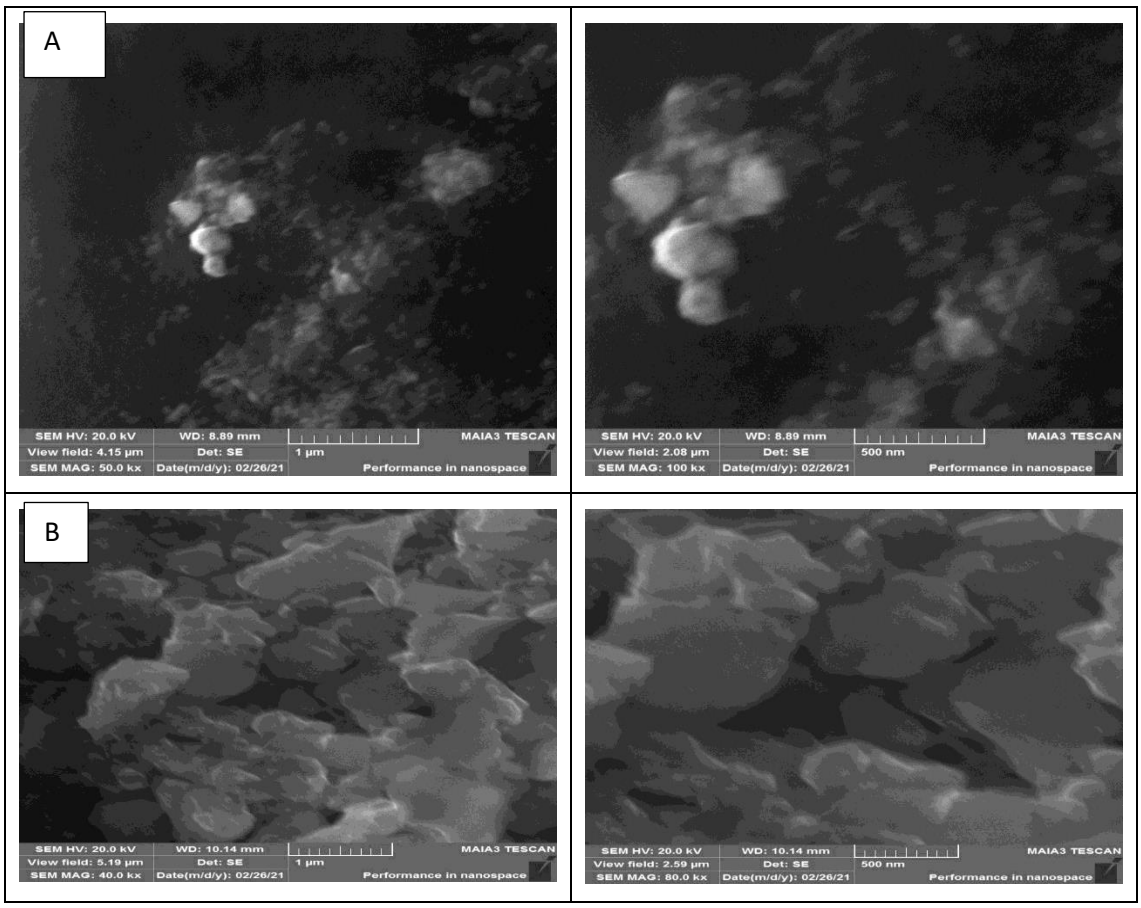

Figure 3. SEM images of (A) Cs Blank and (B) Cs/AC composite beads

3.2 Structural Analysis of Composite Beads

The structural analysis (the interaction between composite constituents) of the composite beads was conducted

using FTIR Spectroscopy. Figure 4A&B. shows the spectra of Cs blank and Cs/AC composite beads for comparison. Several characteristic peaks confirmed the presence of chitosan polymer. Notably, the bands at 3298 cm^{-1}, 2905 cm^{-1}, 1570 cm^{-1}, 1377 cm^{-1}, and 1033 cm^{-1} corresponded to N-H stretching, C-H stretching, NH bending, C-O-C, and C-OH, respectively (Ali & Ismail 2022; Swathi et al. 2021). The presence of activated carbon (AC) contributed to bands observed in the region of 3200-3300 cm^{-1}. The composite formation may take place as a result of interactions between OH groups on the surface of the activated carbon and OH and/or NH_2 groups on Cs.

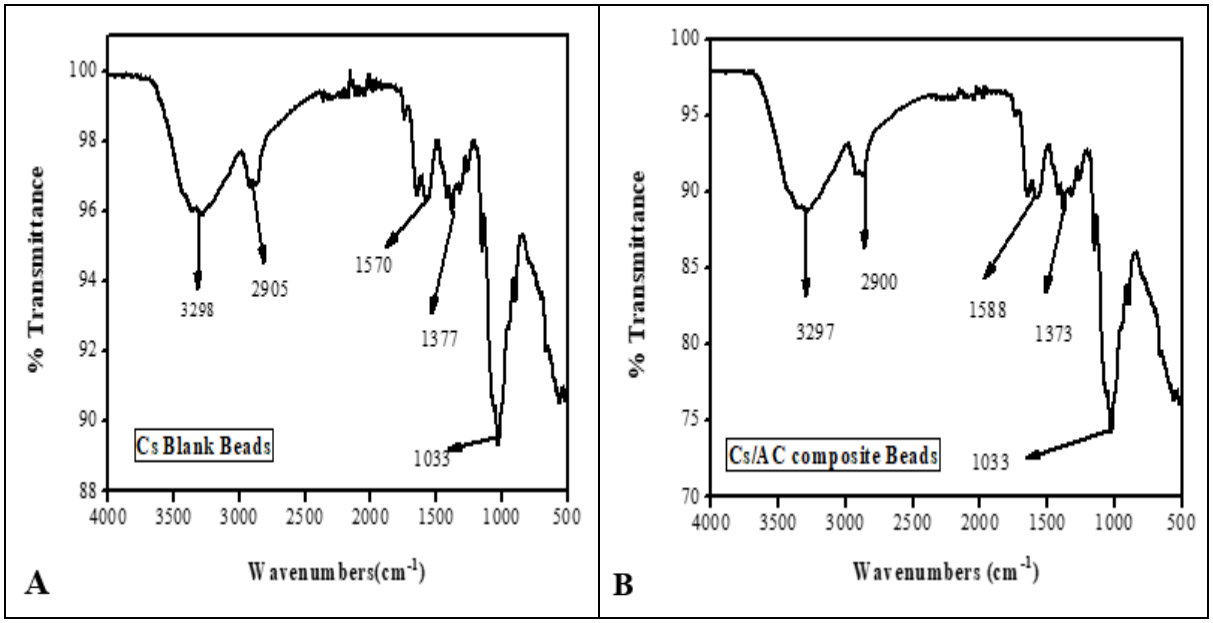

Figure 4. FTIR spectra of (A) CS blank and (B) Cs/AC Composite Beads

3.3 Swelling Behavior of Composite Beads

The swelling behavior of Cs blank and Cs/AC beads was examined, as depicted in figure 5. It's evident that Cs blanks exhibited a higher swelling capacity compared to Cs/AC. This is attributed to the inherent polymeric nature of Cs blank, which results in a higher swelling value. In contrast, the incorporation of AC within the chitosan composite beads led to a reduction in swelling. This highlights how the swelling capacity is altered when polymers are combined, and fillers are introduced into the composites.

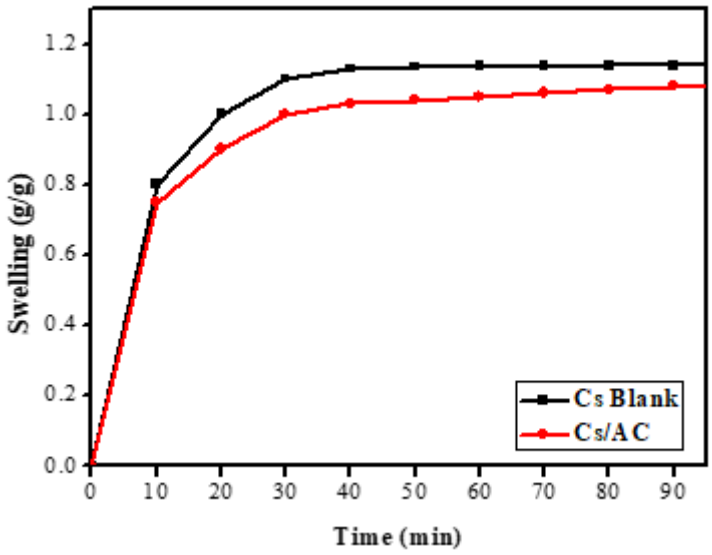

Figure 5. Swelling response of Cs blank (black line) and Cs/AC (red line) composite beads

3.4 Adsorption of Methylene Yellow Dye

Dye removal efficiency of the developed chitosan/activated carbon composites beads in comparison with pure chitosan (Cs) towards methylene yellow was evaluated by examining the adsorption performance of the prepared

samples. Activated carbon embedded in chitosan showed excellent adsorption efficiency for methylene yellow dye as observed in UV-vis spectroscopy. Various parameters affecting the adsorption process were optimized to achieve maximum degradation efficiency. These parameters are discussed as:

3.4.1 Determination of Maximum Wavelength

According to the report of Priyadharshini, et al. (2021) λmax for methylene yellow is 403 nm and during this study the λmax also appeared at 400nm (Figure 6).

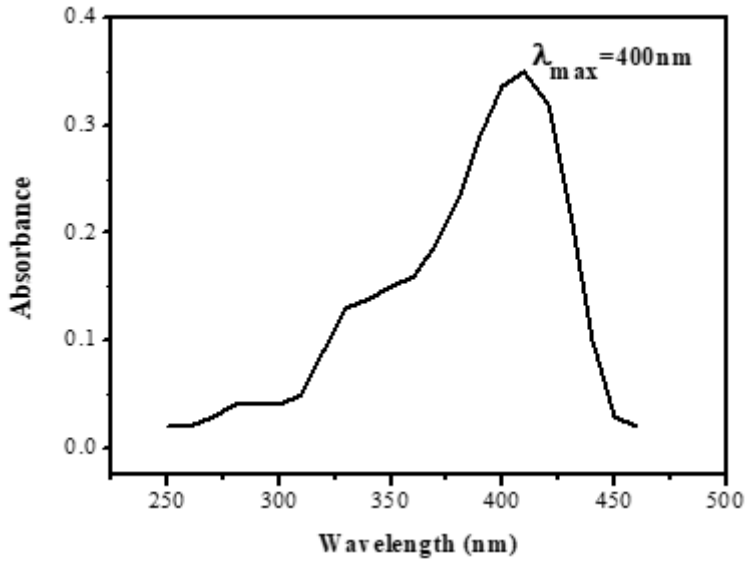

Figure 6. Determination of λmax for methylene yellow

3.4.2 Effect of Contact Time on Adsorption

Contact time is an important variable in adsorption processes. The adsorption of methylene yellow dye increased with an increase in contact time as can be seen in figure 7. It is apparent that an increase in contact time continuously decreases the absorbance, which confirms that the adsorption/removal of methylene yellow dye increases with an increase in contact time to the adsorbent. The spectrum showed that there was continuous adsorption/removal of methylene yellow dye started on exposure to Cs/AC composite beads and there was almost complete removal of dye after 150 minutes of exposure. So, this time was considered as optimum irradiation time for further study. At optimum adsorption time, 92% of removal was achieved. Therefore, it can be concluded that activated carbon incorporated with chitosan is an efficient adsorbent for adsorption of high concentration of methylene yellow dye in 150 minutes as indicated in figure 7.

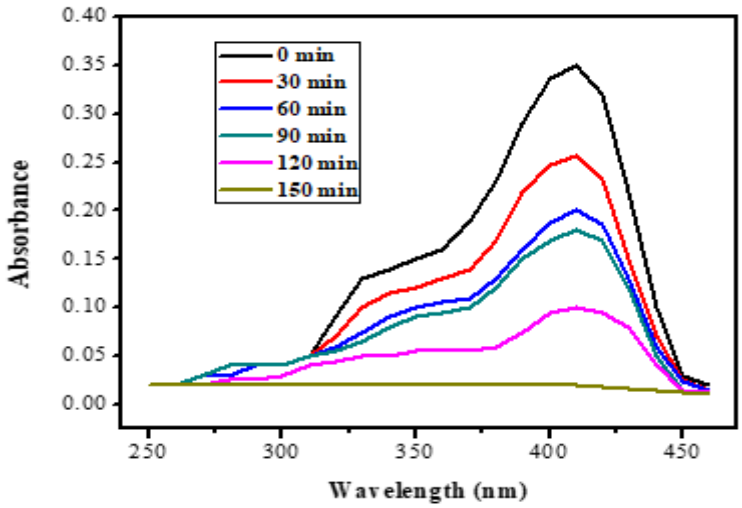

Figure 7. Effect of contact time on the adsorption of methylene yellow dye

3.5 Effect of pH on Adsorption Efficiency

The pH-dependent nature of adsorption is evident in Figure 8, highlighting its substantial impact on methylene

yellow dye adsorption and removal. The pH of the solution plays a pivotal role in the entire adsorption process by influencing the surface charge of the adsorbent and the dissociation of functional groups on its active sites (Huang et al. 2017). With an increase in pH from 1 to 6, there was a significant rise in adsorption rates, which stabilized at approximately pH 6. However, a slight decline was observed at pH levels exceeding 6. These findings suggest that the adsorbent exhibited substantial removal efficiency for methylene yellow over a broad pH range (3.0–9.0). Previous research has often reported the optimal pH range for chitosan-based adsorbents to be around pH 3–6 (Huang et al. 2017; Javed et al. 2011; Zhu et al. 2010). This phenomenon may be attributed to the protonation of amine groups in chitosan prior to adsorption. Notably, in this study, the highest removal efficiency (95%) was achieved at pH 6. Consequently, pH 6 was identified as the optimum condition for further investigation, as illustrated in Figure 8.

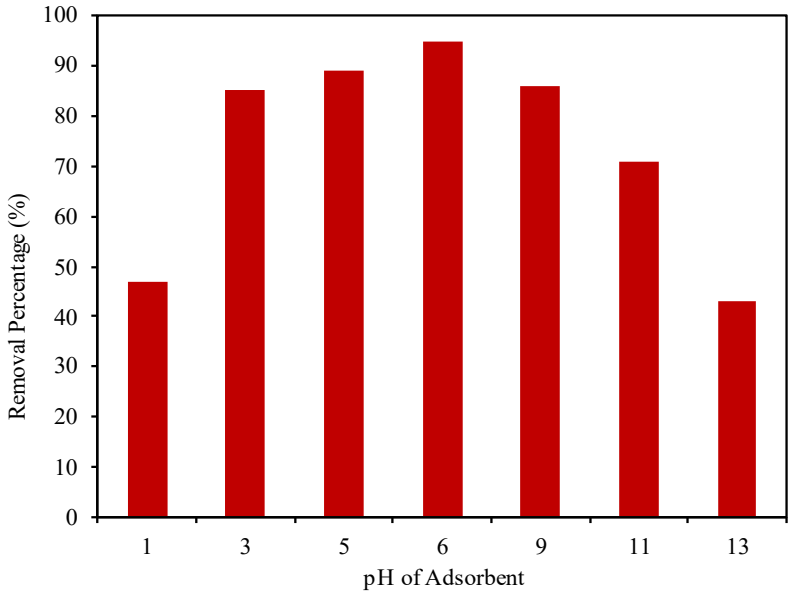

Figure 8. Effect of pH on %degradation of methylene yellow dye

3.6 Effect of Adsorbent Dose on Adsorption

Different quantities of adsorbate dose (ranging from 0.1 to 2.0g) were employed to assess their impact on methylene yellow dye adsorption, as depicted in figure 9. It is evident that the removal of the dye increases with higher adsorbent concentrations.

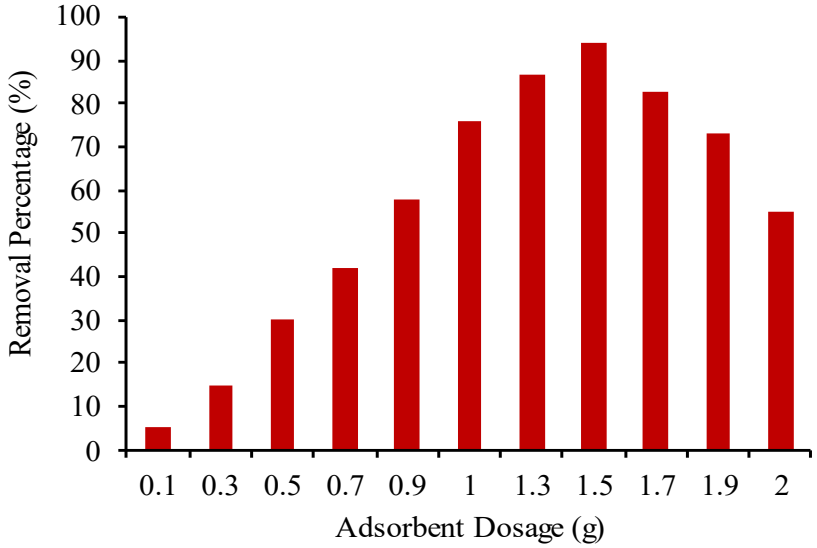

Figure 9. Effect of adsorbent dose on the adsorption of methylene yellow dye

This can be attributed to the increased adsorbent a surface area and the availability of a greater number of adsorption sites (Huang et al., 2017). Notably, at an adsorbent dosage of 1.5 g, methylene yellow was almost

completely removed. The adsorption capacity (in mg of dye adsorbed per gram of adsorbent) exhibited a decreasing trend as the adsorbent dosage increased beyond 1.5g. This decline in adsorption capacity could be ascribed to the overlapping or aggregation of adsorption sites, which led to a reduction in the overall available surface area for dye adsorption and an increase in the length of the diffusion path (Crini and Badot, 2008). Given the high removal percentage and superior adsorption capacity, we selected 1.5 g of adsorbent dosage for subsequent experiments.

4. CONCLUSIONS

In this study, Cs/AC composite beads were synthesized, which effectively removed methylene yellow dye from water. Optimal removal occurred at 150 minutes of exposure time, with no further improvement beyond this duration. This study concluded that pH played a crucial role, with maximum removal (95%) achieved at pH 7. These findings hold promise for addressing water pollution in Pakistan.

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