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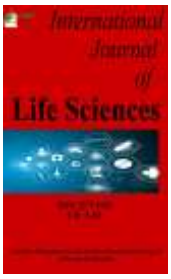

Full Length Research Paper

Phyto Mediated Synthesis of Nanocomposite for the Catalytic Sorption of Direct Dyes

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ARTICLE DETAILS

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nanocomposites, Commiphora wightii, photo catalytic activity

ABSTRACT

Synthetic dyes are colouring agents mainly used in textile industries which generate a huge amount of wastewater in the process of dyeing. Different dyes used in textile industry usually have a synthetic origin and complex aromatic molecular structures which make them more stable and more difficult to be biodegraded and thus polluting the environment. To overcome the deleteriouseffects of such dyes, it is necessary to decolorize them. In the present study, azo dyes were decolourized by nanocomposites prepared using plant Commiphora wightii as reducing agent. Production and characterization of nanocomposites was analysed by UV-visible spectroscopy, Fourier transform infra-red spectroscopy and SEM-EDX analysis. Photo catalytic degradation process showed significant dye degrading efficiency. At the end of 24 hours, nanocomposites showed 99.6% of degradation, followed by increased degradation of about 75% at the end of 7th day of incubation. Results confirmed the dyes were degraded into simple, non-toxic compounds. In conclusion, Commiphora wightii synthesized nanocomposites can exhibit excellent photo catalytic activity against dye molecules and can be used in water purification systems and dye effluent treatment.

1. Introduction

Nowadays, pollution of water resources by dyes or dye-based effluent discharged from many industries is already a worldwide problem. Today, across the world there are more than 10,000 commercially available dyes with over 7×105 tones of them being annually synthesized (Robinson et al. 2001). Non-biodegradable and toxic nature of most of these synthesized dyes affects water quality at as little concentration as 1ppm (Mehra and Sharma, 2012; Fosso-Kankeu et al. 2015) which poses great environmental concern. The water stream and environment get polluted by dye based effluents due to the lack of biodegradability because of their complex molecular structures and their synthetic origin. Various type of dyes used in several industries include acid dyes, basic dyes, reactive dyes, direct dyes, vat dyes, azo dyes and disperse dyes.

In recent decades, dye degradation has become necessary to control environment water pollution. The conventional chemical processes are effective but produces toxic intermediate products and the physical processes are less efficient with high operational cost. Biological processes have received more interest by today because of their cost effectiveness, lower sludge production and environmentally friendly. Microbial systems (bacterial and fungal species either as pure or mixed cultures) with efficient decolorization or degradation of colorants were well documented. The dye adsorption process is performed through the interactions between the dye molecules and the adsorbent and mainly includes hydrogen bonding, electrostatic bonding interactions, and π-π interactions (Al-Degs et al. 2008). The adsorption process is one of the most effective processes for separating due to its high efficiency, ease of operation, and cost- effective.

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Nanotechnology is a relatively new field of science and technology that studies tiny objects (0.1-100nm). Due to various positive attributes displayed by the biogenic synthesis of nanoparticles such as cost-effectiveness, none to negligible environment hazards and biological reduction served as an attractive alternative to its counterpart chemical methods. Nanomaterials with desired size and morphologies have drawn immense attention due to their unique morphology and size-dependent physicochemical properties and their importance in basic scientific research and potential applications (Mohapatra et al. 2010). Various transition metal oxide nanoparticles exhibit high chemical stability, ecofriendly nature, good photocatalytic activity and high surface area. The applications of nanotechnology can be very beneficial and have the potential to make a significant impact on society. Nanotechnology has already been embraced by industrial sectors, such as the information and communications sectors, but is also used in food technology, energy technology, as well as in some medical products and medicines. Nanomaterials may also offer new opportunities for the reduction of environmental pollution.

Nanocomposite is a matrix to which nanoparticles have been added to improve a particular property of the material. The properties of nanocomposites have caused researchers to consider using this material in biodegradation. Removal or recovery of organic and inorganic substance from solution by biological material which can include living or dead microorganisms and their components, seaweeds, plant materials, industrial and agricultural wastes and natural residues. The nanocomposite materials usedin this study were synthesized at room temperature and used as adsorbents to remove contaminants from aqueous solutions.

Commiphora wightii, commonly known as the Guggul tree, is a medicinal plant having various therapeutic applications including antimicrobial, anticancer and anti- inflammatory activities and environmental applications. It has been used in nanoremediation to degrade colours of dyes owing to its rich content of numerous phytoconstituents *viz.,* terpenoids, flavonoids, steroids, carbohydrates etc. The present study aimed at the synthesis of nanocomposite using *Commiphora wightii* extract and evaluating their potential applications in which the decolourization and degradation potential of nanocomposites to be studied.

2. Materials and methods

2.1 Collection of Samples and Preparation of Extract

Fresh green leaves (Commiphora wightii) of good health were collected from a nearby farm. They were rigorously washed to get rid of dust particles and then rinsed thrice with double distilled water and weighed afterwards. Five (5g) of powdered sample was soaked with 50 ml of water, ethanol and acetone separately. The entire mixture was incubated at 4°C for 48 hr. After the incubation period was over, the mixture was filtered and centrifuged at 10,000rpm at 4°C. The extracts were dried and stored at 4°C until further used.

2.2 Phyto-synthesis of Nanocomposite

Preparation of iron-aluminium nanocomposite was similar to the route followed for preparation of iron NPs in our previous study (Mondal and Purkait, 2018). In brief, 40 ml of prepared Commiphora wightii extract at pH 4 was mixed with a solution containing 0.025 (M) FeCl3 (5 ml) and 0.025 (M) Al2O3 (5 ml) (1:1 vol ratio). The reaction starts as the solution was kept at 70oC for 10-15 min and after then without disturbing the content it was again left for 30-40 min. Few minutes later a clear phase separation was observed with light colour solvent at the top and green thick precipitates at the bottom. After filtering, the retentive green portion was freeze dried at 15oC.

Powdered nanocomposite was formed by using a vacuumed lyophilizer chamber maintained at temperature 50oC and pressure 0.04 mbar. Finally the nanocomposite powder was homogenized to pH 7, dried and kept within vacuum desiccators for further use.

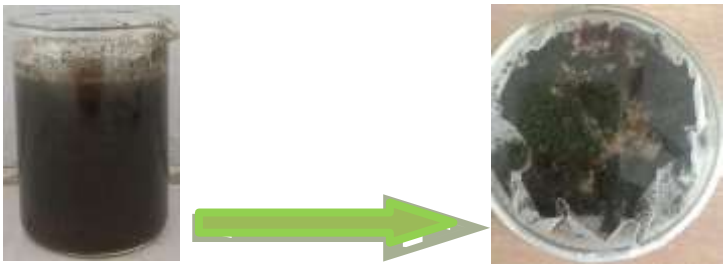


Fig 1. Iron-Aluminium Nanocomposite

The Ferric chloride and Aluminium oxide in 25ml of distilled water each. Both the solution were mixed and kept in a magnetic stirrer for 30 minutes at pH 7 in room temperature at 650 rpm. Then add 5g of Activated Carbon and green leaves (Commiphora wightii) powder extract to the solution and again kept in the magnetic stirrer for 4 hrs in room temperature at 1100-1300 rpm. The solution was filtered and dried overnight and further heated at 400°C in a Muffle

furnace for 10 minutes. Then it is converted into powder form, the nanocomposites are synthesized.

3. Characterization of Nanocomposite

3.1 Scanning Electron Microscopy-Energy Dispersive X-ray Spectrometry Analysis

The microstructure and composite homogeneity of the obtained samples were investigated using a SEM/EDX scanning microscope JEOL-JSM 64000 LV. Energy dispersive X-ray analysis measurements were performed under standard conditions. The silver nanoparticles were centrifuged at 10,000 rpm for 30 min and the pellet was redispersed in 10 mL ethanol and washed 3 times with sterile distilled water to obtain the pellet. The pellet was dried in an oven and thin films of dried samples (10 mg/mL) were used for compositional analysis.

4. Fourier Transform Infrared Spectroscopy Analysis

Spectroscopy for the Fourier transforms infrared (FTIR) spectroscopy analysis, the vacuum dried AgNPs were mixed with potassium bromide (KBr) and the spectra were recorded with a Perkin Elmer Spectrum Express version 1.03.00. The scanning data were obtained from the average of 47 scans in the range 4000–400 cm-1 with the resolution of 4 cm-1.

5. Adsorption Study

5.1 Preparation of Dye solution

The stock solution of dye was prepared by dissolving 0.1 g of direct orange dye and direct green dye in 500ml of distilled water. The working solutions were prepared by serial dilution of this stock solution.

6. Experimental study

The working solution of different concentrations 50 mg/l, 100 mg/l, 150 mg/l, 200 mg/l, 250 mg/l were prepared by serial dilution of stock solution. The five factors initial concentration of dye, pH, contact time and adsorbent dose were varied. The adsorption tests were carried out by shaking 30ml working dye solution in a conical flask. The conical flasks were placed on rotary shaking machine for desired time at 150 rpm. The progress of adsorption during the experiment was determined by removing the flask after desired contact time and analysing the solution spectrophotometrically at 520nm.

The spectrophotometric readings were recorded and further calculations were done to see the removal efficiency of the adsorbents. The dye removal efficiency was calculated by using the formula:

% Removal efficiency (η) = $\frac{Ci-Cf}{Cf} \times 100$ ---------- (3)

Where, Ci is the initial concentration of the dye in solution and Cf is the final concentration of the dye in the solution.

6.1 Adsorption Isotherms of Nanocomposites

Adsorption isotherms were used to model colour adsorption. The adsorption isotherms were tried to fit to the experimental adsorption data. The non-linear forms of Langmuir and Freundlich were applied to describe the equilibrium adsorption data. So, the experimental data were analysed according to the equations:

$$\frac{Ce}{Qe} = \frac{1}{KlQm} + \frac{Ce}{Qm} \quad (4)$$

$$\ln Qe = \ln Kf + \frac{1}{n} \ln Ce \quad (5)$$

Where Qm (mg g-1), KL (L mg-1), KF [(mg g-1) / (mg L-1)1/n] and n are the maximum monolayer adsorption capacity, the Langmuir constant, the Freundlich constant and an empirical constant respectively.

The dimensionless separation factor, RL, is an essential characteristic of the Langmuir isotherm, which is given as follows:

(6) $$Rl = \frac{1}{1+KlC0}$$

The value of RL indicates the type of the isotherm to be either favourable (0 < RL < 1), unfavourable (RL >1), linear (RL = 0).

6.2 Adsorption Kinetics of Nanocomposites

There are two models, i.e. pseudo-first order and pseudo-second order, were used to describe the adsorption process. The pseudo-first order rate equation is given as

ln (Qe – Qt) = lnQe- k1t (7)

The pseudo-second order rate equation is given as

(8) $$\frac{t}{Qt} = \frac{1}{k2Q^2e} + \frac{t}{Qe}$$

where Qt and Qe (mg g-1) are the theoretical amounts of adsorbed dye by the nanocomposites at time t and equilibrium, respectively. k1and k2 (g mg-1 min-1) are the adsorption rate constants for the pseudo-first order and the pseudo-second order models.

7. Results and discussion

7.1 Synthesis and Characterization of Nanocomposites

The present study revealed that the adsorption capacity of the plant mediated nanocomposite. The synthesized nanocomposites were initially confirmed by visual observation by colour change. It was observed that the colour of the reaction mixture was changed from light colour to dark colour (Figure). Further, the synthesized nanocomposites were characterized by Fourier Transform Infrared Spectroscopy (FT-IR) and SEM-EDX.

Fig 2 Iron-Alumina Nanocomposite

7.2 Scanning Electron Microscopy-Energy Dispersive X-ray SpectrometryAnalysis

Figure shows a micrograph of Iron-Alumina nanocomposite with a nanospherical shape and rough surface morphology. The surface morphology and shape of nanocomposite are similar to those observed in previous studies 17,18. SEM-EDX analysis was performed to determine the mass percent of each element in the synthesized compound, as shown in Figure 5.6. The compositions of C, Fe, Al, Cl and O are 6, 26.8, 13, 17 and 8.2 wt.%, respectively. To support the SEM-EDX results, the percentage of mass was calculated, and the results for the elemental mass percentages of Al, Fe and O. Therefore, the successful synthesis of the Iron-Alumina nanocomposite is confirmed by the similarities between the mass percentages obtained in this study.

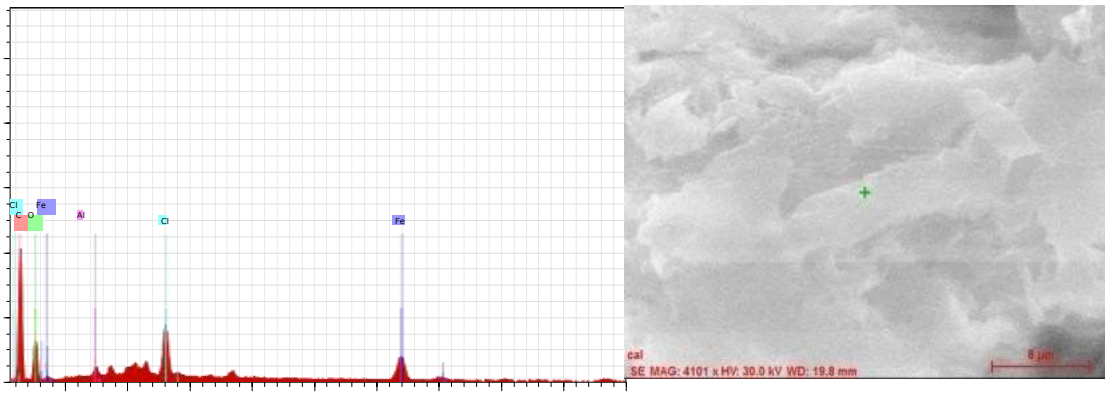
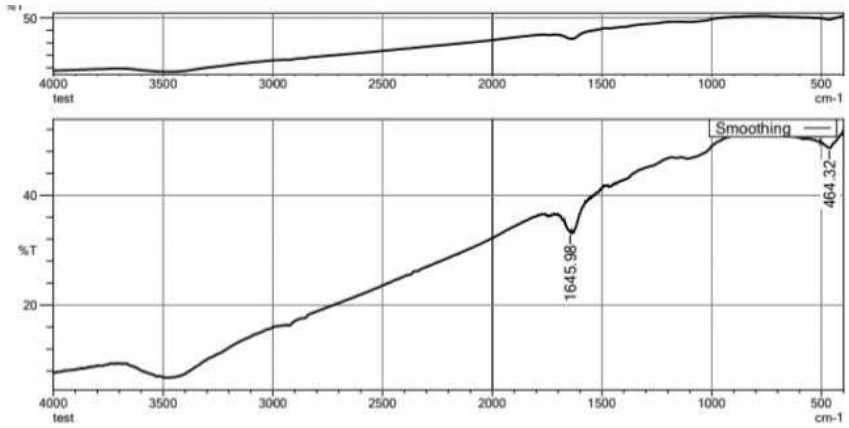


Fig 3 SEM-EDX analysis of Nanocomposite

7.3 FTIR analysis

FTIR spectroscopy was carried out to determine the potential biomolecules responsible for the reduction and capping of the nanocomposite synthesized. The FTIR spectra of plant extracts show absorption bands characteristics of functional groups such as alcohol, phenol, amine and carbonyl group. The vibrational bands corresponded to bonds, such as alcohols (–O–H), alkenes (>C=C), amines (=N–H), flavonoids, and amines (–NH2), which are all in the range of 800–3496/cm. The absorption band at 3496.52/cm in the spectrum might be attributed to the stretching vibrations of secondary amines of N–H bond and bonded hydroxyl (–OH) groups of phenols and carboxylic acids (Azizi et al., 2017). Bonded hydroxyl (–OH) groups of carboxylic acids and phenols could produce absorption bands at 3496.52/cm. In the spectrum, the new band at 1645.98/cm might suggest a new C=O group (ketone or aldehyde).



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	Peak	Intensity	Corr. Intensity	Base (H)	Base (L)	Area	Corr. Area	Comment
1	464.32	48.63	1.78	506.01	403.95	5139.275	93.938	
2	1645.98	33.30	0.51	1670.42	1640.23	1994.327	13.692	

Fig 4 FTIR analysis of Centella asiatica mediated Nanocomposite

7.4 Effect of various parameters on the adsorption of Direct dyes

Effect of Contact time

In adsorption study, the effect of contact time relates to the amount of dye dsorbed on to an adsorbent with respect to the amount of time to reach equilibrium (Nandi et al. 2009). The variation of the percentage removal against contact time at an initial dye concentration of 10mg L-1 is shown in Figure 5.8. It is clear that the adsorption of dyes was rapid at the initial stage to 60 min of the contact period and gradually slows down when it reaches equilibrium beyond 60 min. The maximum removal of 99% was observed at 60 min. Rapid adsorption at the initial stage is due to the availability of large amount of surface sites for adsorption, resulting in dye molecules being adsorbed onto the external surface of adsorbent through boundary layer adsorption (Kyzas et al. 2012). As the contact time increases, the surface of adsorbent gets saturated. Hence, there is limited number of surface sites available for dye adsorption, due to the presence of some repulsive forces forming between dye molecules on the surface of composite and dye molecules present in the solution (Nandi et al. 2009).

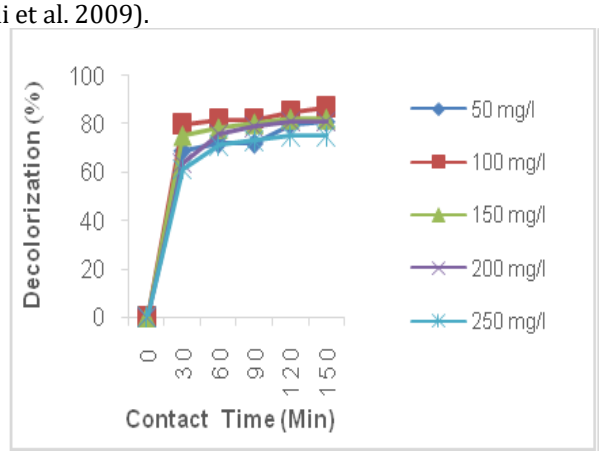

Fig 5 (a) Effect of Contact time and Initial DG dye concentration

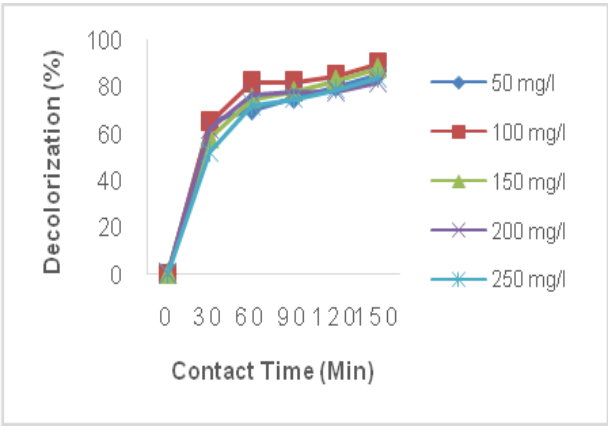

Fig 5 (b) Effect of Contact time and Initial DO dye concentration

7.5 Effect of pH

The initial pH did not affect the adsorption of Direct dyes on nanocomposite surface and the % Direct dyes removal at different pH (6–10). Zhang et al. (2011) reported that the maximum adsorption of malachite green on pine wood decayed by Poria cocos observed at pH 8 and was about 74.3%, corresponding with our results for CoPAC nanocomposite. The

present study suggests the applicability of nanocomposite for the treatment of dye bearing effluents at different pH. From the Figure 5.9, it is observed that the adsorbent showed good adsorption capacity (pH 6) in neutral/slightly basic medium than the acidic medium. The percentage of removal of DO dye by adsorption on these adsorbents progressively increased as the pH of the solution increased from 5 to 8. The consistent dye removal in the pH range 5-8, could be due the effect of electrostatic interactions between adsorbent and the DO dye. It is clearly indicated that with decrease in pH of the solution, the positive charge density on the surface becomes negatively charged. During the adsorption a surface complex is formed between adsorbate-adsorbent interface by interaction of the hydroxylated surface, H+and dye anions at different pH range.

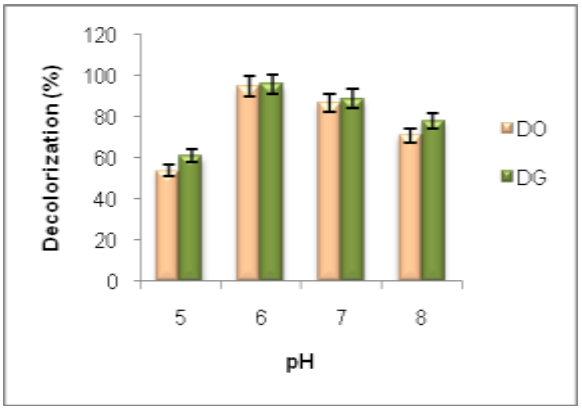

Fig 6 Effect of pH for DO and DG dye

7.6Effect of temperature

The effect of temperature on adsorption of Direct dyes was studied at 20, 30, 40 and 50 ◦ C in which the nanocomposite showed maximum dye adsorption at 30 ◦ C (Figure). Gobi et al. (2011) reported that the highest adsorption of methylene blue on waste activated sludge was observed at 30 ◦ C and it exhibited lower adsorption rate at 20 and 50 ◦ C. The results shown that DO and DG solution at 30 ◦ C had the highest adsorption (80%) on nanocomposite.

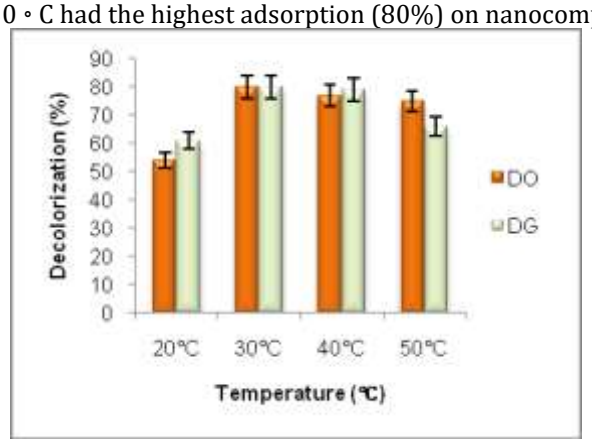

Fig 7 Effect of Temperature for DO and DG dye

7.7 Effect of Adsorbent Dosage

The study of effect of adsorbent dosage is necessary and very useful in identify the optimum of adsorbent required for the removal of dye. The removal of dye by adsorption onto nanocomposite samples in the range of 0.25 to 1.0 mg with 100 mg/l and 200 mg/l of initial dye concentrations and agitation time of 60 and 120 min respectively at pH 6.0 at room temperature were studied. The results revealed that the maximun adsorption for the percentage (85%) removal of dye versus adsorbent dose (0.25 g L-1) are given in the Figure .

7.8Adsorption kinetics

The isothermal models and adsorption kinetics are shown in Table 5.5. The results showed that dyes fitted according to Freundlich isotherm model (R2=0.98). The R2 of kinetic models suggested that the pseudo-second-order model mechanism is predominant which means the uptake process follows the pseudo second-order expression with correlation coefficients were always greater of 0.9482.

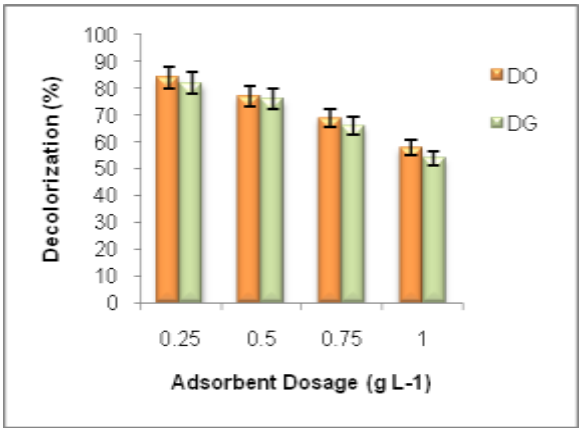

Fig 8 Effect of Adsorbent dosage for DO and DG dye

Fig 9 Biosorption of Direct green dye

Fig 10 Biosorption of Direct orange dye

Table 1 Freundlich and Langmuir parameters for DO and DG dye removal

Dye	Freundlich			Langmuir		
	R^2	K_F	n	R^2	a	Qm
Direct Orange	0.9844	0.024	0.7542	-	-	-
Direct Green	-	-	-	0.9888	0.0941	49.44

Table 2 Pseudo first order and second order parameters forDO and DG dye removal

Dye	R^2	K_1(min $^{-1}$)	K_2(mgg^{-1} min $^{-1}$)
Direct Orange	0.9482	0.0482	-
Direct Green	0.9288	-	0.0058

8. Conclusion

Catalytic activity of these green synthesized nanocomposites was evaluated for the degradation studies of Direct dyes. Different parameters affecting the dye degradation procedure were investigated and optimized. Fourier transform infrared spectroscopy studies identified the functional groups present in bioactive compounds which were responsible for the reduction and stabilization of the nanocomposite. The green synthesized nanocomposites were characterized by SEM-

EDX and FTIR analysis. The extracts showed significant antibacterial activity on both Gram-positive and Gram- negative bacteria. This promises a potential use of the nanocomposite in the pharmaceutical, biomedical, and industrial fields, such as bandages, wounds dressing, and dental tools. In addition, the applications include also food and water storage as well as wastewater treatment. Based on the above findings and arguments, it is to be concluded that Iron-Alumina nanocomposite could be employed as an effective and inexpensive sorbent for the removal of direct dyes. But in fact this sorbent possesses a more significant efficiency on the removal of direct orange than that of direct green.

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