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Effective Sequestration of Acid Orange-7 Dye from Wastewater by using Ricinus Communis Biochar along with Zinc Oxide Nanocomposites

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ABSTRACT

Water is critical to the survival of life on Earth. Due to increased industrialization, overpopulation, and overexploitation, water quality and assets have deteriorated. To satisfy water demands, it is critical to treat effluents with cost-effective and environmentally friendly adsorbents. In this study, Ricinus communis biochar (RCB) and its nanocomposites with zinc oxide (RCB/ZnO) were employed to remove Acid Orange 7 dye on a batch basis (AO7). The effects of adsorbent dose (1 - 4g/L), dye starting concentration (25 - 500 mg/L), pH (2 - 8), and contact period (15 - 180 min) on the adsorption potential of different adsorbents were investigated and compared. When the IC was varied from 25-200mg/L, the findings showed that the elimination of AO7 by utilizing RCB was 90-70 percent. While the elimination of RCB/ZnONPs were found to be 99-89 percent effective in removing AO7. When compared to earlier investigations, the proposed materials are more efficient and have a higher adsorption capacity. The use of nanoparticle composites for AO7 cleanup at the industrial level has been suggested.

INTRODUCTION

Water Contamination is a worldwide problem with adverse consequences for animals, plants and human health. In recent years, many developing countries have faced serious challenges in providing their populations with a sustainable supply of drinking water, as their natural water resources have been severely polluted by the effluents discharged from industrial and agricultural wastewater (Gani et al. 2016). Various industries such as textiles, plastics, pulp, cosmetics, paints, rubber, pesticides, pharmaceuticals and paper produce large amounts of wastewater containing synthetic dyes (Muthirulan et al. 2013). With the development of the dyeing industry, a large number of dyes in China will be used for a variety of crops each year (Hu et al. 2017). Synthetic dyes have a wide structural range and can be divided into azo, anthraquinonoid, Sulphur, indigo, and phthalocyanine derivatives on an industrial scale (Oros et al. 2004).

Most of the synthetic dyes used in industry today are azo dyes and their derivatives because they are very stable on cleaning, resistant to light and resistant to deterioration under natural conditions (Garcia et al. 2013). The textile dyeing industry produces large amounts of colored wastewater, which increases the likelihood of contaminating clean water (Asghar et al. 2015). Over 15% of the dyes are produced in various fiber manufacturing processes, contributing to the creation of colored wastewater streams (Vasseghian et al. 2018). Today, there are over 100,000 different dyes and pigments commercially available, more than 7 x 105 tons produced each year around the world (Naushad et al. 2014).

AO7 is a mono-azo dye [p-(2-hydroxy-1-naphthylazol) benzene sulfonic acid] that is the most commonly used anionic dye due to its water solubility. Its molecular formula is$C_{16}H_{11}N_2NaO_4S$, and its molar mass is 35.32 g/mol. It is widely used to dye a wide range of materials, including nylon, wool, cosmetics, aluminum, detergents, and silk (Gupta et al. 2006). It is frequently released into industrial wastewater, which poses a serious threat to human health. AO7 is a toxic compound, and its slow degradability in the environment can result in its presence for an extended period of time (Fernandez et al. 2015). It is highly toxic; therefore, ingestion may cause irritation of the eyes, skin, mucous membranes and upper respiratory tract; severe headache, nausea, water-borne diseases such as dermatitis and bone marrow loss leading to anemia.

Purification of wastewater containing AO7 dye is becoming an increasingly important goal in order to avoid potential environmental threats. Many countries strictly regulate wastewater emissions contaminated with AO7 azo dyes for aesthetic reasons. The dramatic increase in toxic substances from industrial outlets has spawned various technologies for eliminating waste from wastewater outlet (Almasian et al. 2014). In the field of color removal of fiber effluent from industrial wastewater, various physical, chemical, biological, and electrochemical processes have been used (Collivignarelli et al. 2019) such as Coagulation, ozone treatment, bio solution, filtration, agglutination process, etc. widely used for wastewater treatment in the textile industry. However, due to limitations such as operating costs, the formation of dangerous by-products, intensive energy requirements, and limited adaptability to a wide range of wastewater, the application of these methods is somewhat limited. Although these processing techniques are not always effective at removing dyes, adsorption is the most widely used and versatile technique (Imran et al 2019). If the adsorbent is cheap and readily available, it is feasible.

Adsorption is a surface phenomenon primarily related to the use of surface forces. When a solution containing an absorbent solute, also called an adsorbate, comes into contact with a solid called an adsorbent, which has a highly porous surface structure, the solute concentrates on the surface of the solid due to the liquid-solid intermolecular attractive forces. The use of biochar as an adsorbent to remove toxic compounds from water is highly recommended due to its properties; large porous spaces, large surfaces, more active sites for anchoring contaminants. Recently, biomass-based biochar has received special attention in restoring various dyes from wastewater due to its renewable and abundant properties, economic feasibility, and efficiency.

Biochar (BC) can be prepared from a wide variety of biomass, including organic waste, crops, wood-based materials, algae, defatted cakes, seed covers, perilla leaves and aquatic weeds. (Huang et al. 2019). Research on the synthesis of biochar-based adsorbents for the uptake of metals and dyes has increased dramatically (Srivatsav et al .2020). Several factors, such as heating temperature, residence time and heating rate, affect the efficiency, morphology and potential of biochar. *Ricinus Communis*, also known as castor, is an annual oilseed crop. It's commonly referred to as castor bean, but it's not a genuine bean. Castor, a member of the Euphorbiaceous spurge family, can grow in a variety of environments (Anjani et al. 2014). Temperatures between 20 and 25 °C are good for castor growth, however temperatures below 12 °C or above 38 °C have an impact on germination and production (Severino et al., 2012; Yin et al., 2019).

Recently, the use of *Ricinus Communis* seeds for castor oil production has increased because of their applications in beauty products and biofuels. Consequently, the cultivation of castor crops has increased, and its processing results in the accumulation of huge amounts of dry biomass residue (0.8 to 10 Mg ha−1) in terms of stalks and leaves (Hilioti et al. 2017). In this study, RC leaf-based biochar was developed for the adsorption of dyes from waste effluents, such as textile wastewater, to provide beneficial use of these residues. Some recent studies show 69% degradation of AO7 during 140 min of the experiment when reacting with CdO50ZnO50-SCP (Payam et al. 2018).

Literature review revealed that biochar improves the adsorption capacity of the acid orange 7 (AO7) dye. Adsorption was used to investigate the removal of AO7 dye using unmodified (Pea-B) and modified (Pea-BO-NH-2) biochar derived from pea Pisum sativum peels. The percentage of AO7 removed by using modified biochar is approximately 99 percent greater than that of unmodified biochar. The results of a mechanistic study of AO7 adsorption over ANP revealed that it can remove AO7 dye up to 97.6 percent at 2 pH under equilibrium conditions.

As a result, the purpose of this study was to see how successful RCB and RCB/ZnONPs are at removing AO7 from synthetic wastewater. The effects of several processes, such as initial dye concentration, solution pH, contact time, and adsorbent dose, were determined to determine the performance of the material for decontamination of AO7 dye-contaminated water. To simulate the obtained data, existing isothermal equilibrium and kinetic sorption models were used. The adsorption potential of RCB and RCB/ZnONPs was compared to the adsorption potential of biochar composites utilized in the literature, and the reusability of RCB and RCB/ZnONPs was tested in five adsorption/desorption cycles.

MATERIAL AND METHODS

Chemical and Preparation of Synthetic Wastewater

Merck, Faisalabad, provided zinc sulphate heptahydrate ($ZnSO_4.7H_2O$), potassium hydroxide, sodium hydroxide (NaOH), hydrochloric acid (HCl), and AO7. The stock solution of AO7 (1000 mg/L) was prepared using double distilled water, and solutions of its various working concentrations were prepared from the stock solution.

Preparation of Biochar

Ricinus Communis (RCB) biomass was collected from the surrounding locations. Using a fodder machine, the RCB was cut into smaller pieces. To eliminate contaminants clinging to the surface of biomass, the smaller pieces of RC were rinsed twice in distilled water. The air dried material was placed in the biochar unit and heated to 350°C for 90 minutes to make RC biochar. After 90 minutes, the biochar machine was turned off, and the created biochar was allowed to cool for 24 hours before being ground and sieved with a fine sieve. To remove dissolvable elements from the biochar, the fine material was rinsed with distilled water and oven-dried for further 12 hours at 85°C. The dried RCB was saved for composite purposes.

Preparation of Composites RCB/ZnONPs

The precipitation process was employed to make the RCB composite with ZnO nanoparticles (RCB/ZnONPs). For the synthesis of RCB/ZnO, a solution of 0.1 M ZnSO4 and 0.12 M KOH was produced. After mixing a 100 ml solution of ZnSO4 in 0.5g of RCB for 10 minutes, the combination was titrated against a 100 ml KOH solution. This procedure was continued until 1000 ml of each solution had been titrated using the above method. What man filter 42 was used to filter out the RCB/ZnONPs composite, and the RCB/ZnONPs were oven dried for 24 hours at 85°C. RCB and RCB/ZnONPs were calcined in a furnace at 300°C for 30 minutes and stored in plastic containers for further testing to remove AO7.

Batch scale Acid Orange 7 Adsorption Study

Under laboratory settings, a standard solution of AO7 was made by dissolving 1.0 g of dye in 1 L distilled water. Diluting the standard solution yielded the various AO concentrations (25, 50, 100, 200, and 500 mg/L). A series of batch scale adsorption experiments were conducted to eliminate AO7. The effects of process variables such as dye starting concentration, adsorbent material dose, solution pH, contact time, and material type were investigated. The dye solutions were placed in 250 mL conical flasks and mechanically shaken for 3 hours at 140 rpm. The AO7 elimination equilibrium time was determined in preliminary studies, and 5 mL samples were obtained from each. Initially, the AO7 elimination equilibrium period was determined, and 5 mL samples were obtained from each flask at various times, including samples at equilibrium. The samples were stored in 10 mL plastic vials and were used to calculate the amount of residual AO7 in water samples. AO7's maximum absorption wavelength (max) was determined by scanning its solution (200 to 700 nm) with a UV-visible spectrophotometer (PerkinElmer 25 series) and running standard AO7 solutions to obtain a calibration curve. The experiment was repeated twice (n = 2), with the calibration curve used to convert sample absorbance to AO7 concentration.

Effect of Initial Concentration of AO7 and Adsorbent Dosage

The effect of AO7 initial concentration was studied using various initial concentrations (25, 50, 100, 200, and 500 mg/L) at constant dosage (25mg), pH (6), and contact time (180 min). To determine the dosage effect, experiments were performed at 1, 2, and 4 g/L concentrations of AO7 (80 and 320 mg/L) and pH 8 at equilibrium.

Effect of Contact time on Removal rate

Two concentrations of AO7 (100 mg/L) were employed at dosages of 1 g/L and pH 8 to determine the impact of contact time (optimum values). After 15, 30, 60, 120, and 180 minutes of shaking, samples of each substance were obtained. At 486 nm, the sample was measured with a UV-1600 spectrophotometer.

Effect of pH on Removal Rate

To test the effect of pH on AO7 removal, 0.025g of RCB was added to a 250 ml Erlenmeyer flask containing 200ml of 10mg/L AO7 and shaken at 140 rpm/min on a mechanical shaker. The pH effect of AO7 containing synthetic wastewater was measured using pH 2, 6, 8, and 10. All other variables were held constant. It was then measured at 486 nm with a spectrophotometer.

Data Analysis

The data used in the analysis was derived from triplicate sets of experiments. The initial (Co) and final (C_f) concentrations of AO7 in mg/L, the mass (g) of adsorbent, and the volume of solution (V) in L were used to compute the experimental adsorption (qe). (Ahmad et al. 2017; Shah et al. 2018).

$$q_e = C_o - C_f / M_b \quad x\ V$$

Using the provided equation (Imran et al. 2018; Shah et al. 2018), the initial (Co) and final (Cf) concentrations of AO were used to calculate its removal (R percent) by each adsorbent material.

$$R\% = C_o - C_f / C_o \quad x\ 100$$

RESULT

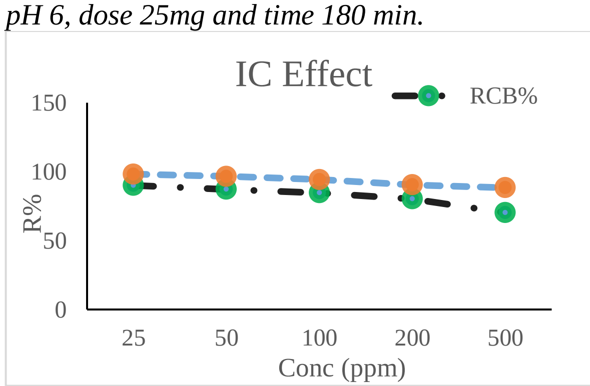
Effect of Initial Concentration

The effect of IC was determined by varying solution IC from 25 – 500 mg, while all other factors were kept constant such as pH (6), dose (0.025g/l) and time (180 mints). The removal percentage of AO7 by RCB was 90%, 87.2%, 84.6%, 80.25% and 70% respectively. The result showed that AO7 removal is maximum at 25 ppm concentration while the removal efficiency of RCB decreased with increasing IC.

However, the removal percentage of AO7 by RCB/ZnONPs was 99.6%, 98.2%, 94.4%, 92.6% and 89.4% respectively when IC was changed 25-500ppm of AO7. The results show that AO7 removal is greatest at low IC and decreases with increasing initial AO7 concentration. Under the same experimental conditions, RCB/ZnONPs demonstrated greater AO7 adsorption potential than RCB. It could be because there are fewer active sites on the RCB surface than on the RCB/ZnONPs. When the IC level varies from 25 to 100mg/L, there is a small change in AO7 removal by RCB/ZnONPs due to its higher potential, whereas at higher concentrations (500 mg/L), there is a clear decline in AO7 removal.

Figure 1

Removal of AO7 by RCB and RCB/ZnONPs at different initial concentrations of AO7 at constant pH 6, dose 25mg and time 180 min.



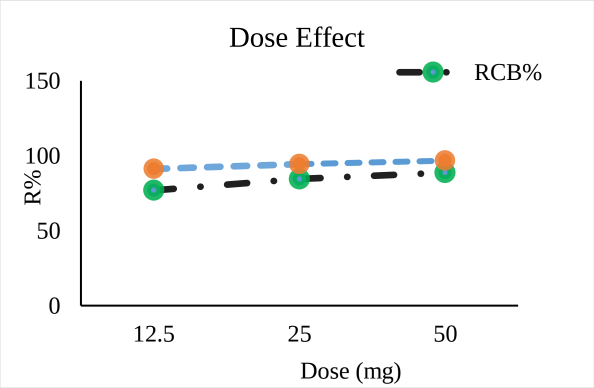
Effect of RCB and RCB/ZnONPs Dose on AO7 sequestration

The dose effect of AO7 from wastewater is determined by increasing the dose from 12.5 to 50 mg while maintaining the AO7 initial level at 100mg, pH 6, and ambient temperature at equilibrium. The removal percentage of AO by RCB is 76.9%, 84.5% and 88.7% respectively. The AO7 removal is maximum at 50mg dose. The result shows that AO7 removal increases from 76.9 to 88.9% with the increase in adsorbent dose. While, the removal percentage of AO7 by RCB/ZnONPs is 91.2%, 94.4% and 95.7% respectively on 12.5mg, 25mg, 50mg dose. This shows that with increase of adsorbent dose, there is an increase in removal of AO7.

Furthermore, even at low doses, RCB/ZnONPs is clearly more effective than RCB. The RCB/ZnONPs material exhibits an efficient increase in removal (91.2-95.7 percent) with increasing adsorbent dose (12.5-50mg) and a minor increase (91-94 percent) with increasing adsorbent dose (912.5-25mg). This slight increase could be attributed to particle interaction, such as aggregation.

Figure 2

Removal of AO7 by RCB and RCB/ZnONPs at different doses at constant IC 100 mg/L, pH 6 and time 180 min.

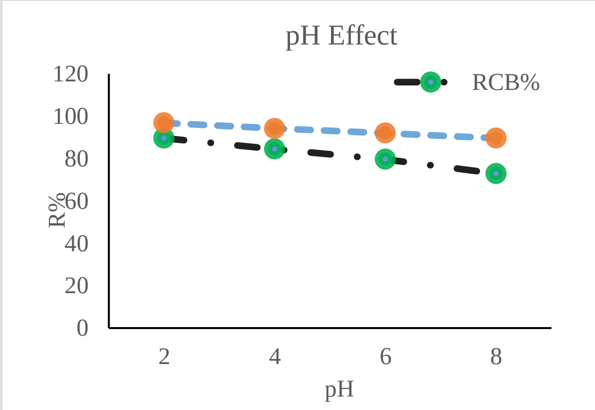


Effect of RCB and RCB/ZnONPs pH on AO7 Sequestration

The pH effect of AO7 from wastewater is determined by varying the pH from 2 to 8 while keeping the AO7 starting concentration at 100 mg/L, the dose at 25 mg, and the ambient temperature at equilibrium. The elimination percentages of AO by RCB are 89.6%, 84.5 percent, 79.6%, and 72.9 percent, respectively. At 2 pH, the AO7 elimination is at its greatest. This could be related to AO7's anionic nature. The finding demonstrates that as pH rises, AO7 elimination reduces from 89.6 to 72.9 percent. On 2pH, 4pH, 6pH, and 8pH, the elimination percentage of AO7 by RCB/ZnONPs is 96.9%, 94.4 percent, 93.1 percent, and 92.1 percent, respectively. This indicates that as the pH of the adsorbent increases, the removal of AO7 decreases slightly.

Figure 3

Removal of AO7 by RCB and RCB/ZnONPs at different pH at constant dose 25 mg, IC 100 mg/L and time 180 min.

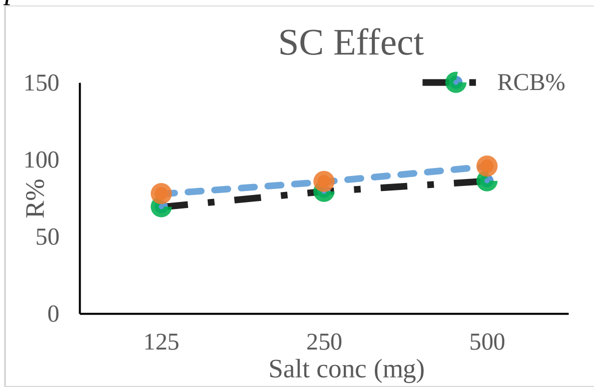


Effect of Salt Concentration on AO7 Sequestration

Figure shows how RCB and its composites with ZnO nanoparticles was used to remove AO7 dye from wastewater using IC. The effect of salt concentration SC was determined by varying solution SC from 125, 250 and 500 mg, while all other factors were kept constant such as pH (6), dose (0.025g) and time (180 mints). The removal percentage of AO7 by RCB was 90.5%, 93.9% and 93.1% respectively. The result showed that AO removal is maximum at 500mg, the removal efficiency of RCB increases by increasing SC. While, the removal percentage of AO7 by RCB/ZnONPs was 98.3%, 97.6% and 97.4% respectively on 125mg, 250mg, and 500mg concentration of AO7 is observed. The results show that removal is greatest at high SC and increases with increasing initial AO7 concentration.

Figure 4

Removal of AO7 by RCB and RCB/ZnONPs at different SC at constant dose 25 mg, IC 100 mg/L, pH 6 and time 180 min.

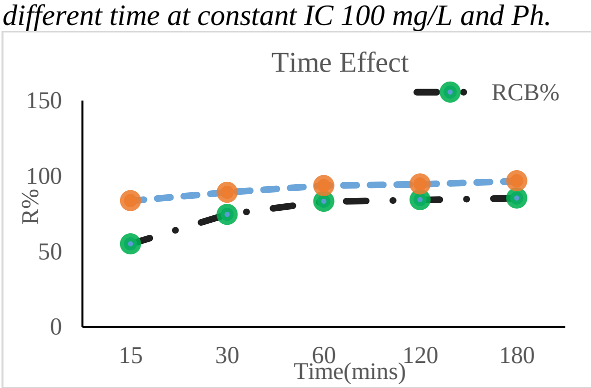


Effect of Time on AO7 Sequestration

For Acid Orange7 dye (AO7), samples were taken at the interval of 15, 30, 60, 120, and 180 minutes and the (R%) through use of RCB is 54.9%, 74.5%, 83%, 83.9%, and 84.7% that shows that with the increase of time removal can be more effective. While, the removal percentage of AO7 by RCB/ZnONPs was 83.3%, 89.8%, 93.6%, 94.3% and 94.4% respectively on 15min, 30min, 60min, 120min and 180min is observed. The results show that AO7 removal is greatest at long time intervals.

Figure 5

Removal of AO7 by RCB and RCB/ZnONPs at different time at constant IC 100 mg/L and Ph.



DISCUSSION

Water contamination is a worldwide problem which leads to many diseases in animals, plants and in humans. It is highly documented that anthropogenic and industrial action are the key sources of surface and ground water contamination all over the world. From industries like leather, textile, smelting etc. chemicals are directly discharged into water bodies which potentially affect water quality**.**

In this study it was noticed that the removal percentage of AO7 was significantly decreased with the increasing concentration of IC by keeping other factors constant. At low IC, there is an abundance of active sites on the adsorbent surface; as IC increases, the number of active sites decreases, resulting in less AO removal from wastewater. The findings of this study match with Supriya et al. (2016). According to her research, as the concentration of dye increases, the adsorption capacity of dye decreases due to a decrease in the number of active sites available. Hence the removal percentage decreases using activated carbon and conducting polymer composite.

The effect of solution pH on AO7 sorption is obvious. In this study low pH shows higher removal than high pH. By increasing pH, the removal percentage of AO7 decreases. These results showed that the acidic medium is favorable for sorption of AO7. These findings are also in line with the previous study of Ghiasvand et al. (2014). He used activated carbon with ZnO for the removal of AO7 and revealed that the adsorption of AO7 by ACZnO was increased at pH 3 (91.48 percent) and decreased at higher pH. The adsorption process was pH dependent, with optimum AO7 removal obtained at pH 2. This pattern of results corresponds to Hamzeh's previous study (2012). In his study he observed that adsorption capacity decreased by increasing pH from 2 to 9. The maximum adsorption was found to be at pH 2.5, indicating the adsorption was strongly pH-dependent.

The effect of contact time shows that as time increases from 15 min to 180 min the AO7 removal percentage increases. This is due to the fact that the concentration of acid orange 7 on the surface of the RCB is highest during its initial stage. The result was in line with the previous study Santhosh et al. (2020). In his research, the effect of contact time on the removal effectiveness of AO7 dye and Cr(VI) ions by modified sludge and woodchips was investigated at different time intervals up to 200 minutes. During the first 10 minutes, the adsorption of AO7 dye rose fast, with a removal effectiveness of nearly 40%. Following that, the adsorption rate gradually decreased until it reached equilibrium around 160 minutes later, with a maximum removal effectiveness of 90%.

Adsorbent dose calculation is a critical step in determining whether adsorbent capacity exists for a given IC of adsorbate. It was discovered in this study that raising the concentration of adsorbent dosage causes the AO7 to be removed more efficiently. The more bio sorbent in the solution, the more active sites for AO7 are available, resulting in increased AO7 removal. Tilaki et al. found comparable results (2014). He investigated the effect of biosorbent dosage on AO7 biosorption on dried Rice Stem to determine an ideal biosorbent dosage. The biosorbent dosages used in the study ranged from 1 to 10 g/L, with a starting AO7 concentration of 10 mg/L and a contact time of 90 minutes. Increasing pattern of AO7 elimination % by increasing SC is visible in the salt concentration. The removal percent is 93.1 with a greater salt concentration of 500mg, which is higher than the removal percent at 125mg. Due to the greater surface area for segregation, RCB/ZnONPs has a higher removal rate than RCB.

CONCLUSION

Results of this study indicated that composites with ZnO showed better performance for the removal of inorganic dye Acid Orange 7 from wastewater. While RCB/ZnONPs found to be more efficient in the removal of AO7. To overcome with the contaminated water with AO7 dye, adsorption method was used-the most recommended, inexpensive, low energy and less time-consuming method. Different parameters effect like pH, Dose, IC, SC and contact time was observed under batch scale study. It is concluded that nanocomposite with ZnO should be used on a large scale to remediate contaminated water with dyes.

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