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Research Article

Efficient removal of Congo Red Dye from water using walnut shells activated carbon/MgO-Fe_2O_3 adsorbent

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ABSTRACT

In this study, the efficiency of walnut shells activated carbon modified with MgO and Fe_2O_3 was investigated for treatment of dyes contaminated water. Dyes are chemical molecules that are poisonous, long-lasting, and difficult to decompose. Congo red, an anionic dye with a complicated molecular structure containing different diazo aromatic groups, is widely utilized in the textile industry. There are multiple methods available to treat dye-containing water such as nano-filtration, photo-degradation, coagulation, ozonation and others, however, the adsorption method is a compelling approach with multiple benefits including its versatility and wide range of feasibility. The use of biomass as adsorbents such as nutshells has been tested as efficient material as compared to commercially available adsorbents in terms of cost and environmental impact. In the present study, the efficacy of WS based activated carbon modified with MgO-Fe_2O_3 was studied for the removal of Congo red dye from synthetic wastewater. The dye removal was optimized for various factors, including time, pH, dye concentration, temperature, and catalyst dose. It was found that the highest adsorption was achieved within 120 min with WS-AC/MgO-Fe_2O_3 at a dose of 0.075 g/L. At dye concentration of 5 ppm, pH 6.0 and temperature 35 ^oC, the optimal conditions were met and about 100 % removal of Congo red dye was achieved. Overall, this study showed a remarkable potential of WS based AC modified with MgO-Fe_2O_3 for removal of Congo red dye from wastewater and can be used in future wastewater treatment plants.

Keywords: Walnut shells; activated carbon; agricultural biomass; adsorption; MgO-Fe_2O_3; congo red dye.

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INTRODUCTION

Pakistan is one of the largest walnut producers where 29,724 tons of walnuts production was recorded in 2019 with an average expected increase of 1.67%. In Pakistan 3,478 hectares of land is dedicated to walnut farming. Dyes and pigments have long been used by humans, with early uses of natural dyes dating back to pre-3000 BC, whereas synthetic dyes and pigments are now widely used to impart color to various man-made and natural materials (Rasilingwani et al., 2024). As a result, the dyes and pigments industry is rapidly expanding, with a current market size of $38.2 billion in 2022 and a relatively high compound annual growth rate of more than 5 % up to 2030 due to increased demand from related industries such as tanneries and textiles, paint and coatings, and plastics (Nagrale, 2023). Textile industries are the worst polluters of all industrial sectors when it comes to discharge volume and effluent composition. Dyes released from textile industry are often resistant to biological degradation and also exhibit stability to light (Aragaw & Bogale, 2021).

The wastewater from various industries such as textile, varnish, cosmetics, food, pharmaceutical, leather, paint, rubber etc., significantly contribute to water pollution. Thousands of dye particles are discharged in the environment as effluents during the dying process. Dyes are usually synthetic and contain a complex aromatic molecular structure, making them persistent and difficult to break down. China and India are the global highest and 2nd biggest producers and exporters, respectively. It has been estimated that around 100,000 different dyes are commercially available (Ho, 2020). Disperse Violet 26, Methylene blue, Congo Red, rhodamine B, methyl red, methyl orange, and crystal violet are among the most commonly used dyes. Concurring a recent appraise, the annual production of dyes approximately 70 lakh tons globally. These dye wastewaters are toxic and few of them are also thought to be genotoxic, allergic, mutagenic and carcinogenic (Ho, 2020; Dutta et al., 2021).

Due to the fact that synthetic dyes are indispensable, they contribute the most to the organic contaminants in the environment. Hence, it is crucial that dye wastewater be treated before discharged into the environment or groundwater. For this purpose, several treatment methods including physical and chemical methods have been deployed over the years for the removal of dyes (Kaur et al., 2012). A few of them include electrocoagulation, biochemical degradation, electrochemical degradation, oxidative degradation, adsorption (Dutta et al., 2021) and photoctalysis (Anjum et al., 2018, 2023; Barakat et al., 2020; Nawaz et al., 2023a,b, 2024a,b). However, the use of activated carbon has proven to be a very effective option for dye removal but due to its high cost in terms of both, production and recovery, and the fact that it is non- renewable, it is not a suitable option in developing countries. Therefore, the use of adsorbents from agricultural biomass that is also a cheap, renewable and sustainable, provides a very efficient way of treating wastewater in terms of dye removal (Tang et al., 2017; Ho, 2020; Aragaw & Bogale, 2021).

Congo Red is the sodium salt of benzidinediazo-bis-1-naphthylamine-4-sulfonic acid, a diazo dye that is red in alkaline solution and blue in acid solution and is employed as a biological stain and indicator (Gharbani et al., 2008). It is an azo dye that is harmful to a wide range of organisms and is suspected of being a carcinogen and mutagen. One of Congo Red's application is as pH indicator since it turns from blue to red at pH 3.0-5.0. It has a high affinity to cellulose fibers However, Congo Red has long been discontinued from usage in the cellulose industries (cotton textiles, wood pulp, and paper industry), mostly due to its ability to change color when touched by perspiring fingers and also due to its toxicity. However, it is still used for diagnostic purposes (Alam et al., 2015; Steensma, 2001).

WS has shown to be a very effective adsorbent for dye removal. Walnut shell has been effectively used for the production of activated carbon because of its availability as a renewable resource, strong stability, and high stiffness (Ghasemi et al., 2015). Produced on the walnut tree (*Juglans regia* L), it is Central Asia's native plant that also stretches across Europe, China, Afghanistan and Iran. While almonds occupy the first rank as the highest produced nuts worldwide, walnuts stand at the second rank, producing above 3.7 million tons worldwide in 2019 (Chudhary et al., 2020). China as the largest producer of walnuts produces about 1.06 million tons annually, while USA produces about 600 tons and Iran, almost about 405 tons (Queiros et al., 2020). The WS constitute about 67% of the nut's total weight and are majorly composed of cross-linked polymeric compounds. These are usually disposed-off without any further consideration or use. These WS exhibit great adsorption potential and consist of lignin, cellulose, tannins and hemicellulose, much similar to wood biomass. WS adsorbents not only prove effective in dye removal but are also highly efficient in the removal of emerging contaminants that surfaced not very long ago.

To enhance the adsorption capacity of WS, the present study was designed with the objective of synthesizing a modified WS based activated carbon. The WS Activated carbon was prepared using alkali activation method followed by temperature treatment. The prepared WS activated carbon was further modified with MgO/Fe_2O_3. Furthermore, the synthesized WS-AC/MgO/Fe_2O_3 adsorbent was determined for its efficiency to remove Congo Red Dye from water under varying operating conditions.

MATERIALS AND METHODS

The materials used include walnut shell (WS) powder, synthetic wastewater containing Congo Red dye, NaOH, Nitric Acid, $FeCl_3$ and $MgCl_2$. The dye, chemical, acid and salts were obtained from the laboratory. Equipment used includes digital balance (Model; SES224, Brand; Saffron), pH meter (Model; PHS-3C, Accuracy; 0.01), incubator shaker (Model; SI-100R) and spectrophotometer (Model; E-1000UV, Voltage; AC 220V/50Hz). WS is required in three forms of samples i.e., raw sample, activated carbon sample and the modified form.

Synthesis of Walnut Shells Based Activated Carbon

The walnut shells were obtained from the local market which were initially washed and dried, followed by crushing to a fine powder. For preparation of activated carbon a chemical activation, the method mentioned by Bedia et al. (2020) was adopted (Figure1). The first step involves the dry mixing of NaOH and walnut powder at 1:1. In the second step, calcination of walnut shell is performed in a muffle furnace at 550 °C for 2 h. After calcination, the material was ground into a fine powder form with the help of mortar and pestle.

After activation of walnut shell, the activated carbon was subjected to washing with to remove contaminants from surface of activated carbon. Secondly, by inserting a hydrophilic functional group such as an acid or a base group, it enhances surface chemistry. Moreover, it expands the surface area by enlarging the pores. The method mentioned by Allwar et al. (2017) was used for washing, the activated carbon sample was washed by alternatively adding distilled water and methanol 5-7 times to ensure higher efficiency of the process. Washing helped remove any water-soluble components in the sample as filtrate, as the insoluble sample remained on the filter paper as residue. The filter paper was then removed from the filter funnel. Finally, the samples were dried in an oven at 100 °C for 3 h.

Synthesis of Walnut Shells AC-MgO/Fe_2O_3

For iron modification, the method mentioned by Barjasteh-Askari et al. (2021) was followed. The synthesized activated carbon powder (3g) was added to 70 mL of 36% nitric acid and maintained at 80 °C for 1 h with the help of magnetic stirrer. It was then allowed to settle for about half an hour and then filtered by washing with distilled water till the filtrate appeared clear. The resulting residue was then left to air dry for 24 h. In second step, 3g of dried powders were added to 70 mL of 3 M $FeCl_3$ and stirred for 3 h at room temperature at 300 rpm using magnetic stirrer. It was then filtered and washed until the green color of the filtrate appeared clear. The residue was then dried at 100 °C for 90 min. For MgO modification, the method mentioned by Ghalehkhondabi et al. (2021) was followed. The MgO/AC composite was made using the sol–gel–thermal deep-coating process. Magnesium oxide was deposited onto AC as the support media, where magnesium chloride serving as the precursor. First 5 g of $Mg(NO_3)_2.6H_2O$ was dissolved in 50 mL deionized water, then 3 mL of NaOH (1N) was added while constantly stirring at 50 rpm. After stirring for 10 min to generate a homogenous gelatinous suspension of $Mg(OH)_2$, 1.326 g of Iron modified-AC was added and gently swirled for about 1 h. Then the suspension was allowed to settle for 2 h before being released as supernatant. The MgO/Fe_2O_3/AC-WS was dried in the oven at 100 °C for 2 h after. Finally, to form MgO nano-crystals from $Mg(OH)_2$, the modified AC was subjected to calcination at 600°C for 1 h. The detailed synthesis method is summarized in Figure 1.

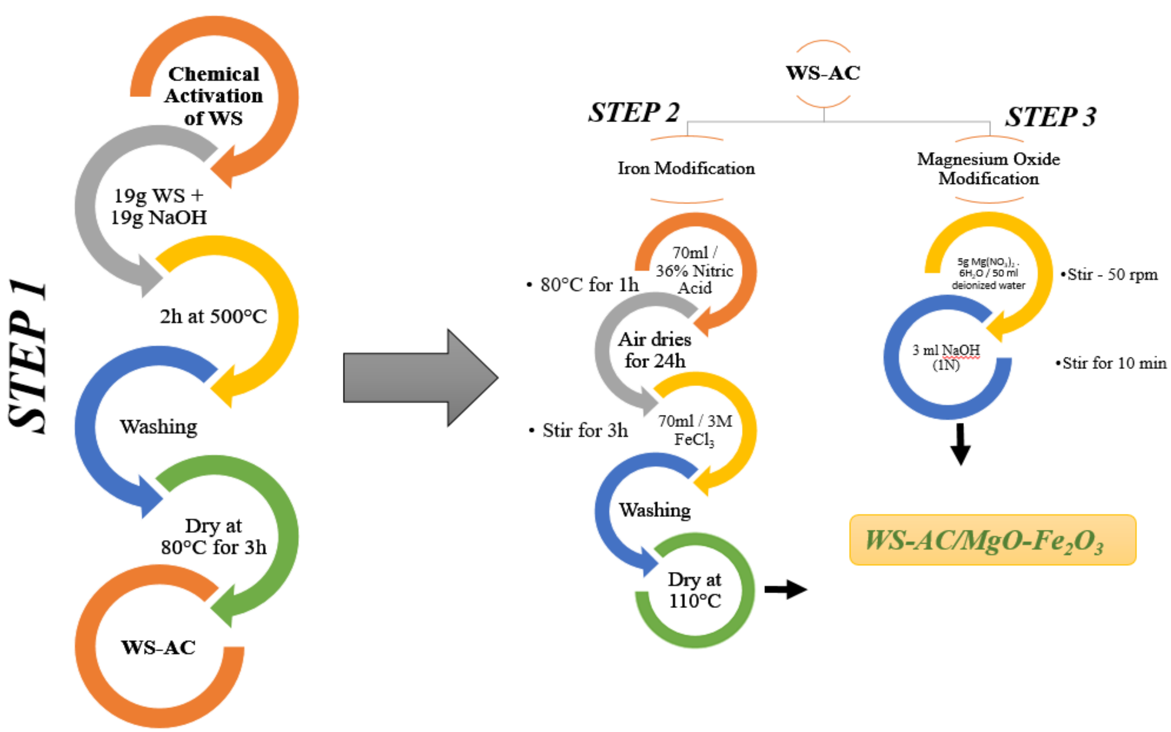

Figure 1. Synthesis of WS-AC and WS-AC/MgO-Fe_2O_3.

Preparation of Wastewater

To prepare synthetic wastewater, Congo Red Dye was used. A stock solution of 100 ppm was prepared by adding 0.001 g of Congo Red Dye to 100 ml of distilled water. The stock solution was further used during experimentation by making required dilutions.

Adsorption Experiments

Batch experiments were performed to analyze the adsorption capacity of raw, activated and modified (AC-WS/MgO-Fe_2O_3) walnut shells by adjusting various conditions such as contact time, adsorbent dose, dye concentration, temperature and pH. The detail experimental setup is described in Table 1. For analysis about 5 ml of sample was taken at regular interval of time. The samples were filtered using a syringe filter and analyzed using a spectrophotometer.

For spectroscopic analysis, the standard solutions (1, 5, 10, 15 and 20 ppm) of Congo Red Dye were prepared from the stock solution. The wavelength of Congo Red Dye was 497nm that provided maximum adsorption (99%). Similarly, the standard curve was developed at 497 nm and the concentration of Congo red dye remained in the samples after absorbance was measured.

Table 1. Experimental Setup.

Experiments	Treatments Details	Experimental conditions
Exp. 1: Effect of contact time and adsorbent	Unit 1: WS raw (Time: 0-120 min) Unit 2: WS-AC (Time: 0-120 min) Unit 3: AC-WS/MgO-Fe_2O_3 (Time: 0-120 min)	Adsorbent dose: 0.05 g/L Dye Concentration: 10 ppm pH: 6.0 Temp: 30 °C
Exp. 2: Effect of adsorbent dose	Dose 1: 0.025g/L Dose 2: 0.05g/L Dose 3: 0.075g/L	Adsorbents: AC-WS/MgO-Fe_2O_3 Time: 0-120 min Dye Concentration: 10 ppm pH: 6.0 Temp: 30 °C
Exp. 3: Effect of dye concentration	Dye 1: 05 ppm Dye 2: 10 ppm Dye 3: 15 ppm Dye 4: 20 ppm	Adsorbents: AC-WS/MgO-Fe_2O_3 Adsorbent dose: 0.075 g/L Time: 0-120 min pH: 6.0 Temp: 30 °C
Exp. 4: Effect of temperature	Temp: 25 °C Temp: 30 °C Temp: 35 °C	Adsorbents: AC-WS/MgO-Fe_2O_3 Adsorbent dose: 0.075 g/L Time: 0-120 min Dye Concentration: 10 ppm pH: 6.0
Exp. 5: Effect of pH	pH: 3.0 pH: 5.0 pH: 6.0 pH: 7.0 pH: 9.0	Adsorbents: AC-WS/MgO-Fe_2O_3 Adsorbent dose: 0.075g/L Time: 0-120 min Dye Concentration: 10 ppm Temp: 35 °C

RESULTS AND DISCUSSION

Effect of Synthesized Adsorbents and Contact Time on Adsorption Capacity

Contact time is the first and one of the most important parameters to determine, since with increasing the time, the rate of adsorption increases at first and then tends to become constant. Therefore, to determine the optimum contact time, 3 units (Unit 1-WS raw, Unit 2- WS-AC, Unit 3- AC-WS/MgO-Fe_2O_3 were prepared with pre-determined conditions, dye: 10 ppm, pH = 6, dose = 0.05g at 30°C temperature. To measure the removal of ongo red dye, a 5 ml sample was obtained regularly from all 3 experimental units at 0h, 30min, 60min, 90min and 120 min. It was found that the adsorption increased to maximum with the AC-WS/MgO-Fe_2O_3 (modified adsorbent) as compared to the raw and activated carbon adsorbent (Figure 2). The removal of Congo red dye was initially increased from 74% to 93% and finally to 98% with AC-WS/$MgO-Fe_2O_3$. After 120 min the modified sample had completely removed the dye and turned the sample color-less.

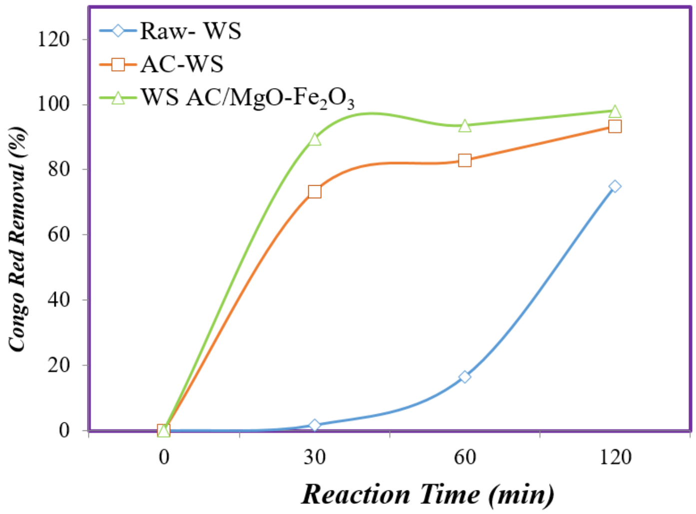

Figure 2. Effect of time on adsorption of Congo Red Dye using AC-WS/$MgO-Fe_2O_3$.

Effect of Adsorbent Dose on Adsorption Capacity

Adsorbent dose is also a critical factor for dye adsorption in water, where with increasing adsorbent dose more adsorption sites become available. In this experiment, the optimum quantity of adsorbent required for effective adsorption was determined by using various adsorbent dosages. Three different doses (0.025 g/L, 0.05g/L, 0.075g/L) of the AC-WS/$MgO-Fe_2O_3$ were added to three units containing 10 ppm of Congo Red Dye, at pH 6.0 and 30 °C of temperature.

Absorbance values obtained from the samples taken at 0h, 30min, 60min, 90min, 120min. Fig. 3 indicates that increasing the dosage from 0.025g to 0.05g increased the dye removal from 99.01% to 99.3%. Increasing the dose increased adsorbent surface area and the availability of more adsorption sites, thereby, resulting in enhanced adsorption (Kaur et al., 2012). Further increasing the dosage to 0.075g resulted in dye removal of 99.6%. Thus, providing us with the maximum optimum dose of 0.075g. In another study, for a contact time of 2 hours, the effect of walnut shell dosage on Methylene Blue adsorption was investigated (Tang et al., 2017). When the adsorbent dosage increased from 0.10 to 1.25 g/L, the methyl blue dye removal % improved from 26.8% to 99.8%. Sharma and Uma. (2010) determines the impact of various doses of rice husk AC on the adsorption of Methylene blue by using various adsorbent dosages (0.40-0.60 g) in 50 mL of dye solution. They claimed that increasing the dosage from 0.40 to 0.60 g caused the removal to rise from 86.75 % to 99.83 %.

Effect of Dye Concentration on Adsorption Capacity

The direct relationship between dye concentration and the accessible binding sites on the surface of adsorbent determines the influence of the initial dye concentration factor (Salleh et al., 2011). With increasing initial dye concentration, the dye removal often decreases. In this experiment, four experimental units with 5 ppm, 10 ppm, 15 ppm and 20 ppm of dye concentrations were tested against AC-WS/$MgO-Fe_2O_3$. The other operating conditions, including 0.075 g of the adsorbent dose (as determined as optimum in previous experiment), pH 6.0 and temperature 30°C were maintained for 120 min adsorption process. Samples of 5 ml were taken at 0h, 30min, 60min, 90min and 120 min. Figure 4, indicates that removal of Congo Red Dye decreases with increasing the dye concentration as the % removal went from 99 % at 5 ppm to 94 % at 10 ppm, 85 % at 15 ppm, further decreasing to 81 % at 20 ppm. Therefore, concluding that optimum dye concentration is 5 ppm. The active sites required for the dye molecule to bind to the adsorbent's surface are occupied at low concentrations and are unavailable when the dye concentration increases (Kannan and Sundaram, 2001).

Kaur et al. (2012) investigated the potential of ground nutshell and eichhornia charcoal for removal of Congo Red in relation to the impact of dye concentration. The experiment was conducted with an adsorbent dosage of 1 g/L. They found that as Congo Red concentration increased, the percentage of Congo Red adsorption decreased. The percentage of removal reduces as a result of the rise in Congo Red concentrations and saturated active sites of the adsorbent.

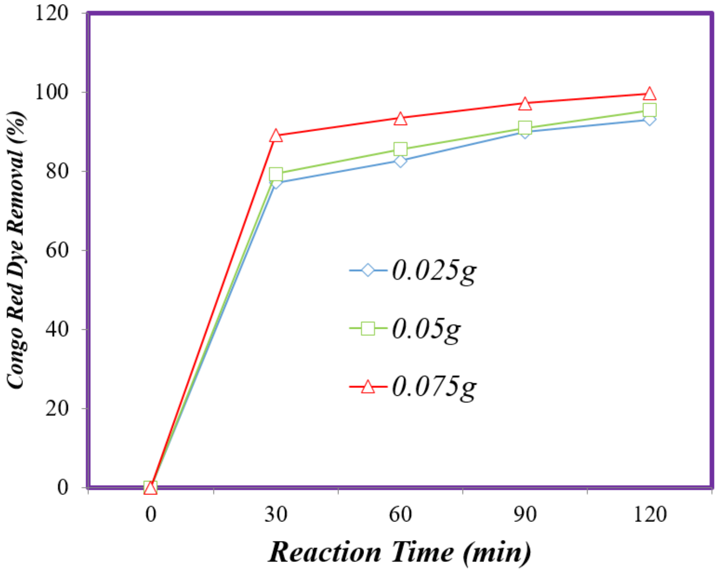

Figure 3. Effect of adsorbent dose (AC-WS/$MgO-Fe_2O_3$) for removal of Congo Red Dye.

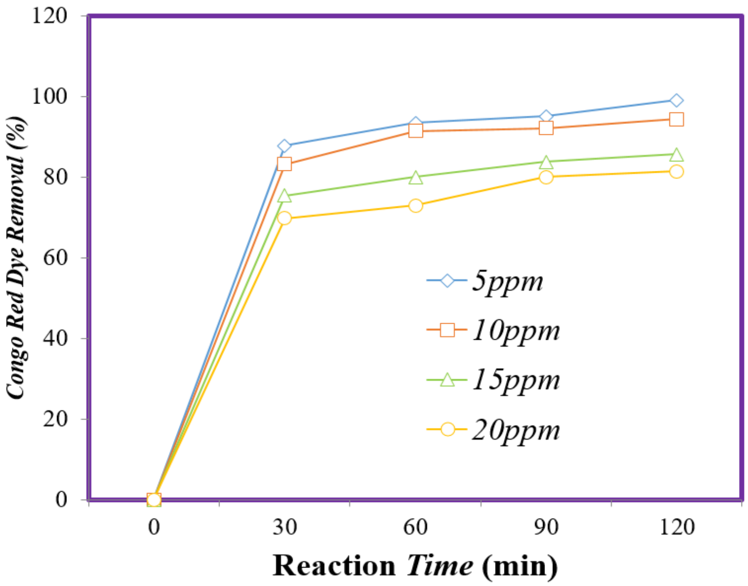

Figure 4. Effect of dye concentration on adsorption of Congo Red Dye using AC-WS/$MgO-Fe_2O_3$.

Effect of Temperature on Adsorption Capacity

The effect of temperature on adsorption capacity has been documented by several researchers, stressing the endothermic character of the adsorption process employing. The adsorption process is thought to be endothermic in nature; increases in adsorption capacity are attributable to the increased mobility of adsorbate at higher temperatures. To determine the optimum temperature, three experimental units at 25°C, 30°C and 35°C respectively were set at 0.075g of the adsorbent dose, 10 ppm dye concentration (as determined in the previous experiment), pH 6.0 and for 120 min. The results obtained are illustrated in Figure 5. It was found that removal of Congo Red Dye increased with increasing the temperature, the dye removal increased from 89% at 25°C to 95% at 30°C and 99% at 35°C. Thus, providing the maximum optimum temperature i.e., 35°C.

Li et al. (2020) tested the influence of temperature on two kinds of dyes; Congo red and methylene blue and found that the temperature of the solution has a significant impact on dye removal. Both dyes had the same result, indicating that dye adsorption capability increased with increasing temperature. The increasing dye diffusion within the adsorbent, resulting in more incessant contacts among active sites and dye molecules on the adsorbent's surface.

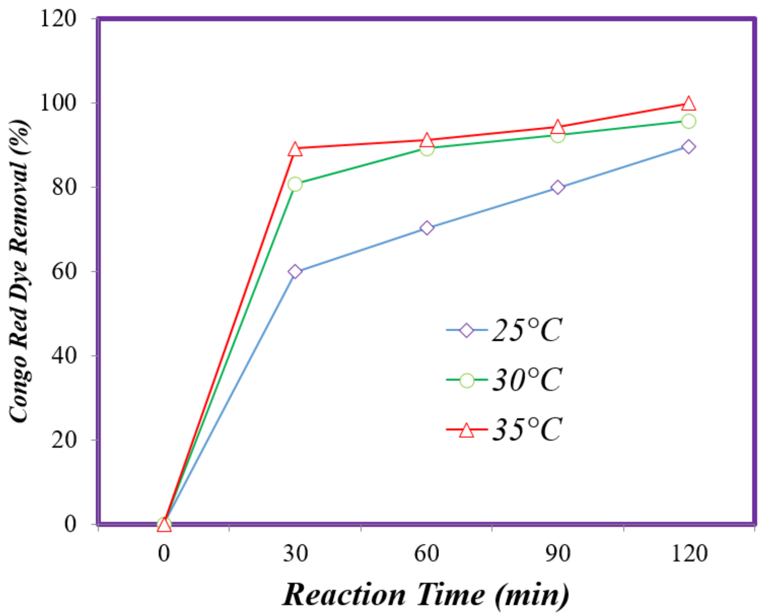

Figure 5. Effect of temperature on adsorption of Congo Red Dye using AC-WS/$MgO-Fe_2O_3$.

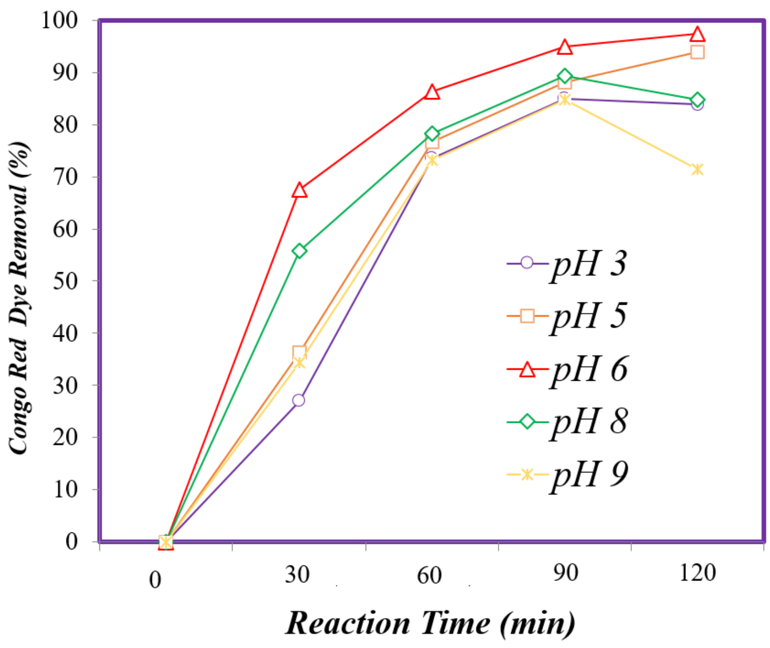

Figure 6. Effect of pH on adsorption of Congo Red Dye using AC-WS/$MgO-Fe_2O_3$.

Effect of pH

According to recent research, the pH of the solution has a significant impact on adsorption capacity. The surface characteristics of the adsorbent can have a big impact on adsorption. To determine the optimum pH, five experimental units with pH 3.0 5.0, 6.0, 8.0 and 9.0 were set at 0.075g of the adsorbent dose, with 10 ppm dye concentration, at 35 °C temp (as determined in the previous experiment). 5 ml samples were taken at 0h, 30 min, 60 min, 90 min and 120 min. The obtained values described in Fig. 6, indicated that adsorption capacity of Congo Red Dye increased with increasing pH from 3 to 6. However, it then appears to decrease as the pH increases up till 9. The data shows that removal increases from 83% at pH-3, to 93% at pH-5 and then further increasing to 97% at pH-6. However, it then decreases from 97% to 84% at pH-8 and further to 71% at pH-9.

Congo Red is an anionic dye and the adsorption capacity of an anionic dye is high at low pH values, thereby, demonstrating maximum removal at acidic pH values and minimum removal at basic pH values (Albatrni et al., 2022). Hence, the experiment indicates that incase of Congo Red Dye and WS- modified adsorbent, acidic i.e., pH-6 proves to be the maximum optimum pH. Miyah et al. (2020) also studied the absorption of three dyes with varying net charges. Cationic dyes methylene blue and crystal violet, and anionic dye methyl orange. The results showed that adsorption rate was low for cationic dyes and higher for anionic dyes at acidic pH values ranging from 2.5 to 5.5. Methylene blue adsorption was shown to be increased at high pH levels i.e., 6.5 to 12. Because methylene blue is a cationic dye, electrostatic repulsion between it and positively charged adsorbents develops at low pH values, lowering the adsorption capacity. Zawani et al. (2009) studied that Remazol black 5 adsorbed on palm kernel shell AC at an optimal pH of 2, with a maximum uptake of 27.44 mg/g. After that, with an increase in pH, a decreased in uptake has been recorded.

CONCLUSION

In this study a modified walnut shell activated carbon i.e. AC-WS/MgO-Fe_2O_3 was successfully prepared for removal of Congo red dye from wastewater. It was revealed that modified AC has the capability to remove dye completely within 120 min. The optimum operational conditions for adsorption were adsorbent dose 0.075 g/L, dye concentration 10 ppm, temperature 35 °C and pH 6.0. Overall, it can be concluded that the walnut shell in its modified forms can be employed as an effective adsorbent for the removal of Congo red dye. The agricultural biomass can be used while also replacing costly commercially manufactured adsorbents. In future, the recycling WS can help to reduce the negative impacts caused by the industrial sector's commercial processing of various activated carbons, demonstrating that agricultural waste WS can be utilized as an efficient and low-cost material for development efficient adsorbent for wastewater treatment of textile and leather processing industries.

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