PHYTOPRODUCTION OF IRON NANOPARTICLES FOR METHYL ORANGE REMOVAL AND ITS OPTIMIZATION STUDIES

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ABSTRACT

In the present study, iron nanoparticles have been synthesized using the leaf extract of potential weed *Datura inoxia* to evaluate their feasibility for methyl orange removal. This method approves that the green synthesis method must be adopted for the more efficient and rapid synthesis of metal nanoparticles. A simple process of bio reduction has been involved, the leaf extract of *Datura inoxia* used as a precursor for reducing metal iron. The UV-visible spectral analyses for iron nanoparticles have shown a peak at 240 nm wavelength. Spherical shaped iron nanoparticles are formed as shown by transmission electron microscopy. Batch studies were investigated for optimization study of methyl orange removal on selected parameters i.e., pH (1-10), adsorbent dose (0.02-0.14g), initial dye concentration (5-100ppm), contact time (15-120 minutes) and temperature (20-50°C). The result from the present study approves easy and fast dye removal of 98 % with kinetic data following a second order removal rate. The thermodynamics parameters supported the spontaneity with a negative value of ΔG i.e., -14.87 kJ mol⁻¹ and exothermic (ΔH -7.094 kJ mol⁻¹) nature of the reaction. Thus, it can be concluded that the use of *Datura inoxia* for the phyto production of iron nanoparticles is efficient for various commercial applications in environment sector.

Keywords: Antioxidant activity; ABTS; Bryophyllum pinnatum; DPPH; Lectin; SDS-PAGE.

INTRODUCTION

Pure water is good for humans and their health and also essential feedstock used in many industries (Cao and Li, 2014). Azo dyes are being used in the leather, textile, food, plastic, cosmetics, and paper and pharmacology industries for coloring purposes (Kim and Choi, 2017). The effluent containing dyes are released into the water bodies, intensify its chemical oxygen demand (COD), biological oxygen demand (BOD) and suspended solids etc. In an investigation by Bhatia et al. (2018) on textile effluent on 2 sites in Ludhiana, Punjab, recorded pH in the alkaline range (8.58-8.33) and suspended solids (143.5 ± 75.01 and 139.66 ± 71.87 mg L⁻¹) in autumn and lowest (86.50 ± 15.10 mg/L) in the rainy season. A study also found out that the effluents were having values of BOD and COD ranged from 121–580 to 240–990 mg L⁻¹, respectively. These values are higher than the water quality standards provided by world health organization i.e., BOD - 30 mg L⁻¹and COD - 250 mg L⁻¹.

Also, it hinders the entry of light into the water; affect photosynthesis in aquatic plants, microbial growth, fish and other organisms’ aquatic toxicity etc. The most important, it is also carcinogenic and mutagenic for human beings as well (Sajab et al., 2011). An azo (–N=N) group is present in azo dyes. According to the World Bank, estimation nearly 17–20% of water pollution contribution is related to dyeing industries and textile finishing (Kant, 2011). In a survey by Ecological and Toxicological Association of Dyes and Organic Pigments Manufacturers (ETAD), out of 4000 dyes tested 90% had their LD50 values more than 2×103 mg kg⁻¹. However, the rate of toxicity was higher in tests done for azo, basic and direct dyes. About 15% (1000 tons) of non-biodegradable and toxic dyes are discharged into the water bodies through textile waste effluents annually (Ajmal et al., 2014). Production rate of dyes per annum is higher than 7 × 10⁵ metric tons globally (Yao et al., 2016). Specific features that contribute to mutagenicity of azo dyes are related to differences in substituton sites, and the number and position of hydroxyl and sulpho-groups adjacent to the azo bond. Dyes are more toxic which have hydroxyl group at the ortho position in comparison to hydroxyl group at para position (Tauber et al., 2005). Precursor compounds used for manufacturing many azo dyes are known carcinogens, for e.g., naphthalene, benzidine and other aromatic compounds. Aromatic amines are released after cleavage of azo bonds by microflora containing azoreductase (Prasad and Aikat, 2014). Moreover, in living creatures whenever azo dyes react with sweat, gastric juices and saliva aromatic amines are synthesized (Pieliesz et al., 2002). High resistant of aromatic amines towards conventional wastewater treatment strategies makes them more persistent in the environment than dyes (Chen et al., 2009). Also, water-soluble azo dyes get reduce into aromatic amines by the intestinal microflora in the gastrointestinal tract, which is reabsorbed and forms tumors. \( \text{N, N-dimethyl-p-phenylenediamine (DMPD)} \) (Figure 1) a mutagen produced from methyl...
orange by intestinal anaerobes (Feng et al., 2012). Methyl orange (MO) is a toxic water-soluble azo dye which has use in laboratories, paper and textiles industries (Fan et al., 2009). Discharge of MO through effluent from dye using industries into water bodies is causing many health hazards as MO is toxic, mutagenic and carcinogenic (Mathur et al., 2012). This has led to the use of several removal techniques for azo dyes from the environment. Various conventional and advanced treatment techniques have been used for treating dye-containing textile effluent like flocculation, adsorption (activated carbon sorption), UV-light degradation (Atul et al., 2012), fenton oxidation, membrane filtration, phytoremediation, bioremediation, photochemical, electrochemical oxidation (Ghaly et al., 2014). Youssef et al., (2016) has reported the oxidation of MO using a Fenton reaction and achieved a removal of 97.8%. The use of cork powder for MO removal by Kriya and Benlahbib (2015) proved to be an improved study with good adsorption capacity of cork for MO 16.66 mg g⁻¹ at pH 2, 298 K or 25 °C and 5.00 g cork dosage, particle size of d=0.08 mm and contact time of 240 minutes in optimal conditions. However, these removal methods have some limitations like photochemical degradation forms toxic byproducts, flocculation method produce sludge while electrochemical oxidation is too expensive (Raman and Kanmani 2016).

Currently, a novel field has been fabricated called nanobiotechnology by converging nanometer scale technologies with biological technologies. This new field mainly focuses on creating, manipulating and using materials at the nanometre scale for highly developed biotechnology (Goodsell 2004). Moreover, nanobiotechnology is based on the principles of biology with chemical and physical methods to create nanoparticles (NPs) of unambiguous properties (Kathiresan et al., 2009). However, “A nanoparticle can be defined as any intentionally produced particle that has a characteristic dimension from 1 to 100 nm and has properties that are not shared by non-nano scale particles with the same chemical composition” (de Medecine 2009). The smaller size is associated with intensification in number of atoms on the surface and demarcates the groups of NPs (Lin et al., 2005). The most important property of (Daniel and Astruc 2004). NPs are to act as a catalyst or to catalyze the reactions which are impossible to achieve 9. Kaur et al., (2013) evaluated the potential of zinc oxide nanoparticles for MO removal biphotocatalytic degradation and attained a complete degradation in 80 minutes. Recently, metal NPs synthesis from leaf extract of different plants is an alternative to other synthesis methods and promises inexpensive and non- toxic reduction process (Machado et al., 2013). Hence, the green synthesis approach for NPs fabrication by means of phytochemicals extracted from weeds that act as reducing agents is striking one. These phytoc constituents can transform metal ions into metal NPs (Mittal et al., 2013) by the process of reduction. Even, there is no need for ligand exchange before biological applications as they act as capping agent as well (Sebastian et al., 2018). Metal NPs of several shapes and size are being formed by means of reduction of metals in the presence of phytochemicals (Pattanayak and Nayak 2013a). Mondal (2015) reported the biosynthesis of silver nanoparticles using aqueous shoot extract of Parthenium hysterophorus at room temperature along with using it for degradation of MO dye.

Nowadays, iron nanomaterials due to their versatile properties and high catalytic activities and the higher intrinsic reactivity of its surface sites have received great attention from researchers in different fields such as medical uses (Silva et al., 2016), degradation of environmental organic contaminants (Wang et al., 2015), catalysis (Walker and Zaleski 2016), magnetic storage media (Yu et al., 2016), magnetic field-assisted separations (Massoud and Mahmoud 2017). Iron oxide nanoparticles as dye removing materials are used for maintaining a healthy environment (Ebrahiminezhad et al., 2018). Green-synthesized Fe NPs has been examined for dye degradation and because of the easy availability of plants in nature; it makes them more applicable (Saif et al., 2016). Ebrahiminezhad et al., (2018) used Cupressus sempervirens for synthesis of iron nanoclusters of mean size 19nm. The potential of green synthesized iron nanoclusters was analysed for MO removal.

The present study aimed to prepare a phytochemical extract from the leaves of potential weed of Rohtak i.e. Datura inoxia to reduce iron salt precursors into FeNPs. Datura inoxia (D. inoxia) is a potential weed and a well-known Indian medicinal plant belonging to the family Solanaceae. Many different bioactive molecules found within its extract are responsible for the reduction of the metal iron to Fe NPs. Furthermore, the use of Fe NPs for methyl orange (MO) removal from textile wastewater indicates that they have good phytochemical content which leads to new interactions amid dye species and metal NPs. A methodical study of the influence of pH, adsorbent dose, contact time, initial dye concentration and temperature on MO dye uptake by Fe NPs was explored in this study. However, to the best of our knowledge, Fe NPs synthesized using D. inoxia species have not been explored towards the removal of MO removal so far.

MATERIALS AND METHOD

Chemicals Used

Ferric chloride (anhydrous) was purchased from Ranbaxy Fine Chemicals Ltd. Double distilled water was used for extract preparation as well as synthesis process. Methyl orange [4-dimethylaminoazobenzene-4-sulfonic acid, sodium salt] Hazardous Substances Data Bank Number: 4322] is an orange powder (Figure 2) (NTP 1992). In double distilled water, stock solution of MO (1000 mg L⁻¹) was prepared.
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**Leaf Extract Preparation**

Fresh leaves were collected of *D. inoxia* for the extract preparation. For removal of any dirt and organic contaminants, the leaves were cleaned with running tap water and kept in a sieve for some time to remove extra water (protecting the leaves from degradation), chopped into small pieces and then shade dried. To make the powder, leaves were oven dried at 60° C. Addition of 5% (w/v) powder of leaves with double distilled water is a much-generalized ratio for the preparation of leaf extracts (Ebrahiminezhad *et al.*, 2017). For this, 5 g dried leaves were boiled in 100 ml double distilled water for 15 minutes on a hot plate. The prepared extract was left for an hour at room temperature for cooling. The extract prepared was centrifuged at 2000 rpm for 5 minutes (at room temperature) to remove leaf micro particles (Beheshtkhoo *et al.*, 2018).

**GC-MS Analysis**

The carrier gas was helium (99.999%), used at a flow rate of 1.2 ml min⁻¹ with split mode (10:1). 1 μl of methanol sample was injected into column at 250°C injector.
Green synthesis of Iron Nanoparticles

Ferric chloride (FeCl₃) (anhydrous) (Ranbaxy Fine Chemicals Ltd. CAS: [7705-08-0]) was used for metal ion solution. FeNPs formation was screened by mixing of ferric chloride solution (0.10 M) with the leaf extract (2:3) by continuous stirring for half an hour with further addition of NaOH. The solution turned into a black color.
solution indicating the formation of FeNPs. The FeNPs were separated from the solution through centrifugation at 15000 rpm. The pellet of FeNPs obtained was washed three times with double distilled water and dried (Shahwan et al., 2011).

**Characterization**

D. inoxia leaf extract was analyzed by Gas chromatography-Mass spectrometry (GC-MS) (Thermo Fisher) to detect the presence of phytoconstituents. Spectroscopic analysis was performed by UV-vis spectrophotometer (LabIndia, UV) and the wavelength range was set from 200 to 600 nm. For size determination of FeNPs, these were subjected to transmission electron microscopy (TEM) (Talos 200kv Cryo TEM). The crystallinity of the sample was investigated with X-ray diffraction (XRD) analysis (Rigaku Ultima IV, Ri).

**Batch adsorption studies**

Batch experiments were performed for investigating the effects of parameters i.e., pH, adsorbent dose, initial dye concentration, temperature and contact time on dye adsorption. Batch adsorption studies were performed by suspending FeNPs (0.02–0.14 g L\(^{-1}\)) in MO working solutions of different initial dye concentrations (5–100 ppm) of different pH values (1-10). The solutions were rotated at 150 rpm at constant temperature (298 K). The desired pH of the solutions was set up by 0.01 N HCl and 0.01N NaOH. The solutions were filtered using Whatman filter paper No 1 for minimizing the effects of suspended particles in solution. The concentration of MO in the supernatant was estimated by UV/visible spectrophotometer at 464 nm (MO maximum wavelength) using a calibration curve. The results presented here are the mean of triplicate determination.

**Estimation of removal efficiency**

The percentage removal (% R) of the dye solution and amount of dye adsorbed (qe, mg g\(^{-1}\)) on the adsorbent were calculated by equations (Eq) (1) and (2) respectively:

\[
R(\%) = \left( \frac{c_0 - c_e}{c_0} \right) \times 100 \quad \text{Eq. (1)}
\]

\[
q_e = \frac{(c_0 - c_e) \cdot V}{W} \quad \text{Eq. (2)}
\]

The adsorption capacity (qe) is defined as “the amount of adsorbed material per mass of adsorbent” (do Socorro et al., 2016). Where qe (mg MO g\(^{-1}\) adsorbent) is “the amount of dye adsorbed on per gram adsorbent at the time of equilibrium”, V (L) is the volume of solution and C\(_0\) and C\(_e\) (mg L\(^{-1}\)) are the initial and at equilibrium dye concentrations respectively, W denotes dry weight of adsorbent (g).

**RESULTS AND DISCUSSION**

**GC-MS Analysis**

The GC-MS analyzed that D. inoxia leaf extract was rich in phyto constituents like phenols and alcohols which were responsible for the reduction of FeNPs (Figure 4). The peak at 8.33 (Retention time, RT) is of 2-methoxy-4-vinylphenol that is a plant metabolite, a member of the class of phenols. The peak at 14.68 (RT) shows D. inoxia leaves are rich in phytol or 3, 7, 11, 15-tetramethyl-2-Hexadecen-1-ol. Phytol is acyclic diterpene alcohol while compound n-hexadecanoic acid also found with RT 26.26. Hexadecanoic acid is a potential antioxidant as well (Sundararajan et al., 2017). On the parallel lines, Bagewadi et al., (2019) also analyzed phytol (RT-14.78) and hexadecanoic acid (RT 5.094) in D. inoxia leaf extract.

**UV-visible spectral analysis**

After adding ferric chloride solution to D. inoxia leaf extract, the color changes to black, confirms Fe NPs fabrication. UV- visible spectroscopic analysis was carried out and a sharp peak obtained at 240 nm for FeNPs whereas at 290 nm for leaf extract (Figure 5). Likewise, Pattanayak and Nayak (2013b) monitored the UV-vis peaks between 216-265 nm wavelengths for bio reduction of Fe\(^{3+}\) which were similar to the UV-visible peak of metal iron.

**FT-IR Spectroscopy**

The FT-IR analysis was carried out to know the presence of functional groups in D. inoxia extract which played the role of reducing, capping and stabilizing agents in FeNPs synthesis (figure 6a). FT-IR spectra of FeNPs synthesized from D inoxia extract is carried out as well (figure 6b). Broad peak at 3342 and 3416 cm\(^{-1}\) refers to O-H stretch of H bonding in alcohols and phenols while the peaks at 2975 cm\(^{-1}\) and 2897 cm\(^{-1}\), 2924 cm\(^{-1}\) and 2855 cm\(^{-1}\) (Figure 6a, b) can be ascribed to the C-H stretching vibration of a methylene group. 1647 cm\(^{-1}\) peak is slightly shifted to 1631 cm\(^{-1}\) as it shows the presence of C=C stretching. The peak at 1044 cm\(^{-1}\) representing C-O stretching vibration of primary alcohols. This peak is not well formed; it may conclude that primary alcohols have been used in the synthesis of FeNPs. This indicates the putative role of alcohols and phenols played significant role in FeNPs fabrication.

**Transmission Electron Microscopy**

The size as well as the morphology of green synthesized FeNPs was assessed with the help of TEM. TEM micrograph of the FeNPs synthesized by D. inoxia leaf extract is shown in Figure 7 (a). A single drop of FeNPs was positioned on a copper grid coated with carbon and dried (at room temperature) before processed for TEM. TEM images showed that the majority of FeNPs were spherical
shaped in a chain like structures under nanoparticle size range (1-100nm). A fine layer of biomatrix surrounding the FeNPs confirms the presence of plant biomolecules present in *D. inoxia* leaf extract which reduced Fe ions to FeNPs. Nanoparticles subjected to transmission electron microscope were coupled to energy dispersive X-ray spectroscopy (EDX).

The EDX of FeNPs was done for determining the chemical composition (Figure 8). An EDX spectrum shows intense peaks of Fe, Oxygen, carbon and chlorine as well. Atomic percentages as given by EDX: Fe (7.25%), O (14.85%), C (65.29%) and Cl (9.32%). Oxygen is also present suggesting surface oxidation of the FeNPs (Njagi et al., 2011). Chlorine might be originated from FeCl₃. Presence of copper and carbon peak is due to a carbon-coated copper grid used in TEM analysis. Selected area electron diffraction (SAED) pattern confirms the FeNPs are amorphous in nature (Figure 7 b).

**Field Emission Scanning Electron Microscopy (FE-SEM)**

FE-SEM was done for morphological analysis the of the fabricated FeNPs. Figure 9 shows the granular and spherically shaped FeNPs with mean size 14 nm (mean: 14 nm). In addition, the capping of plant biomolecules was vital for avoiding the FeNPs aggregation which enhanced their stability as well (Ali et al., 2018). To study the morphology of the synthesized FeNPs Freyria et al., (2017) has done the FE-SEM and analyzed that spherical shaped FeNPs were formed with size 110nm.

**X-Ray Diffraction**

Figure 10 illustrates the XRD pattern of Fe NPs; the scanning range used for the sample analysis was 10° ≤ 2θ ≥ 80°. The characteristic peaks at 2θ = 32° corresponded to iron hydroxides while 2θ = 45° shows the formation of an
Figure 6 FT-IR spectra of (a) D. inoxia leaf extract (b) Iron Nanoparticles

Figure 7 Transmission electron microscopy image of (a) FeNPs and (b) SAED pattern
Figure 7 Transmission electron microscopy image of (a) FeNPs and (b) SAED pattern

Figure 8 Energy Dispersive X-ray Spectroscopy

Table 3. Linear forms of Freundlich and Temkin isotherm models

<table>
<thead>
<tr>
<th>Isotherms</th>
<th>Model Parameters</th>
<th>Values</th>
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<td>Freundlich</td>
<td>1/n</td>
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<td></td>
<td>N</td>
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<tr>
<td></td>
<td>ln K_F</td>
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<td></td>
<td>Ln A_T</td>
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<td></td>
<td>A_T</td>
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<tr>
<td></td>
<td>R²</td>
<td>0.99</td>
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Table 4. Kinetic Adsorption Parameters

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<th>Kinetic models</th>
<th>Model parameters</th>
<th>Values</th>
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<tr>
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<td>q_{total} (mg L⁻¹)</td>
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<tr>
<td></td>
<td>k_1 (min⁻¹)</td>
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<td></td>
<td>R²</td>
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<tr>
<td>Pseudo II order</td>
<td>q_{e calc} (mg L⁻¹)</td>
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</tr>
<tr>
<td></td>
<td>k_2 (min⁻¹)</td>
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</tr>
<tr>
<td></td>
<td>R²</td>
<td>0.99</td>
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</table>
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Figure 9 Field Emission Scanning electron microscopy image of FeNPs

Figure 8 Energy Dispersive X-ray Spectroscopy

Figure 10 XRD spectra of Iron nanoparticles (a) (b) (c) (d) (e)

Figure 11 Plots showing effects of (a) pH (b) adsorbent dose (c) ionic concentration (d) contact time (e) temperature on methyl orange removal using Fe NPs
amorphous Fe phase (Kim and Choi 2017) which is ably supported by SAED pattern too. Kim and Choi (2017) also analyzed during XRD studies that a broad peak at $2\theta = 45^\circ$ depicts the iron is in amorphous phase. Also, Kheshtzar et al., (2019) investigated in his optimization studies for fabricating green synthesized iron nanoparticles that FeNPs were amorphous but not crystalline in nature.

**Batch Studies for Dye removal**

**Influence of pH**

Solution pH takes the important part in the adsorption of the dye MO by Fe NPs as it affects the aqueous chemistry in addition to surface binding-sites (OF adsorbent). At pH 2, the solution of MO achieved maximum decolonization efficiency of 72% within 60 minutes of reaction time. But on increasing the pH to 7 the dye removal decreases to 5% only and becomes constant for a further increase in pH up to 10 (Figure 11 a). At lower pH, iron surface becomes positively charged (Li et al., 2006) while MO (an anionic dye) molecules become negatively charged. Hence,
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Figure 13. (a) Pseudo I order (b) Pseudo II order plots for MO removal

Figure 14. Arrhenius plot showing relationship between ln Kc versus 1/T for the MO removal using FeNPs

making favorable for the process of dye adsorption onto the surface of adsorbent (FeNPs). Conversely, when solution pH is alkaline, the Fe exterior loaded with negative charge (alkaline pH causes the corrosion products to cover the Fe surface (Fan et al., 2009). This result suggests that acidic pH is favorable for MO removal, while reaction in alkaline conditions may retard. The study done by Debnath et al., (2016) also proves that the removal of MO using α-Fe₂O₃ NPs favors acidic medium.

Influence of Adsorbent dose

With other parameters kept constant a dosage range was selected. In figure 11(b) with an increase in FeNPs dosage qe (adsorption capacity, mg g⁻¹) value decreases, it is because of increase in surface area while keeping the adsorbate concentration constant (Saha et al., 2011). During the reaction as more FeNPs are loaded, results in increase in surface area i.e. active and adsorptive sites. Hence, dye removal increases with increase in FeNPs loading within the same reaction time. Within a time of 60 minutes reaction reaches at equilibrium, efficiency of dye removal was 62%, 68%, 72%, 74% and 79.41 % respectively for the dosage 0.02, 0.04, 0.06, 0.08 and 0.1g.

Influence of ionic concentration

Figure 11 (c) depicts the effect of ionic concentration on MO removal using FeNPs in aqueous solution. An increase in dye concentration (5-100 mg L⁻¹) results in increase in MO amount adsorbed per unit mass of FeNPs i.e., qe (2.23 to 6.26 mg g⁻¹). More dye molecules transfer towards adsorbent surface with an increase in dye concentration (5-100 mg L⁻¹). A concentration gradient creates at higher concentration between MO molecules in aqueous solution and MO on FeNPs surface. This concentration gradient is the driving force for mass transfer during adsorption process (Luo et al., 2010). Though, the percentage removal decreases (85.55%-74.52%).
Influence of contact time

One of the significant design parameters is the contact time that affects the efficiency of adsorption process between adsorbate (MO) and adsorbent (FeNPs). Keeping the parameters pH, adsorbent dose as well as initial ion concentration constant (putting their optimum values) the variation in contact time was investigated for the performance of FeNPs for MO removal. Figure 11 (d) shows dye adsorption starts within 15 minutes after mixing FeNPs in MO containing solution and attained maximum removal capacity in 75 minutes.

Influence of temperature

Habitually, a chemical reaction shows delicate behavior towards temperature changes, which helps in understanding the mechanism of reaction (Liou et al., 2005). The temperature effect on MO removal was investigated with an initial 10 mg L⁻¹ MO concentration and 0.1 g FeNPs at original pH 2 for 75 minutes. In a temperature range of 20–50 °C experiments were conducted. Figure 11 (e) shows at low temperatures incomplete MO removal was recorded. The removal efficiency increased from 81 % to 98 % due to increase in temperature from 20 to 35°C. Higher temperatures shown to shorten the time needed for MO removal.

Adsorption Isotherm

The adsorption isotherms signify designing the adsorption mechanism and also characterize the adsorbent (Erdem et al., 2005). To design and optimize the process of adsorption it is necessary to develop an appropriate isotherm model. To evaluate the adsorption of any compound at equilibrium some isotherm models have been developed e.g., Langmuir, Freundlich, Temkin, Dubinin–Radushkevich, Redlich–Peterson and Sips etc (Dabrowski 2001). Subsequently, Langmuir, Freundlich and Temkin are generally used for investigating the adsorption isotherm. In this experimental work, results were applied with these 3 adsorption isotherm models in addition isotherm plots were created based on experimental equilibrium data attained. Adsorption isotherm is stated as “the amount of adsorbate taken up per gram of adsorbent (qe mg g⁻¹) to the equilibrium solution concentration (Ce mg L⁻¹) at a fixed temperature”. Constants of these adsorption models offer substantial parameters for envisaging adsorption potential.

Langmuir Isotherm

Langmuir model assumes that “the uptake of adsorbate molecules occurs on a homogenous surface with a finite number of adsorption sites” (Deng et al., 2009). A site stops further adsorption forming amonolayer and reaches at saturation point through achieving maximum adsorption of the surface (Javadian and Taghavi 2014). Langmuir adsorption isotherm linear equation is shown in Table 1. Where Ce denotes adsorbate concentration at equilibrium (mg L⁻¹) whereas qm (q_max) conclude the maximum adsorption capacity (mg g⁻¹) while b denoted for Langmuir constant (L mg⁻¹) and signifies “the energy of adsorption process”. Slopes and intercepts values obtained by plotting the Langmuir isotherm graph was used to calculate qm and b (Figure 12 a). MO removal using green synthesized FeNPs fits to Langmuir adsorption isotherm model. R, i.e., separation factor, is a significant component of Langmuir adsorption isotherm. R is a dimensionless constant and can be expressed as:

\[ R_L = \frac{1}{1 + bC_0} \]  (Eq. 3)

Equation 3 signifies the adsorption behavior i.e., for favorable adsorption, when value of RL is within the range \(0 < R_L < 1\) whereas \(R_L > 1\) and \(R_L = 1\) for unfavorable and linear adsorption respectively (Weber and Chakravorti 1974). RL values calculated were within the range \(i.e.,0.142–0.933\) (Table 2). As the RL values are below 1 so it predicts the adsorption to be favorable for the present study for the under the applied experimental conditions.

Freundlich Isotherm

The Freundlich isotherm a primeval adsorption isotherm model, is suitable to apply for heterogeneous surface describes “relationship between the non-ideal and reversible adsorption” (Ayawei et al., 2015). It is established on multilayer adsorption hypothesis which takes place on heterogeneous surfaces comprising non-uniform sites with dissimilar energy distribution. It is given by the linear equation (Hu et al., 2010):

\[ \log q_e = \log K_F + \frac{1}{n} \log C_e \]  (Eq. 4)

wheren and KF are the Freundlich constants, here n is the heterogeneity factor and is associated with adsorption intensity whereas KF to adsorption capacity (mg g⁻¹). n value indicates the adsorption process is favorable or not, the values below 1 shows favorable adsorption. By plotting the graph between log qe and log Ce, the values for KF and n can be obtained (figure 12 b) and are summarized in table 1.

Temkin Isotherm

The Temkin adsorption isotherm model adopts the phenomenon that “the adsorption energy decreases linearly with the surface coverage due to adsorbent–adsorbate interactions”. The linear equation for Temkin isotherm is as follows (Kiran and Kaushik 2008).

\[ q_e = \frac{RT}{B_T} \ln A_T + \frac{RT}{B_T} \ln C_e \]  (Eq. 5)

...
Where $B_1$ denotes Temkin constant which is associated with adsorption heat (kJ mol$^{-1}$) while $A_{i}$ is equilibrium binding constant equivalent to the maximum binding energy (L g$^{-1}$). $T$ denotes temperature in kelvin whereas $R$ gas constant i.e., $8.314 \times 10^{-3}$ kJ mol$^{-1}$ K$^{-1}$. A Temkin model graph can be plotted between qe and log Ce, (figure 12 c) values obtained are shown in table 3. The higher values of $B_1$ signify high heat of adsorption.

**Kinetics studies**

The kinetic model regulates the rate of reaction. The kinetic study of MO adsorption onto FeNPs was calculated on 10 mg L$^{-1}$ concentrations with pseudo I-order and pseudo II-order kinetic models.

The linear form of “Lagergren” pseudo I-order rate equation is as follows (Hu et al., 2010):

$$
\log(\text{qe} - \text{qt}) = \log \text{qe} - \frac{k_1}{2.303} t \\
$$

(Eq. 6)

Where qe denotes the adsorbed MO concentration at time t (mg g$^{-1}$) whereas $k_1$ denotes rate constant (min$^{-1}$) for pseudo I order reaction. Value of Lagergren constant derived by plotting log (qe −qt) vs t (Figure 13 a) are mentioned in table 4.

While the linear form for pseudo II-order can be expressed as (Hu et al., 2010):

$$
\frac{t}{q_t} = \frac{1}{(k_2 q_e^2)} + \frac{1}{q_e} t \\
$$

(Eq. 7)

Where rate constant is denoted by $k_2$ (mg g$^{-1}$ min$^{-1}$), after analyzing the experimental data for pseudo II-order kinetic model, the plot between t/qt vs t springs a straight line (Figure 13 b). Values for $k_2$ and $R^2$ are obtained from the plots are tabulated in table 4 with quite agreeable calculated adsorption capacity (q cal) with experimental data and higher $R^2$ value which ensures the present study of adsorption follow pseudo II-order. It further confirms that it is a type of chemisorption (Xu et al., 2012):

**Thermodynamics study of adsorption**

For feasibility evaluation of the adsorption process of MO by FeNPs a thermodynamic study was performed. For calculating the thermodynamic parameters following equations were applied (Vimoneses et al., 2009):

$$
K_e = \frac{q_e}{C_e} \\
$$

(Eq. 8)

$$
\Delta G = \Delta H - T \Delta S \\
$$

(Eq. 9)

$$
\ln K_e = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \\
$$

(Eq. 10)

Where, $\Delta G^\circ$ denotes Gibbs free energy change (kJ mol$^{-1}$) while the change in enthalpy by $\Delta H^\circ$ (kJ mol$^{-1}$), $\Delta S^\circ$ denoted by entropy change (J mol$^{-1}$ K$^{-1}$). $T$ is the temperature in kelvin, $K_c$ is adsorption distribution coefficient. By plotting the graph in between ln $K_c$ versus $1/T$ (figure 14), $\Delta H^\circ$ and $\Delta S^\circ$ were intended from its slope and intercept. After getting the values of $\Delta H^\circ$ and $\Delta S^\circ$, value for $\Delta G^\circ$ was calculated as mentioned in table 5. The change in enthalpy determines the nature of (exothermic/endothermic) of the adsorption process. This further helps in differentiating the chemical and physical reaction of adsorption (Tseng et al., 2010). For this adsorption study, negative value of $\Delta H^\circ$ confirms the reaction is exothermic in nature. However, at all temperatures studied $\Delta G^\circ$ values were negative, represents spontaneity of the adsorption process. Change in entropy ($\Delta S^\circ$) predicts “magnitude of changes in the adsorbent surface”, this due to the observed changes in the reversibility (Liu et al., 2010). The positive value for $\Delta S^\circ$ predicts the increased changeability.

**CONCLUSION**

As the studies prove, the organic compounds present in potential weed D. inoxia have a significant impact on the FeNPs stability and metal reduction. On the basis of equilibrium studies, a systematic investigation to determine the potential of FeNPs synthesized using aqueous leaf extract of D. inoxia for methyl orange adsorption has been performed. Characterization of FeNPs revealed they are amorphous in nature (as supported by XRD) having chain like structure with spherical morphology. The adsorption was maximally accessed at pH 2 because of interfacing of cation forming nature of FeNPs and the anionic MO azo dye. Langmuir model of adsorption and pseudo II-order fitted well to the MO adsorption by FeNPs. The adsorption process agreed reasonably well with the Langmuir isotherm and pseudo II-order, and $R^2 = 0.99$. Thermodynamics study proves the reaction is spontaneous and exothermic in nature. Better MO adsorption by FeNPs reaches in 75 minutes at equilibrium is desirable for other adsorption applications. The present adsorption study proposes the FeNPs to be applied as an efficient, substitute and low-cost adsorbent for textile wastewater treatment. It is a plant-based method that does not harm the environment, its structure and man. Hence, an environment friendly approach has been effectively applied.

**CONFLICT OF INTEREST**

No conflict of interest

**ETHICAL CONDUCT**

All co-authors have agreed to submit the manuscript to the journal. The findings have not been published elsewhere. This manuscript is not currently under consideration by
another journal.

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