Topic

Synthesis, characterization and application of Ce-doped Fe2O3 nanoparticle for the removal of methylene blue dye from aqueous solution

# Abstract

Methylene blue (MB) is a hazardous chemical that is widely found in wastewater, and its removal is critical. One of the most common methods to remove MB is adsorption.

# CHAPTER ONE

# INTRODUCTION

## BACKGROUND OF STUDY

Dyes are considered one of the most problematic groups of pollutants because they can be easily identified by the human eyes once they are released to the water bodies but are not easily removed. Furthermore, most synthetic dyes are properly non-degradable even with sunlight (Mogharabi et al., 2012). Recently, there has been an increase in public awareness and concern regarding environmental pollution. Most organic chemicals and pathogens, which are present in aqueous waste effulents discharged from industrial or domestic sources, should essentially be treated or removed prior to the final discharge to the water courses. Hence, a promising treatment techniques is required to overcome such challenge for a safe disposal. Oxidation of such dyes from aqueous industrial discharges is considered a difficult technique since dyes show resistance to various oxidants, chemical, UV light and heat besides being non-biodegradable (Kargi & Ozmıhc, 2004), (Gupta et al., 2011), (Saleh & Gupta, 2012), (Tony et al., 2011).

Conventionally, various techniques were applied for wastewater treatment such as coagulation, reverse osmosis, biological treatment techniques and adsorption methods (Ashour et al., 2014; Tony et al., 2018), waters, which include photodecomposition (Kapdan & Kargi, 2002; Mulugeta & Belisti, 2014), electrolysis (Qingdong et al., 2017), adsorption (Ahmadi, Rahdar, et al., 2019; Ahmadi & Kord Mostafapoor, 2017), oxidation (Ahmadi et al., 2018; Ahmadi, Igwegbe, et al., 2019) and other processes. However, those methods are not widely recommended as they are expensive, transferring the pollutants phase, or they are not effective with high organic loads (Rahman et al., 2009; Tony & Mansour, 2019). Amongst the different physical and chemical processes, adsorption is an effective technique, which is successfully used for the removal of colors from wastewaters (Elnasri et al., 2013; Rahdar, Samani, et al., 2018). The adsorption method is widely used due to its simplicity, low cost, and removal of color and other pollutants with great efficiency (Samadi et al., 2013). Adsorption can be either physisorption (which involves fairly weak intermolecular forces), or chemisorption (which involves basically the formation of a chemical bond between the sorbent molecule and the surface of the adsorbent (Karine, 2001). Activated carbons have been used successfully to remove organic and mineral pollutants (Han et al., 2006; Igwegbe et al., 2015) but they are hardly regenerated (Ahmadi & Kord Mostafapour, 2017). Nanoparticles are referred to as particles with a diameter of less than 100 nm (Igwegbe et al., 2018). Nanoparticles have been revealed to have a high potential in adsorbing organic compounds especially colors from wastewater and sewage tanks due to their high surface to volume ratio than other adsorbents (Rahdar, Igwegbe, et al., 2018).

Methylene blue (MB) is an aromatic heterocyclic basic dye with the chemical formula C16H18N3SCl. It is also referred to as cationic or primary thiazine dye.



Figure 1. Chemical structure of methylene blue

The presence of negative polar sites on water molecules causes an attraction for the cationic dye, resulting in the separation of positive ions and the creation of a stable solution with water at room temperature (Yusop et al., 2021).

MB is recognized as a popular cationic dye utilized in a variety of sectors, including the pharmaceutical, food processing, paper, paint, printing, dyeing, and medicine (i.e., diagnostic and therapeutic medicine for both humans and animals) industries (Khan et al., 2022). In the textile industry, MB adheres well to the interstitial gaps of cotton fibers and remains stable on fabric. Hence, MB is one of the most used apparel colors.

Methylene blue dye-containing effluent from various industries such as textile, rubber, plastic, paper-making are established to be carinogenic and also create toxic effects on living organisms (P. S. Kumar et al., 2014). Methylene blue is a cation color with a complex aromatic structure, which is used for colouring cotton and silk (Srivastava, 2008). This compound can cause impaired respiration. Further, direct exposure to it causes permanent damage to human and animal eyes; it also local burns, nausea and vomiting, mental disorders, and Methemoglobinemia (Mulugeta & Belisti, 2014; Rafatullah et al., 2010).

However, because MB is poisonous, carcinogenic, and non-biodegradable, it may create a variety of environmental hazards in both aquatic and terrestrial life. The danger of MB can also damage human health in a variety of ways, including respiratory discomfort, metal poisoning, stomach pain, blindness, and digestive issues. Furthermore, MB poisoning causes nausea, diarrhea, vomiting, cyanosis, and other symptoms (Al-Tohamy et al., 2022)

In the present work Cerium-doped Fe2O3 nanoparticles with different concentration were prepaped with co-precipation method. Structural and adsorbing properties were studied for the prepared particles. Then Cerium-doped Fe2O3 nanoparticle were efficiently used to adsorbed organic dye Methylene blue. These organic dye are released in to water streams by textile, food, printing industries etc. The dye polluted water is harmful for aquatic life and is carcinogenic to human beings (Phuruangrat et al., 2018).

* 1. AIM AND OBJECTIVES

### 1.2.1 AIM OF STUDY

The aim and objective of this work is the investigation of the effectiveness of Ce-doped ZnO Nanoparticle on the removal of Methylene from aqueous solution and the applicability of Linear adsorption isotherm and Kinetic models on the process.

1.2.2 Specific objectives of Study

The specific objective of this work includes:

1. To synthesis and characterize the Ce-doped Fe2O3 nanoparticle by varoius technique such as X-ray diffraction (XRD), Ultra Violet Spectroscopy and Fourier Transform infrared Spectroscopy (FTIR).
2. Evaluate the effectiveness of Ce-doped Fe2O3 nanoparticles in removing methylene blue dye through adsorption experiments. This includes determining the removal efficiency at different initial dye concentrations and contact times and utilize UV-Vis spectroscopy to quantify the amount of methylene blue adsorbed onto the nanoparticles.
3. Investigate the influence of experimental parameters such as initial methylene blue concentration and contact time on the adsorption capacity of the Ce-doped Fe2O3 nanoparticles.
4. Applying linear adsorption isotherms (e.g., Langmuir, Freundlich) to understand the interaction between the dye and the nanoparticles.
5. Based on the findings, propose potential areas for future research to further explore and improve the Ce-doped Fe2O3 nanoparticle system for methylene blue removal or its application for the removal of other pollutants.
   1. JUSTIFICATION AND SIGNIFICANCE OF THE STUDY

# CHAPTER TWO

# LITERATURE REVIEW

## 2.1 ADSORPTION

Adsorption is a phenomenon that describes the interaction between two different phases that forms an interface layer by transfer of a molecule from a fluid bulk (liquid or gas) to a solid surface so, it is classified as a surface process (Alaqarbeh, 2021).

The mechanisms of adsorption process occurred by adhesion of material either gaseous, liquid, or solid called substrate on the surface of solid, or liquid, called sorbent or adsorbent (Dąbrowski, 2001).

There are different adsorption systems, liquid-gas or liquid-liquid. If a liquid material is an adsorbent, so the interfacial layer called film, micelle, or emulsion. The other system is solid-liquid or solid-gas; the adsorbent is a solid material, so the approved mechanism for

adsorption process is interfacial layer model (Alaqarbeh, 2021).

**Physical Adsorption**: also called physisorption, the bonding between substrate and adsorbent is a weak Van der Waals forces, no changes of chemical structure for both substrate and sorbent(Rajpoot & Bajpai, 1999).

**Chemical Adsorption**: also called chemisorption, the chemical bonding formation between substrate and adsorbent, by rearrangement of electron density between the adsorbent and substrate, the nature of this bond is ionic bond or covalent bond(Rajpoot & Bajpai, 1999).

Both models explain the adsorption mechanism; based on experimental physical criteria results the suitable adsorption model is determined for a system. The physical criteria used to compare two models are thermodynamic or adsorption isotherm studies and kinetics or equilibrium adsorption studies.

Thermodynamic or adsorption isotherm studies are represented by the degree of coverage (θ),

Kinetics or equilibrium adsorption studies are used to explain the adsorption mechanism and adsorption characteristics.

Both thermodynamic and kinetic experimental results distinguish between physical adsorption and chemical adsorption. The results determine bonding type, binding specificity, temperature effect, enthalpy of the bonding process, concentration or pressure effect, saturation of the interfacial layer, and kinetics of the process (Rajpoot & Bajpai, 1999). Indeed, there is a

difference between physical values for the two models as shown in table below.

|  |  |  |
| --- | --- | --- |
| Criteria | Physical Adsorption | Chemical Adsorption |
| Specificity | Non-specific. | Highly-specific |
| Nature of adsorption | Depend on nature of adsorbent. | Depend on nature of adsorbent. |
| Reversibility | Reversible process. | Mainly irreversible |
| Enthalpy | Low (20-40 kJ/mol). | Higher than physical  adsorption (40-300  kJ/mol). |
| Activation energy | Does not require high activation  energy. | Require high activation  energy. |
| **Layer of adsorption of**  **interfacial region**  (saturation) | Multi layers. | Mono layer. |

Source from (Alaqarbeh, 2021)

## 2.2 FACTOR AFFECTING ADSORPTION CAPACITY

## 2.3 ADSORPTION KINETIC MODEL

The adsorption kinetic study provides information of the adsorption rate, the performance of the adsorbent used, and the mass transfer mechanisms. Knowing the adsorption kinetic is essential for the design of the adsorption systems (Wang & Guo, 2020). The adsorption mass transfer kinetic includes three steps, as shown in Figure. 2. The first step is the external diffusion. In this step, the adsorbate transfers through the liquid film around the adsorbent. The concentrations difference between the bulk solution and the surface of the adsorbent are the driving force of the external diffusion. The second step is the internal diffusion. The internal diffusion describes the diffusion of the adsorbate in the pores of the adsorbent. The third step is the adsorption of the adsorbate in the active sites of the adsorbent (Wang & Guo, 2020).

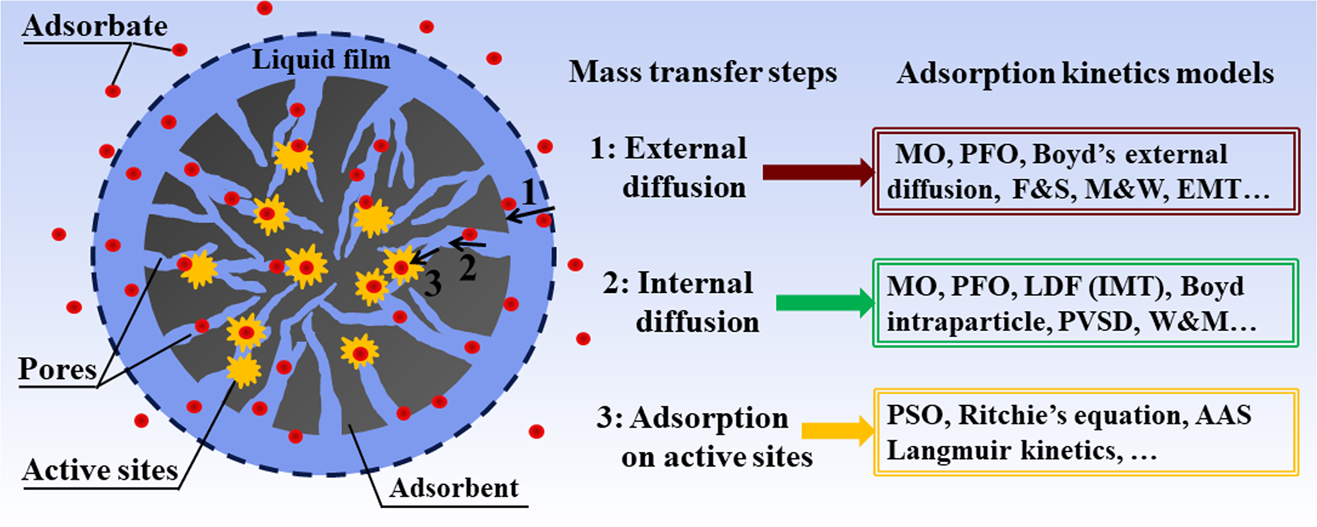


Figure 2 Adsorption mass transfer steps.

Source from (Wang & Guo, 2020)

Various adsorption kinetic models, such as the pseudo-first-order (PFO) model (Lagergren, 1898), the pseudo-second-order (PSO) model(Y. Ho Wase, DAJ &. CF Forster, CF, 1996), the mixed-order (MO) model (Guo et al., 2019), the Ritchie’s equation (Ritchie, 1977), the Elovich model (Elovich & Larinov, 1962), and the phenomenological mass transfer models (Blanco et al., 2017; Marin et al., 2014) have been developed to describe the ad- sorption kinetic process. However, some problems are existed in the applications of these kinetic models. The first one is that the most ap- plied PFO and PSO models are empirical models and lack of specific physical meanings. We cannot investigate the mass transfer mechanisms by these empirical kinetic models. Therefore, the physical meanings of the empirical kinetic models should be established. The second one is that the differential kinetic models, such as the phenomenological external/internal and adsorption in active sites models have specific physical meanings, but the solving methods are complicated.

#### 2.3.1 Pseudo-first-order (PFO) model

The PFO model was firstly proposed by Lagergren (1898). The differential form of the PFO model is described by Eq. (1) (Lagergren, 1898)

(1)

The linearized form of the PFO model is presented as follows

(2)

The above equation has been frequently used to fit the kinetics data and to calculate the parameters *q*e and *k*1, by plotting ln(*q*e-*q*t) vs. *t* (Ersan et al., 2019; Ma et al., 2018)*.* However, the linearization process may cause inaccurate estimations of the parameters (El-Khaiary et al., 2010, 2010; K. V. Kumar & Sivanesan, 2006). The nonlinear method which can provide accurate estimations for model parameters, is provided in the following section.

The PFO parameter *q*e is the equilibrium adsorption amount estimated by the PFO model. (Rodrigues & Silva, 2016) reported that the PFO model was theoretically consistent and equaled to the linear driving force (LDF) model, when the adsorption isotherm could be re- presented by the linear model (Eq. (3)).

(3)

The PFO parameter *k*1 is frequently used to describe how fast the adsorption equilibrium is achieved (Plazinski et al., 2009). However, as shown in Eq. (1), the adsorption rate d*q*t/d*t* is related to both *k*1 and (*q*e- *q*t). Small value of *k*1 and big value of (*q*e-*q*t) could be obtained when the adsorption is slow. Therefore, it is more precise to calculate the PFO rate by Eq. (4), instead of describing the adsorption rate by comparing the values of *k*1.

PFO rate = K1(qe – qt) (4)

### 2.3.2 . Pseudo-second-order (PSO) model

The PSO model Eq. (4) was firstly applied to model the adsorption of lead onto peat (Y. Ho Wase, DAJ &. CF Forster, CF, 1996). Then the PSO model was widely adopted to describe the adsorption processes. Most published papers used the PSO model to predict the adsorption experimental data and to calculate the adsorption rate constants.

)2  (4)

The integrated PSO model is described as following:

(5)

In order to calculate the model parameters, the nonlinear PSO model is always transformed to the linear form Eq. (6).

(6)

The linearization of the PSO model changes the weight of qt  and introduces propagated errors, which to the inaccurate calculations of the model parameters (El-Khaiary et al., 2010; Y. S. Ho, 2006). and Sivanesan, 2006; Guo and Wang, 2019c).

### 2.3.3 Mixed-order (MO) model

The mixed-order (MO) model has the following form (Guo & Wang, 2019):

) + )2 (7)

The PFO and PSO rate of the MO model can be calculated by Equation (8) and (9)

PFO rate = ) (8)

PFO rate = )2 (9)

In most cases, the PFO rate and PSO rate describe the diffusion step and the step of adsorption on active sites, respectively (Guo & Wang, 2019). 2019a). In addition, the MO model represents the overall adsorption process. The following conditions satisfy the assumption of the MO model: (1) arbitrary stage of the adsorption; (2) the rate controlling step is the diffusion or the adsorption; and (3) arbitrary initial adsorbate concentration in solution (Guo & Wang, 2019).

|  |  |  |
| --- | --- | --- |
| Model | Differential equation | integrations form or nonlinear form |
| PFO Model |  |  |
| PSO Model | )2 |  |
| MO Model | ) + )2 | --- |
|  |  |  |

## 2.4 ADSORPTION ISOTHERM MODEL

The well-known adsorption isotherms along with some latest developments are discussed in this section.

### 2.4.1 Henry’s Isotherm

It is a one-parameter model and the most basic adsorption isotherm. It proposes a linear relationship between the adsorbed amount and the adsorbate’s bulk concentration, as presented by equation 1 (Ruthven, 1984).

(1)

where *q*e is the adsorbed amount at equilibrium in mg/g, *K*HE is Henry’s adsorption constant in L/g, and *C*e is the adsorbate’s equilibrium concentration in mg/L.

A plot of *q*e versus *C*e produces a straight line, with a slope equal to *K*HE.

Henry’s model can be used when the coverage ratio of the adsorption sites is minimal. It approximates the data trend only at low solute concentrations. Hence, it shows monolayer adsorption at initially low adsorbate concentrations. This simplest model is invalid at the high concentrations of surfactant.

### 2.4.2 Langmuir Isotherm

The Langmuir isotherm was initially developed for gas–solid interaction but is also used for various adsorbents. (Elmorsi, 2011). It is an empirical model based on kinetic principles; that is, the surface rates of adsorption and desorption are equal with zero accumulation at equilibrium conditions.Based on the following assumptions

(a) monolayer adsorption

(b) homogeneous sites

(c) constant adsorption energy

(d) no lateral interaction between the adsorbed molecules

the Langmuir isotherm can be written as

(2)

where *q*o is the maximum amount of adsorbed surfactant in mg/g and *K*L is the Langmuir constant in L/mg. The linearized version of equation 3 is

(3)

A plot between *C*e/*q*e versus *C*e will generate a straight line with a slope of 1/*q*o and an intercept equals to 1/*K*L*q*o.

The monolayer assumption requires identical adsorption sites, and only one molecule can be adsorbed at each site. There is no more adsorption in a site once a surfactant molecule has occupied it. This model converts to Henry’s model at very low concentrations (*K*L*C*e ≪ 1).

An important parameter related to the Langmuir model is the separation factor or equilibrium parameter, denoted as RL, which is used to check if surfactant adsorption is favorable or unfavorable(Gunawardene et al., 2021). Mathematically, it can be shown as

(4)

where *K*L and *C*o are the Langmuir constant and highest initial concentration of surfactant, respectively.

In general, *R*L < 1 indicates that adsorption is favorable; *R*L ∼ 0 indicates that adsorption is irreversible; *R*L = 1 indicates that the adsorption isotherm is linear, and *R*L > 1 corresponds to unfavorable adsorption.

### 2.4.3 Freundlich Isotherm

Unlike the Langmuir isotherm, this empirical model can be used for multilayer adsorption on heterogeneous sites. It assumes that the adsorption heat distribution and affinities toward the heterogeneous surface are nonuniform(Foo & Hameed, 2010).

The mathematical model can be shown as

(5)

where *b* is the adsorption capacity in L/mg and 1/*n* is the adsorption intensity or surface heterogeneity. When 0 < 1/*n* < 1, adsorption is considered favorable. Unfavorable adsorption occurs when 1/*n* > 1 and is irreversible at 1/*n* = 1.

The linearized form can be written as

In (6)

A plot of ln *q*e versus ln *C*e produces a straight line with a slope = 1/*n* and intercept = ln *b*.

The linearized form is easy and straightforward. On the other hand, the linearization process generates propagating errors, which results in erroneous predictions of parameters. Therefore, the use of nonlinear regression to solve the nonlinear Freundlich model is recommended for the calculation of the model parameters(Wang & Guo, 2020).

The Freundlich isotherm describes multilayer adsorption and assumes exponential decay in the energy distribution of adsorbed sites. However, it is not valid for a large range of adsorption data (Al-Ghouti & Da’ana, 2020).

### 2.4.4 Temkin Isotherm

The Temkin model, which presumes a multilayer adsorption process, considers interactions between the adsorbent and the adsorbate, but it ignores very small and very large concentration values. (Foo & Hameed, 2010). The nonlinearized form of the Temkin isotherm is expressed by

(7)

where R is the universal gas constant in J/(mol K), T is the temperature in K, b is the Temkin constant related to sorption heat in J/mol, and Km is the Temkin isotherm constant in L/g.

The linearized form can be written as

(8)

Plotting *q*e versus ln *C*e will produce a straight line with slope =  and intercept = .

As the surface coverage increases, the Temkin model assumes that the heat of adsorption of all molecules in the layer reduces linearly instead of logarithmically.(Foo & Hameed, 2010)

**Table 1. Summary of Adsorption Isotherms**

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Adsorption isotherm | Number of parameters | X axis | Y axis | Slope | Intercept | Summary |
| Henry | 1 | *q*e | *C*e | *K*HE | No-intercept | 1. the simplest adsorption isotherm; assumes a linear relationship between adsorbed amount and adsorbate bulk concentration 2. applicable for low solute concentrations o |
| Langmuir | 2 | Ce/qe | Ce | 1/*q*o | 1/ K1q1 | 1. monolayer adsorption 2. homogeneous solid surfaces |
| Freundlich | 2 | ln *q*e | ln *C*e | 1/*n* | ln b | 1. applicable for multilayer adsorption 2. suitable for heterogeneous surfaces 3. not valid for a large range of adsorption data |
| Temkin | 2 | *q*e | ln *C*e |  |  | 1. considers interaction between adsorbent and the adsorbate 2. with increase in surface coverage, the heat of adsorption of all molecules in the layer is decreases linearly instead of logarithmically |

## 2.5 ADSORPTION THERMODYNAMICS

Thermodynamic parameters such as free energy (∆Go), enthalpy change (∆Ho) and entropy change (∆So) were estimated using the following equations:

∆ Go = - RT ln Kd (1)

ln Kd = (ΔS°/R) – (ΔH°/RT) (2)

Where R is the gas constant (8.3145 J.mol–1K–1), T is the temperature in Kelvin and Kd is the thermodynamic distribution coefficient, as in equation (3):

= (3)

The values of ∆Ho and ∆So are calculated from the slope and intercept of the linear variation of ln Kd with reciprocal temperature. The ln Kd was calculated from the intercept of ln (qe/Ce) vs qe (Boparai et al., 2011).

# Chapter three

## 3.1 Material and Reagent used

## 3.2 Apparatus and Equipment

## 3.3 Chemicals

## 3.4 Synthesis of Cerium doped Iron (Fe2O3) Nanoparticle

## 3.5 Characterization and Analysis

## 3.6 Adsorption Studies

### 3.6.1 Determination of the effect of Initial Concentration

### 3.6.2 Determination of the effect of contact time

### 3.7 Calculation of Percentage Removal and Adsorption Capacity