Green synthesis of Fe nanoparticles by using *Mangifera indica* extract and its application in photo-catalytic degradation of dyes

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**ABSTRACT**

An exceedingly facile green approach that produces a reliable adsorbent based on a transition metal such as Iron (Fe) using *Mangifera indica* leaf extract at room temperature is described. A single pot method was used for synthesis with no capping agents, surfactants or other templates. The main intention of this study is to synthesize iron nanoparticles from leaf extract (*Mangifera indica*) and examine its degradation potential for photo-catalytic removal of dyes (Congo red and brilliant green) from wastewater. Characterization of synthesized nanoparticles was executed by pHpzc, scanning electron microscopy and Fourier transform infrared spectroscopy studies and results confirm the presence of iron nano-sheets with biomolecules. All photo-catalytic experimental results were assessed by sum of squared estimate of errors and simple linear regression R² with dye concentration, pH, contact time and dose rate as dependent and independent variables. Adsorption experimental data was verified by kinetics and isothermal models. Results showed that Langmuir and pseudo second order models give best fitness towards the photo-catalytic adsorption procedure. Thermodynamics revealed that adsorption mechanism is endothermic, described by the values of changes in Gibbs free energy, enthalpy and entropy, and is chemisorption in nature, with spontaneous processes. Overall photo-catalytic adsorption execution with synthesized iron nanoparticles and simple biomass of *Mangifera indica* gives satisfactory results for treating dye wastewater.

**Key words** | brilliant green, Congo red, endothermic, isotherms, Fe-NPs, *Mangifera indica*

**HIGHLIGHTS**

- *Mangifera indica* extract was put to use for green synthesization of Fe-NPs by a single pot method.
- Fe-NPs and powdered biomass of *Mangifera indica* were adopted for photo-catalytic degradation of synthetic dyes.
- Green synthesized Fe-NPs form dense nano-sheets with thickness of about 20–50 nm.
- Maximum % photo-catalytic degradation was 72.6 and 80.87% for Congo red and 72.88 and 82% for brilliant green with biomass and NPs, respectively.

**INTRODUCTION**

In the last few years, the aquatic environment has been frequently polluted by anthropogenic wastewater contaminants, including pesticides, dyes, heavy metals,
Iron nanoparticles (Fe-NPs) for treating wastewater have been used since the 1990s due to their distinctive characteristics such as large specific surface area, unique adsorption properties and wide distributions of reactive surface active sites. Conventional techniques to synthesize Fe-NPs are physical method (attrition), thermal decomposition (Sun & Zeng 2002; Baskoutas et al. 2008; Devatha et al. 2016) and vacuum sputtering (Tosco et al. 2014). These methods have many restrictions such as low production rate, high temperature and pressure or energy necessity, and thus are relatively expensive. In addition to this, limitations of these methods include contamination of precursors and release of harmful by-products to the ecosystem (Thakkar et al. 2010). Synthesis by plant extracts is beneficial because it reduces the possibility of further contamination by lessening the reaction time and also maintaining the cell structure (Ajitha et al. 2015). In consequence the green synthesis is suggested to be a satisfactory alternative candidate to all other conventional methods as there is an increasing requirement for ecofriendly, cost-effective and less toxic procedures for synthesizing NPs. Moreover, green production is a conventional method for synthesis of NPs at large scale with different range of particle sizes, providing more surface active pore sites to reclaim effluents from wastewater at higher efficiency than natural biomass adsorbents. In the recent past due to these effective advantages, green synthesis is gaining more importance in all the fields focusing towards a greener environment (Devatha et al. 2016).

In this work, Fe-NPs from Mangifera indica leaf extract as a catalytic adsorbent and simple powdered Mangifera indica biomass in a photochemical system (CEL-WLAX visible light photochemical system) were studied for adsorptive treatment of BG and CR dyes. The Mangifera indica surface modified by Fe oxides (NPs) proved to be a more effective surface for reduction of dyes from aqueous media compared with biomass, and acted as catalyst for adsorptive removal of synthetic dyes in a photochemical system. In addition, this approach mainly deals with green synthesis and characterization of Fe-NPs with optimization of adsorption parameter variables such as catalyst (adsorbent) dose, dye solution concentration, pH and fixed temperature under the influence of photochemical apparatus.

**MATERIALS AND METHODS**

Ferric chloride (FeCl₃), CR and BG dyes and other chemicals – nitric acid (HNO₃) 0.1 M stock (68% purity)
and sodium chloride (NaCl) 1.0 M – used in the present study were AR grade. Stock solutions of dyes were prepared of 1,000 mg L\(^{-1}\) and further attenuation of solutions were freshly made from stock each time. The chemical structure of BG and CR are presented in Figure 1.

**Preparation of leaf extract**

Fresh leaves of *Mangifera indica* (mango plant) were collected from the University of Agriculture Faisalabad. The collected leaves were firstly wiped with distilled water then further with deionized water to remove excess impurities and dehydrated on a blotting paper for 4 hours at room temperature. Around 25 g of small pieces of evenly crushed leaves were mixed in 200 mL double distilled water and boiled for 30 min. After cooling at room temperature, these were centrifuged at 12,000 rpm for 15 min at 4°C and filtered through 0.45 µm polytetrafluoroethylene (PTFE) filter. The filtrate was stored at 4–8°C for preparation of NPs and used as reducing or stabilizing agents (Groiss et al. 2017).

**Preparation of iron nanoparticles**

FeCl\(_3\) of analytical grade was used as precursor for green synthesis of Fe-NPs. A solution of 0.10 mg L\(^{-1}\) of FeCl\(_3\) was developed and homogenized with leaf extract in 1:2 ratio at 15°C temperature. The instant black color emergence indicates the formation of Fe-NPs (Xio et al. 2016). Samples without exposure to sunlight were preserved as control and no color transition was spotted (Jayapriya et al. 2019). To predict the type of green synthesized Fe-NPs, the following chemical transitions can be assumed.

\[
\begin{align*}
2\text{FeCl}_3 \text{ (solution)} + 3\text{H}_2\text{O} & \rightarrow \text{Fe}_2\text{O}_3 \text{ (solid)} + 6\text{HCl} \text{ (gas)} \\
\text{FeCl}_3 \text{ (solution)} + \text{H}_2\text{O} & \rightarrow \text{FeOCl}_3 \text{ (solid)} + 2\text{HCl} \text{ (gas)} \\
\text{2FeOCl} \text{ (solid)} + \text{H}_2\text{O} & \rightarrow \text{Fe}_2\text{O}_3 \text{ (solid)} + 2\text{HCl} \text{ (gas)}
\end{align*}
\]

Therefore, we can say that *Mangifera indica* contains Fe\(_2\)O\(_3\) modified surface as no crystal formation (FeOCl) was detected during this green synthesis, which was confirmed by Fourier transform infrared (FT-IR) analysis.

**Photo-degradation of dyes**

Photo-catalysis followed by adsorptive degradation of BG and CR dyes was accomplished to explore the effect of irradiation on degradation ability. Effect of photo-catalysis by NPs and powdered biomass on adsorptive reduction of dyes was checked at 228–288 nm light in a photochemical system (CEL-WLAX visible light photochemical system), as previously explained in literature (Liu et al. 2017), in which adsorption medium was exposed to visible light at a specific range of wavelength (228 to 288 nm), promoting adsorption–desorption property in aqueous solution.

In each degradation reaction medium of CR and BG the volume of dye solution (100 mL) was thoroughly mixed with desired catalyst dosage (0.1 g). Samples were treated for a fixed contact time and then filtered with 0.45 µm PTFE filter to remove adsorbent from dye solution. Different

![Figure 1](http://iwaponline.com/wst/article-pdf/83/7/1739/870995/wst083071739.pdf)  
**Figure 1** Chemical structure of Congo red (azo dye) and Brilliant green (basic dye) dyes.
conditions were selected: initial dye concentration (mg L\(^{-1}\)), shaking time (min), pH, adsorbent mass (g) and temperature (K), to investigate adsorption mechanism using Fe-NPs and biomass powder of *Mangifera indica*.

Absorbance was measured for both CR and BG dyes at their \(\lambda_{\text{max.abs}}\) of 497 and 623 nm by a UV-visible spectrophotometer (UV-2600, China), respectively. Photo-catalytic % degradation efficiency of dyes was evaluated from Equation (1):

\[
\% \text{Photo-catalytic degradation} = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)
\]

where \(C_0\) is initial dye amount (mg L\(^{-1}\)) and \(C_e\) is finally measured concentration of dye (mg L\(^{-1}\)) at equilibrium in adsorption degradation medium.

**pH point of zero charge (pHpzc)**

Point of zero charge pH (pHpzc) of Fe-NPs and biomass powder of *Mangifera indica* was determined by applying salt addition procedure. In this method, 0.1 g of adsorbent was added to 40 mL solution of sodium nitrate (NaNO\(_3\)) and pH of solutions was maintained initially from 2 to 12 with the help of 0.1 M acid and base (HNO\(_3\) and KOH) (Kataria & Garg 2017). After 100 min of shaking time at room temperature final pH of solutions was determined by a pH meter and pHpzc of adsorbents was obtained as 6.4 and 8.2 for Fe-NPs and biomass powder of *Mangifera indica*, respectively, by plotting the graph between initial pH and \(\Delta\)pH (pH\(_i\) – pH\(_f\)).

## RESULTS AND DISCUSSION

### Characterization

Characterization of green synthesized Fe-NPs was monitored by scanning electron microscopy (SEM) (Hitachi S 4800) and FT-IR (FTIR-400S Shimadzu) techniques. Figure 2(c) represents a SEM image of green synthesized Fe-NPs of *Mangifera indica*, which shows the formation of spherical shaped morphology of NPs. The spherical shape NPs had average size of 200–400 nm and their diameter...
was in the 0.25 μm range. These spherical shapes combine to form dense nano-sheets with distinctive thickness of about 20 to 50 nm and size of a single sphere is about 3.5 μm. As from previously reported SEM analysis of Mangifera indica powder biomass (Abodunrin et al. 2015), for a specified wavelength under the influence of irradiation of 100 mW cm⁻², film micrograph of Mangifera indica has thickness of 9 μm with particle size of 20 nm, indicating the favorability of CR and BG adsorption, but the pore size of powdered biomass is less than that of Fe-NPs. Therefore, structural morphology of Fe-NPs from Mangifera indica enhances the photo-catalytic degradation of BG and CR dyes as compared to biomass powder of Mangifera indica. From Figure 2(a) (CR) and 2(b) (BG), it is clearly found that dyes could not only effect dispersability of NPs pores but also show impact towards the morphological structure and size of particles. After adsorptive degradation of dyes the average size of green NPs was observed to be from 90 to 100 nm.

The FT-IR spectrum of Mangifera indica Fe-NPs is given in Figure 3. The absorption bands in region of 2,923 cm⁻¹ illustrate C-H and CH₂ bond vibration of aliphatic (alkane, alkene or alkyne or maybe their derivatives) hydrocarbons which maybe long chain hydrocarbons. The peaks at 1,151 and 1,643 cm⁻¹ represent the presence of C-O and C=C aromatic ring with stretching of O-H bonds. The region at 3,557 and 1,095 cm⁻¹ refers to the presence of sulfate and amides with C=O extending vibrations, respectively. The wavelength of 551.6 and 628.75 cm⁻¹ indicates the presence of Fe-O group vibrations, strongly verifying the surficial formation of Fe-NPs. On the other hand, FT-IR analysis of Mangifera indica biomass described in literature (Abodunrin et al. 2015) showed the strong appearance of C-H and C=O bond stretching at 1,735 and 1,041 cm⁻¹ and aromatic C-C groups at 1,535 cm⁻¹ with conjugation at 1,618.33 cm⁻¹. All these observed groups (C=O, C-H, O-H) and indication of biomolecules (aliphatic hydrocarbons, aromatic molecules) recommends the adsorption of BG and CR dyes on Fe-NPs and biomass of Mangifera indica surface via photo-degradation procedure.

The photo-adsorptive behavior of adsorbent is primarily dependent on aggregation of pores in their plane, which was determined by using Brunauer-Emmett-Teller (BET) analysis. Here, green synthesized Fe-NPs were ignited at 573 K for 1 hour for reclamation of water content and other organic pollutants. At 87 to 77 K (constant temperature) the Fe-NPs were analyzed and allowed to absorb N₂ (nitrogen) gas. Adsorption was continuous until equilibrium establishment and then pressure variation in samples was noted. By employing the BJH-model (Barret-Joyner-Halenda) pore volume and surface area of NPs were calculated before and after photo-adsorption and results are shown in Table 1. From, this surface analysis it is noted that the surface area decreases after dye degradation, approximately in ratio of 1:0.347 (CR) and 1:0.30 (BG). These results exhibit the favorability of dye reclamation via photo-adsorptive procedure.

![Figure 3](http://iwaponline.com/wst/article-pdf/83/7/1739/870995/wst083071739.pdf)
Batch photo-catalytic adsorption experiments

pH effect

Influence of pH on photo-catalytic degradation of BG and CR was investigated in pH range from 2 to 12 by proceeding with 50 mg L$^{-1}$ initial dye concentration, 0.1 g of NPs catalyst and biomass and shaking time of 100 min at room temperature (293 ± 1 K). Figure 4(a) represents the effect of pH on photo-catalytic degradation of CR and BG dyes on Fe-NPs and biomass of *Mangifera indica*. In batch experiments, CR degradation increased from 3.72 to 72.6% for biomass and 12.64 to 80.87% in the case of Fe-NPs with rise in pH from 2 to 12, whereas BG degradation increased from 19.08 to 72.88% for biomass of *Mangifera indica* and 26.97 to 80.48% in the case of Fe-NPs with increase in pH from 2 to 6. Both dyes behave differently with biomass and Fe-NPs of *Mangifera indica* as shown in Figure 4(a); no further dye uptake was observed with increase in pH from 8 to 12 in the case of CR and 6 to 12 in BG degradation medium.

Dyes have two intermediates: an aromatic ring and azo group. The solution generally affects the azo-moiety reaction while aromatic rings remain unaffected. Thus, CR degradation becomes more beneficial due to protonation of amino group at pH 8.0, and negative surface charge of Fe-NPs grows as compared to powder biomass (Hasanpoor et al. 2017). Moreover, at lower pH 6.0 sulfamethoxazole molecule in BG gives its an acid conjugate that facilitates electrostatic attraction between dye molecule and catalyst surface of Fe-NPs instead of powdered biomass of *Mangifera indica* (He & Hwang 2016). Therefore, at below pH$_{pzc}$ of adsorbents the development of electrostatic attraction.

| Table 1 | BET-analysis of photo-degradation of dyes by Fe-NPs |
|---------------------------|---------------------------|
| Fe-NPs per dye | Before dye degradation | After dye degradation |
| | Pore volume (cm$^3$ g$^{-1}$) | Surface area (m$^2$ g$^{-1}$) | Pore volume (cm$^3$ g$^{-1}$) | Surface area (m$^2$ g$^{-1}$) |
| Congo red | 0.462 | 11.481 | 0.149 | 3.995 |
| Brilliant green | 0.462 | 11.481 | 0.127 | 3.452 |

![Figure 4](http://iwaponline.com/wst/article-pdf/83/7/1739/870995/wst083071739.pdf)

(a) Effect of pH for photo-catalytic removal of dyes on biomass and Fe-NPs from *Mangifera indica* (0.1 g adsorbent mass, 100 mL solution with concentration 50 mg L$^{-1}$ of dyes at room temperature). (b) Effect of initial dye concentration for photo-catalytic degradation of dyes (0.1 g adsorbent mass, 100 mL dye solution for 100 min shaking time at pH 8.0 for CR and 6.0 for BG). (c) Effect of adsorbent amount for photo-catalytic degradation of dyes (100 min contact time, 100 mL dye solution at pH 8.0 for CR and 6.0 for BG). (d) Effect of contact time for photo-catalytic degradation of dyes (0.1 g adsorbent mass, 50 mg L$^{-1}$ dye concentration, 100 mL dye solution at pH 8.0 for CR and 6.0 for BG).
between Fe-NPs and powdered biomass of *Mangifera indica* with BG and CR dye molecules gives rise to auspicious photo-catalytic degradation, which is chemisorption in nature (Alshammari *et al.* 2020).

**Influence of initial dye concentration**

The photo-adsorptive degradation of BG and CR dyes as a function of initial dye concentration was investigated in the range 5 to 50 mg L\(^{-1}\). Other experimental variables were maintained as 0.1 g adsorbents mass, 100 mL dye solution, and pH 8.0 and 6.0 for CR and BG at room temperature (293 ± 2), respectively. From Figure 4(b) it is clear that dye removal decreased from 61.65 to 24.99% and 59.72 to 20.14% for BG and CR dyes with increase in dye concentration with powdered biomass of *Mangifera indica*. But, the reduction in % degradation was greater in comparison with green synthesized Fe-NPs from *Mangifera indica*. The dye removal was decreased from 72.56 to 39.02% and 70.72 to 32.78% for BG and CR dyes with NPs as a photo-catalyst, respectively (Figure 4(b)). This trend of % dye degradation may be attributed to the fact that at lower concentration excess number of active sites are readily available on surface of adsorbents. By increasing dye concentration the photo-catalytic activity reduced due to engorgement of binding sites with corresponding dye molecules (Kataria & Garg 2017).

**Adsorbent mass effect**

The relationship between adsorbent mass (g) and photo-catalytic degradation of dyes was examined in 100 mL dye solution, 50 mg L\(^{-1}\) of CR and BG and 100 min contact time at temperature 293 ± 2 K with pH 6.0 and 8.0 for BG and CR, respectively. For biomass of *Mangifera indica* the % degradation efficiency continuously increased from 57.81 to 73.45% and 57.21 to 72.6% for BG and CR dyes with rise in adsorbent dose from 0.05 to 0.1 g (Figure 4(c)). For Fe-NPs the % photo-catalytic degradation removal increased from 67.74 to 80.87% and 66.85 to 80.48% for CR and BG with increase in adsorbent amount. Therefore, green synthesized Fe-NPs proved to be a more efficient adsorbent for dye degradation than biomass of *Mangifera indica*. This phenomenon reveals that the availability extent of surface active pore sites increased with rise in adsorbent dose, and the equilibrium point showed direct relation with increase in active sites due to agglomeration of sites on adsorbent surface (Wang & Gu 2015).

**Effect of shaking time**

To explore shaking time effect on photo-catalytic adsorptive removal of BG and CR dyes by powdered biomass and Fe-NPs of *Mangifera indica*, catalytic adsorption experiments were conducted with different contact times ranging from 0 to 200 minutes with 0.1 g adsorbent dose and 50 mg L\(^{-1}\) dye concentration at optimum pH (6.0 for BG and 8.0 for CR) and nearly similar behavior was perceived for both dyes. Percent degradation as a function of variable shaking time is given in Figure 4(d). The photo-catalytic degradation efficiency increased from 9.03 to 75.89% and 13.14 to 83.55% for CR and BG dyes with powdered biomass of *Mangifera indica*, while in the case of green synthesized Fe-NPs from *Mangifera indica* the % degradation efficiency increased from 22.09 to 90.53% and 25.08 to 85.62% for CR and BG, respectively (Figure 4(d)). Initially, the expeditious rise in dye adsorption is possibly due to large availability of surface active pore sites which are more accessible in NPs surface as compared to powdered biomass of *Mangifera indica*.

In addition as time duration reached from 140 to 200 min, the catalytic efficiency was slowed down and eventually attained equilibrium resulting from saturation of adsorbents sites and repulsive forces that may assemble between adsorbent and adsorbate molecules (Kataria & Garg 2017; Tripathy *et al.* 2020).

**Thermodynamic study**

Temperature influence for photo-catalytic degradation of BG and CR dyes was studied in temperature from 0 to 60 °C (273 to 333 K), 100 mL of 50 mg L\(^{-1}\) dye solution and 100 min shaking time with 0.1 g adsorbents amount at optimum pH for both dyes. Both dyes show similar photo-adsorbent behavior with surface of powdered biomass and green synthesized Fe-NPs from *Mangifera indica*. Figure 5(a), shows the temperature change effect on photo-catalytic degradation of BG and CR. As the temperature rose from 0 to 20 °C the degradation values increased from 32.83 to 66.5% and 37.3 to 69.54% for CR and BG dyes with powdered biomass of *Mangifera indica*. While with NPs, degradation increased from 39.89 to 71.51% and 45.3 to 80.09% for CR and BG dyes. But less improvement in catalytic efficiency was observed with further increase in temperature from 40 to 60 °C: 71.69 to 73% and 73.33 to 76.07% for CR and BG with biomass, and 80.78 to 82.09% for CR and 82.5 to 84.6% for BG with Fe-NPs from *Mangifera indica* (Figure 5(a)).
Thermodynamic parameters for photo-degradation of BG and CR with powdered biomass and green synthesized Fe-NPs from *Mangifera indica* were obtained using temperature experiments (0 to 60 °C). The Gibbs free energy (ΔG°), entropy (ΔS°) and enthalpy (ΔH°) were enumerated by the following expressions (Equations (2) and (4)) and their values are given in Table 2.

\[ ΔG° = -RT \ln K_c \]  
\[ K_c = \frac{C_{ads}}{C_{eq}} \]  
\[ \ln K_c = \frac{ΔH°}{RT} - \frac{ΔS°}{R} \]

where \( R (8.314 \text{ J mol}^{-1} \text{ K}^{-1}) \) is general or universal gas constant, \( K_c \) is equilibrium constant, \( C_e (\text{mg L}^{-1}) \) photo-catalytic equilibrium amount of BG and CR adsorbed on biomass and NPs surface and \( T \) is temperature in K. A non-linear plot was obtained by a graph between 1/T and ln \( K_c \) (Van’t Hoff plot), Figure 5(b). Through the slope and intercept value of the plot, positive values of enthalpy and entropy were obtained (Table 2), indicating that adsorption is overall endothermic in nature for photo-catalytic degradation of CR and BG dyes with biomass and Fe-NPs from *Mangifera indica*. Positive value of entropy revealed that there is an increase in degree of randomness at adsorbate-adsorbent interfaces (Chen et al. 2012; Kataria & Garg 2017). Thermodynamic parameter values for both dyes with adsorbents confirm chemical-adsorption as a mechanism of photo-catalytic degradation of dye molecules.

### Kinetic studies

The rate mechanism of photo-catalytic activity of adsorption for BG and CR removal with powdered biomass and green synthesized Fe-NPs from *Mangifera indica* was determined by pseudo first (Equation (5)) and second (Equation (6)) order kinetic rate expressions. These expressions are

Figure 5 | (a) Temperature effect for photo-catalytic degradation of dyes (0.1 g adsorbent mass, 100 min contact time, 50 mg L\(^{-1}\) dye concentration, 100 mL dye solution at pH 8.0 for CR and 6.0 for BG). (b) Van’t Hoff plot for photo-catalytic degradation of BG and CR.

| Temperature (K) | ΔG (kJ mol\(^{-1}\)) | ΔH (kJ mol\(^{-1}\)) | ΔS (J K\(^{-1}\) mol\(^{-1}\)) |
|-----------------|---------------------|---------------------|---------------------|
| 273             | -1.769              | -1.019              | -1.267              |
| 283             | -0.953              | -0.300              | -0.621              |
| 293             | 1.657               | 2.230               | 2.009               |
| 313             | 2.251               | 3.486               | 2.462               |
| 323             | 2.349               | 3.552               | 2.736               |
| 333             | 2.411               | 3.698               | 2.816               |
represented in their linear forms by the following expressions:

\[
\log (q_e - q_t) = \log q_e - \frac{K_1}{20303} t
\]

(5)

\[
t = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t
\]

(6)

where \( q_t \) and \( q_e \) in mg g\(^{-1} \) are adsorption capacity at specified time interval (t) and at equilibrium point. \( K_1 \) (min\(^{-1} \)) and \( K_2 \) (min\(^{-1} \)) are the rate constants for pseudo first and second order rate models, respectively. All kinetic parameters are summarized in Table 2.

In pseudo first order model, the plot between \( \log (q_e - q_t) \) and \( t \) (Figure 6(a)) gives the values of \( q_e \) (mg g\(^{-1} \)) and \( K_1 \) given in Table 3. From Table 3, the values of \( R^2 \) and sum of squared estimate of errors (SSE) indicate less applicability of this model for photo-catalytic degradation of CR (\( R^2 \) of 0.962 and 0.973, respectively) and BG (\( R^2 \) of 0.992 and 0.964, respectively) dyes with powdered biomass and Fe-NPs. The \( R^2 \) values of pseudo second order rate model are greater than for first order model (0.995 and 0.994 for BG and 0.990 and 0.992 for CR with biomass and Fe-NPs, respectively), obtained by plotting the graph between \( t/q_t \) and \( t \) (Figure 6(b)). Therefore on the basis of \( R^2 \) and SSE calculated values (Table 3) pseudo second order rate expression can be declared the more appropriate model to exhibit kinetics of photo-degradation of CR and BG with biomass and green synthesized Fe-NPs from Mangifera indica. The degradation rate of dyes (BG and CR) was approximated by reduction kinetics studies with regard to the dyes alone (pseudo first order) and regarding the dye relation with adsorbent surface at studied time duration (pseudo second order), which indicated that photo-adsorption of dyes was a bimolecular reaction due to the involvement of catalyst surface with respect to corresponding dye molecules on regression basis (Table 3), also revealed in the ‘Photo-degradation mechanism’ section.

### Adsorption isotherms

Photo-catalytic adsorption degradation capability of BG and CR on green synthesized Fe-NPs and biomass of Mangifera indica was determined for dye concentration range 5 to

![Figure 6](http://iwaponline.com/wst/article-pdf/83/7/1739/870995/wst083071739.pdf)

**Table 3** Kinetic parameters for photo-catalytic degradation of BG and CR

| Kinetic models       | Parameters       | Biomass (CR) | Fe-NPs (CR) | Biomass (BG) | Fe-NPs (BG) |
|----------------------|------------------|--------------|-------------|--------------|-------------|
| Pseudo first order   | \( q_e \) (mg g\(^{-1} \)) | 30.34        | 34.01       | 29.67        | 31.76       |
|                      | \( K_1 \)        | 0.962        | 0.973       | 0.992        | 0.994       |
|                      | \( R^2 \)        | 0.458        | 0.274       | 0.432        | 0.196       |
|                      | \( K_2 \) (mg g\(^{-1} \)) | 8.34 \times 10^{-4} | 1.19 \times 10^{-3} | 1.79 \times 10^{-3} | 1.66 \times 10^{-3} |
| Pseudo second order  | \( q_e \) (mg g\(^{-1} \)) | 30.34        | 34.01       | 29.67        | 31.76       |
|                      | \( K_1 \)        | 0.962        | 0.973       | 0.992        | 0.994       |
|                      | \( R^2 \)        | 0.458        | 0.274       | 0.432        | 0.196       |
50 mg L\(^{-1}\), expressed in Figure 4(b), and adsorption behavior between dyes and adsorbent surface is explained by Langmuir (Figure 7(a)), Freundlich (Figure 7(b) and Temkin (Figure 7(c)) isothermal models. The experimental medium (initial dye concentration effect) was kept at room temperature \((293 \pm 2 \text{ K})\) and from temperature based % photo-degradation results (Figure 5(a)) it is clearly demonstrated that with temperature enhancement dye reduction was not much altered; this behavior of adsorbents may be due to the abundance of specific surface biomolecules in Mangifera indica, given in Table 1. Similarly, due to presence of iron in the form of oxides (Fe-NPs) the biomolecular surface provides enhanced attachment sites towards dye (BG and CR) reduction in aqueous media (Turunc et al. 2011). Thus, \(293 \pm 2 \text{ K} \) (room temperature) was kept as suitable temperature for dye degradation as a function of initial dye concentration. The linear expression of the Langmuir isotherm (Equation (7)) (Imran et al. 2013) is:

\[
\frac{C_e}{C_{ads}} = \frac{1}{q_m} \cdot \frac{1}{K_L} + \frac{C_e}{q_m}
\]  

(7)

In above equation, \(q_m \text{ (mg g}^{-1}\)) is the maximum capacity of adsorption of corresponding adsorbent surfaces, \(K_L \text{ (L mg}^{-1}\)) is Langmuir model constant and \(C_{ads} \text{ (mg L}^{-1}\)) is amount of dyes adsorbed in bulk mode. The values of \(q_m\) and \(K_L\) were obtained by plotting the graph between \(C_e/C_{ads}\) along y-axis and \(C_e\) along x-axis; parametric values are given in Table 4.

The Freundlich isotherm (Kismir & Aroguz 2011) (Equation (8)) linear expressions is given as:

\[
\log C_{ads} = \frac{1}{n} \log C_e + \log K_f
\]  

(8)

In Equation (8), \(K_f \text{ (mg g}^{-1}\)) is the Freundlich model constant and \(n\) is the adsorption heterogeneity factor (Kataria & Garg 2017). A linear plot between \(\log C_{ads}\) and \(\log C_e\) was obtained to get parameter values of this model (Table 4). The linear plot of Freundlich suggested that photo-catalytic adsorption mechanism of CR and BG is heterogeneous in nature on the surface of Fe-NPs as well as powdered biomass of Mangifera indica determined on the basis of \(R^2\) and SSE values, which are summarized in Table 3.

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Figure 7 | (a) Langmuir model for photo-catalytic degradation of BG and CR. (b) Freundlich model for photo-catalytic degradation of BG and CR. (c) Temkin model for photo-degradation of BG and CR.
The Temkin isotherm (Coşkun et al. 2019) (Equation (9)) can be represented by the following linear equation as:

$$C_{ads} = B \ln K_T + B \ln C_e$$  \hspace{2cm} (9)

where

$$B = \frac{RT}{K_T}$$  \hspace{2cm} (10)

This model determines photo-catalytic heat of adsorption which is a result of adsorbate-adsorbent molecular interaction. $B$ (J mol$^{-1}$) and $K_T$ (L mol$^{-1}$) parameter values of this model were obtained by linear plot between $C_{ads}$ and ln $C_e$ (Figure 7(c)). The values of correlation coefficient and parameters of photo-catalytic degradation of CR and BG with biomass and green synthesized Fe-NPs from Mangifera indica are shown in Table 4.

By evaluating the comparison on the basis of SSE and regression values of isotherms it is revealed that the Langmuir model is the most favorable isothermal expression for photo-catalytic adsorption data of BG and CR degradation with both adsorbents, biomass and Fe-NPs from Mangifera indica. The $R^2$ values for powdered biomass and NPs is 0.989 and 0.998 with CR dye, whereas in the case of BG the values are 0.950 with biomass and 0.991 with NPs. Thus, the adsorption process is single layer in nature with adsorption capacity 101.1 and 172.4 mg g$^{-1}$ of CR, and 158.5 and 270.4 mg g$^{-1}$ of BG with biomass and green synthesized Fe-NPs from Mangifera indica, respectively, higher than other studies (Table 5).

### Table 4 | Isotherm parameters for photo-degradation of BG and CR

| Adsorption isotherms | Parameters | Biomass (CR) | Fe-NPs (CR) | Biomass (BG) | Fe-NPs (BG) |
|----------------------|------------|--------------|-------------|--------------|-------------|
| Langmuir             | $q_m$ (mg g$^{-1}$) | 101.1 | 172.4 | 158.5 | 270.4 |
|                       | $K_T$ (dm$^3$ mol$^{-1}$) | 0.052 | 0.019 | 0.043 | 0.012 |
|                       | $R^2$      | 0.989 | 0.988 | 0.930 | 0.991 |
|                       | SSE        | 0.317 | 0.0858 | 2.37 | 0.065 |
| Freundlich            | $n$        | 0.571 | 0.290 | 0.325 | 0.191 |
|                       | $K_T$ (mg g$^{-1}$) | $4.26 \times 10^{27}$ | $4.57 \times 10^{49}$ | $1.58 \times 10^{16}$ | $7.2 \times 10^{74}$ |
|                       | $R^2$      | 0.807 | 0.948 | 0.761 | 0.958 |
|                       | SSE        | 1.970 | 0.023 | 0.024 | 0.007 |
| Temkin                | $B$ (J mol$^{-1}$) | 0.248 | 0.332 | 0.274 | 0.357 |
|                       | $K_T$ (L mol$^{-1}$) | 0.026 | 0.366 | 0.106 | 0.778 |
|                       | $R^2$      | 0.804 | 0.950 | 0.798 | 0.962 |
|                       | SSE        | 4.757 | 4.008 | 21.84 | 10.02 |

### Table 5 | Comparison of photo-degradation with other studies

| Adsorbent              | Dye    | Adsorption capacity (mg g$^{-1}$) | Reference |
|------------------------|--------|----------------------------------|-----------|
| Surface modified TiO$_2$ NPs | BG     | 9.80                             | Reza et al. (2017) |
| Ag-NPs-coated          | CR     | 0.69                             | Pal et al. (2013) |
| Ag-NPs                 | CR     | 0.35                             | Albeladi et al. (2020) |
| Ni O-NPs               | CR     | 0.90                             | Roopan et al. (2019) |
| Fe-NPs                 | CR     | 172.4                            | This work |
| Fe-NPs                 | BG     | 270.4                            | This work |
| Mangifera indica       | CR     | 101.1                            | This work |
| Mangifera indica       | BG     | 158.5                            | This work |

### Photo-degradation mechanism

The investigation of mechanism of dye (BG and CR) photo-adsorption on adsorbent surface is complex due to involvement of several factors that lead to adsorbent-adsorbate interactivity (Pal & Deb 2014). The interaction (positive or negative) and attachment of dye molecules with adsorbent surface are determined by properties of adsorbent surface, structure and functional groups present in dyes as well as adsorbent. The studied mechanism may be predicted on the basis of changes in morphological structure (SEM and BET), of green synthesized iron NPs as already explained in the ‘Characterization’ section.

The photo-adsorption phenomenon of dye reduction can be anticipated by band gap energies, which refers to
the generation of conduction ($e^{-}$) and valence ($h^{+}$) bands, when light falls on a photo-adsorptive medium.

$$\text{Fe-NPs + hv (}&>288 \text{ nm)} \rightarrow e^{-} \ (\text{conduction band})$$
$$+ h^{+} \ (\text{valence band}) \quad (11)$$

Oxidative degradation:

$$h^{+} \ (\text{valence band}) + \text{dye} \rightarrow \text{dye}^{-} \rightarrow \text{dye degradation} \quad (12)$$

Reduction degradation:

$$h^{+} \ (\text{valence band}) + \text{H}_2\text{O} \rightarrow \text{H}^{+} + \text{OH}^{-} \quad (13)$$

$$h^{+} \ (\text{valence band}) + \text{OH}^{-} \rightarrow \text{OH} \ (\text{radical}) \quad (14)$$

$$\text{OH} \ (\text{radical}) + \text{dye} \rightarrow \text{dye degradation} \quad (15)$$

In above equations, the holes in valence band ($h^{+}$) serve as oxidizing agent that leads to the oxidative reduction of dyes (Equation (12)), while the conduction band electrons ($e^{-}$) behave as reducing agent that reduces adsorbent surface oxygen, leading to reductive degradation of dyes (CR and BG).

Reusability

The successive cycles for BG and CR photo-degradation were investigated to monitor the reusability–stability of green Fe-NPs under different selected conditions. The results are shown in Table 6. Nanoparticles were filtered after photo-adsorption, washed with ethanol and oven dried at 120 °C for further usage in dye reduction experiments. Four cycles for BG and CR reduction were run and results revealed that CR dye (89.41%) and BG dye degradation (92.80%) was maintained after four cycles of NPs reuse (Table 6).

CONCLUSION

This simple study showed that green synthesized Fe-NPs made by single pot method have spherical shape, dense nano-sheets with thickness of 20 to 50 nm, as shown by SEM and FT-IR analysis. The photo-catalytic degradation efficiency for BG and CR dyes was monitored using both powdered biomass and Fe-NPs from Mangifera indica at specific applied conditions and Fe-NPs were a more effective photo-catalyst than powdered biomass. From the isothermal model analysis, the Langmuir isotherm is the best-fitting adsorption model based on experimental data fitness with regression coefficient and SSE values. The maximum photo-catalytic adsorption capacity for BG was 158.5 (with powdered biomass) and 270.4 mg g$^{-1}$ (with Fe-NPs), whereas for CR dye, 101.1 (with powdered biomass) and 172.4 mg g$^{-1}$ (with Fe-NPs) were obtained. The rate mechanism of photo-catalytic dye uptake efficiency is competently explained by pseudo second order rate model. Thermodynamics of photo-catalytic analysis of both dyes showed that the adsorption process is endothermic, spontaneous and chemisorption with distinctive values of Gibbs free energy. The maximum results of photo-catalytic degradation performance were found to be 72.6 and 80.87% for CR and 72.88 and 82% for BG with powdered biomass and green synthesized Fe-NPs of Mangifera indica, respectively. This work concludes that for both azo-dye (CR) and cationic dye (BG), green synthesized Fe-NPs and powdered biomass of Mangifera indica are economically efficient and are ecofriendly, reusable adsorbents for photo-degradation of both dyes and can be utilized for other dye degradation and dye wastewater treatment.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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