

# Adsorption of Congo Red Dye by Using PPHA-Adsorbent

Saroj P. Sahare

Department of Chemistry, Anand Niketan College, Warora, Maharashtra, India  
sarojsahare04@gmail.com

**Abstract:** Nowadays water pollution is concerning environmental problem for human health as well aquatic ecosystems. There are many reasons for water pollution mainly industrialization, in which textile industries are causing dye containing water pollution. In this work, it is a attempt to reduce this dye water pollution. A pigeon pea hull which is a agricultural waste is utilized to obtain a adsorbent for removal of dye. Congo red dye was chosen as target dye pollutant in this study. Kinetics and adsorption study was done. The prepared PPHA-adsorbent shows good adsorption capacity towards congo red dye and it is cost-effective.

**Keywords:** Congo red dye; adsorption; Pigeon pea leaves ash; Adsorbent

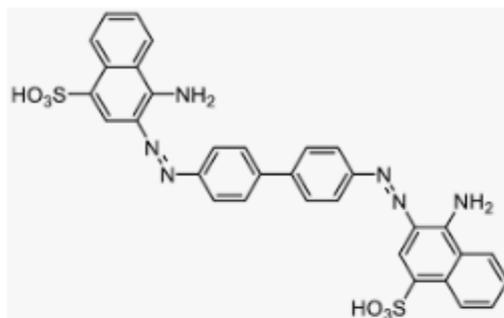
## I. INTRODUCTION

Dyes are basically chemical compounds that can connect themselves to surfaces or fabrics to impart colour. The majority of dyes are complex organic molecules and are required to be resistant to many things such as the action of detergents. Synthetic dyes are widely used in many fields of advanced technology, e.g., in various kinds of the textile, paper, leather tanning, food processing, plastics, cosmetics, rubber, printing and dye manufacturing industries. Synthetic dyes are also employed in ground water tracing for the determination of specific surface area of activated sludge, sewage and waste water treatment, etc.[1]

The toxic effluents can cause considerable damage to human and marine life if they are not treated prior to discharge. With the rapid development of industrial technology, reusing sustainable resources such as water and materials has become an issue of concern around the world and the water pollution has become a serious world wide issue. Water crisis exacerbated by water pollution poses a huge threat to the global economy, manifesting in the instigation of civil or international conflicts and the disruption of operations and supply chains in industries [2].

Congo red (CR) is a typical anionic azo dye. Although CR has been widely used, this dye is intrinsically harmful to living organism. Given its complex aromatic structure and high chemistry and thermal stability, CR-containing wastewater is a type of harmful organic waste water that is difficult to degrade and demands high chemical oxygen [3].

In addition, its degradation product under anaerobic conditions is benzidines, which is a recognized carcinogen. Thus, excessive CR in wastewater must be removed with environmentally friendly techniques for sustainable development [4].



**Figure 1:** Chemical structure of congo red dye



Congo red containing effluents are generated from textiles, printing, dyeing, paper, rubber and plastics industries, etc. Due to its structural stability, it is difficult to biodegrade. Physico-chemical or chemical treatment of such wastewaters is, however, possible. Adsorption is considered an attractive option in treating such wastewater [5].

Congo red is an anionic dye; therefore, if electrostatic attraction plays an important role in the adsorption process, the adsorption will be highly reversible under a certain alkaline environment that was used as a desorbing agent[6].

Wastewaters containing dyes are very difficult to treat, since the dyes are recalcitrant molecules, resistant to aerobic digestion. Another difficulty is treatment of wastewaters containing low concentrations of dye molecules. The presence of very small amounts of dyes in water is highly visible and undesirable. So it is essential to remove color from solution. It is known that adsorption using low-cost adsorbents is an effective and economic method for water decontamination[6].

The tremendous discharge of textile waste water is viewed as one of the main causes of water pollution. Industries are major sources of aquatic pollution. The large quantities of dyes discharged from the textile, clothing, and printing. Most of these dyes are very colorful, but have high biochemical and chemical oxygen demands, smell unpleasant, and are toxic[7].

Dyes are rather difficult to remove from wastewater because of their synthetic origins and complex aromatic structures. Several physical, chemical, and biological techniques have been used to remove dyes from wastewater. These techniques include coagulation, chemical treatment, oxidation electrochemical methods biological treatment adsorption, and ion exchange. Among them, adsorption is considered to be an effective and versatile method for removing dyes from aqueous solutions [8].

Many researchers have studied the feasibility of low-cost, natural materials for dye removal, such as wood, natural coal, peat, clays, and silica. However, these low-cost adsorbents generally have low adsorption capacities. Thus, there is still a need to find economical, easily available, and highly effective alternative adsorbents [8].

The discharge of untreated effluents with a large amount of dye into the aquatic environment poses serious threats to the ecological environment and human health. Due to their toxic effects, dyes have generated much concern regarding its use. It has been informed to cause mutagenesis, chromosomal fractures, carcinogenesis, and respiratory toxicity. Therefore focuses on specific methods and technologies to remove dyes from different kinds of wastewater streams are desired [9].

An ideal dye removal method should be able to efficiently remove large quantities of dye from wastewater in a short time span without producing secondary pollution. It is encouraged to remove pollutants from wastewater with a method that does not produce more hazardous by-products[10].

In recent years, numerous low cost natural materials such as phytophyllite, rice husk, montmorillonite, plant, activated carbon prepared from coir pith, bagasse, fungi, soil, clay, mineral, fruit shell, water hyacinth root, activated carbon prepared from algae, chitosan hydrogel, and other adsorbents have been used and investigated for removal and adsorption of CR from aqueous solution [11].

Pigeon pea hulls (*Cajanus cajan*), a member of the legume family, is an agricultural and industrial waste product that is distributed mainly in semiarid and subtropical areas of the world. Pigeon pea products possess antioxidant, anti-inflammatory, and protein kinase inhibitory activities [12].



Figure 2: Pigeon pea hulls [*Cajanus cajan*]

In this study, a pigeon pea hulls (*Cajanus cajan*) leaves ash prepared and used as adsorbent for removal of Congo red (CR). The adsorption isotherm and kinetics are also studied.

## II. MATERIALS AND METHOD

All material and chemicals were of analytical grade and used without further purification in all experimental work. Congo red dye was used for this work. For the preparation of dye solution calibrated volumetric flask and distilled water used.

### 2.1. Adsorbent Synthesis

Pigeon pea hulls were collected from agricultural waste. The leaves were washed with distilled water, air dried, ground in powder and then heated in hot oven at 180<sup>0</sup> c for 2 hour and form the PPH ash. Finally sieved of 200 mesh particle size. Stock solution of Congo red dye was prepared. The stock solution of congo red dye was Prepared.

### 2.2. Instruments used

#### 2.2.1. Orbital Shaker

A shaker is a piece of laboratory equipment used to mix, blend, or agitate substances in a tube or flask by shaking them. It is mainly used in the fields of chemistry. A shaker contains an oscillating board that is used to place the flasks, beakers, or test tubes. Although the magnetic stirrer has lately come to replace the shaker, it is still the preferred choice of equipment when dealing with large volume substances or when simultaneous agitation is required.

#### 2.2.2. Colorimeter

Colorimetry is the field of determining the concentration of a coloured compound in a solution. A colorimeter, also known as a filter photometer, is an analytical machine that acts as the tool quantify a solutions concentration by measuring the absorbance of a specific wavelength of light.

### 2.3. Adsorption experiment

Adsorption experiments were carried out by agitating 150 mg of adsorbent with 20 mL of CR solution of the desired concentration at 150rpm in rotary shaker. The absorbance measurement before and after experiment was carried out using colorimeter.



Pigeon Pea Hulls



Dried Pigeon Pea Hulls



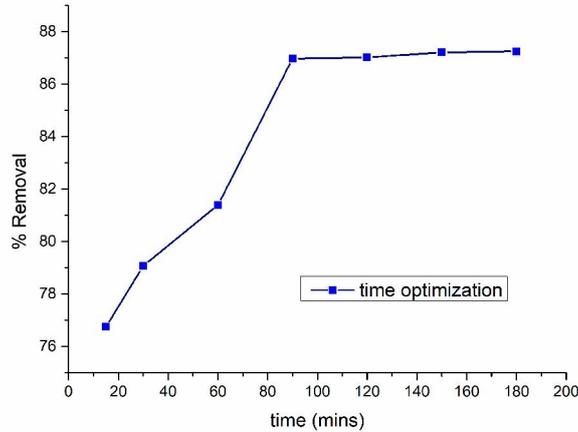
Pigeon Pea Hulls Ash

Figure 3: Pigeon pea hulls at various stages in adsorbent synthesis

## III. RESULTS AND DISCUSSIONS

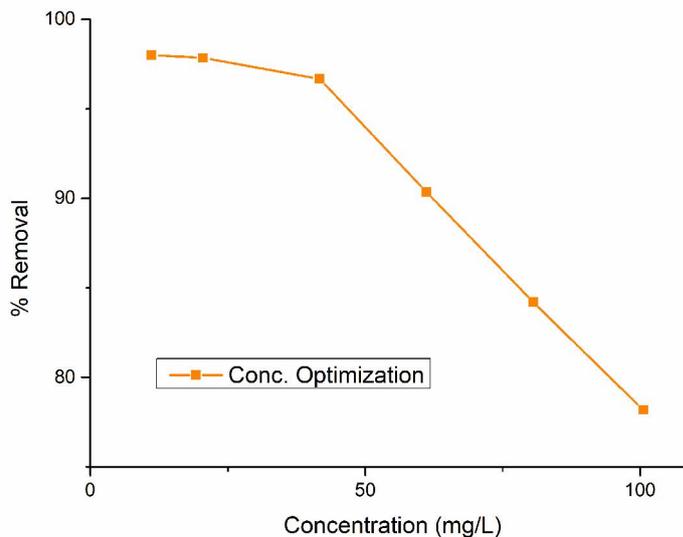
### 3.1 Effect of Initial Parameters

The effect of time enhances the equilibrium adsorption of the pollutants and adsorption kinetic performances between the adsorbate and adsorbent. As the time of agitation increases dye adsorption also increases.



**Figure 4:** Effect of contact time on adsorption of congo red dye on PPHA adsorbent

The effect of concentration of congo red dye uptake by the turmeric leaves ash adsorbent was measured by varying the initial concentration of congo red dye at constant temperature for 90 min in stirring time. The adsorption capacities were increased with increasing an initial congo red dye concentration. The effect of dye concentration shown in graph.



**Figure 5:** Effect of initial concentration on adsorption of congo red dye on PPHA adsorbent

### 3.2 Adsorption Kinetics

The order of adsorbate–adsorbent interactions has been described by using various kinetic models. Traditionally, the well-known pseudo first-order model has found general use, but second-order kinetics has also been applied with success by various authors to describe the interactions. When adsorption is preceded by diffusion through a boundary, the kinetics in most cases follow the pseudo first order rate equation (1). Pseudo second-order kinetics given by equation (2) [13].

$$\log(q_e - q_t) = \log q_e - \left( \frac{k_1}{2.303} \right) t \quad (1)$$

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



Where  $q_t$  and  $q_e$  are the amount adsorbed at time  $t$  and at equilibrium and  $k_1$  is the rate constant of the pseudo first order adsorption process. Where  $k_2$  is the second-order rate constant. The plots of pseudo first order and pseudo second-order kinetics are shown in figures (6) and (7) respectively. The parameters are shown in table 1 and according to found results psuedo second order is applicable for this experiment and having  $R^2= 0.9996$  value.

The variation in the amount of adsorption with time at different initial dye concentrations could be further processed for evaluating the role of diffusion in the adsorption process. Adsorption is a multi-step process involving transport of the solute molecules from the aqueous phase to the surface of the solid particulates followed by diffusion of the solute molecules into the pore interiors. The intra-particle diffusion rate is given by the equation

$$q_t = K_{id} \cdot t^{1/2} + C \tag{3}$$

Where  $k_{id}$  is the intra-particle diffusion rate constant. The  $k_{id}$  values are found from the slopes of  $q_t$  vs.  $t^{1/2}$  plots.

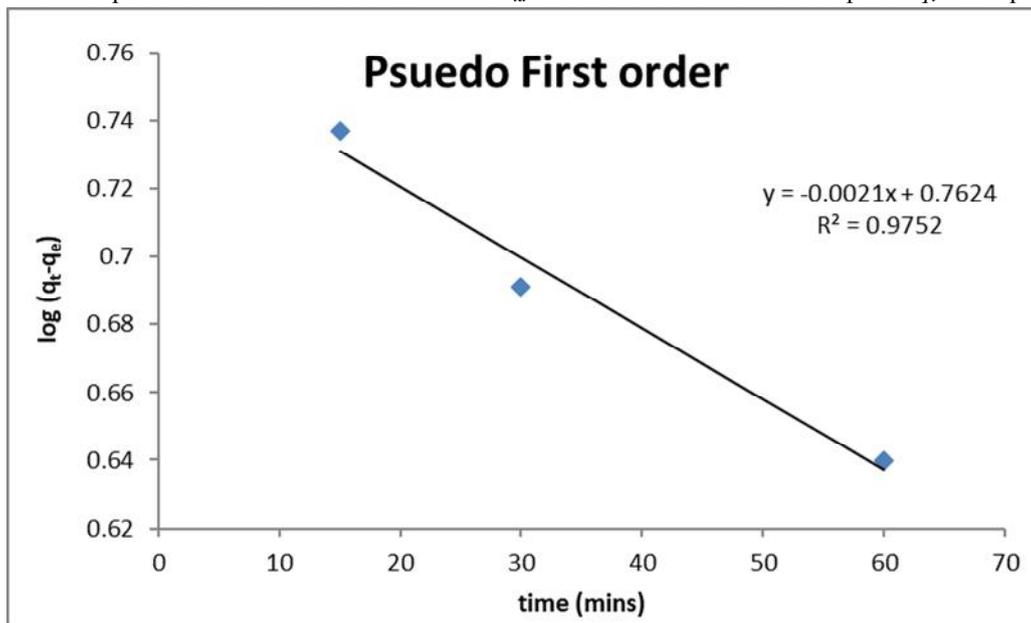


Figure 6: Psuedo first order model for adsorption of congo red dye

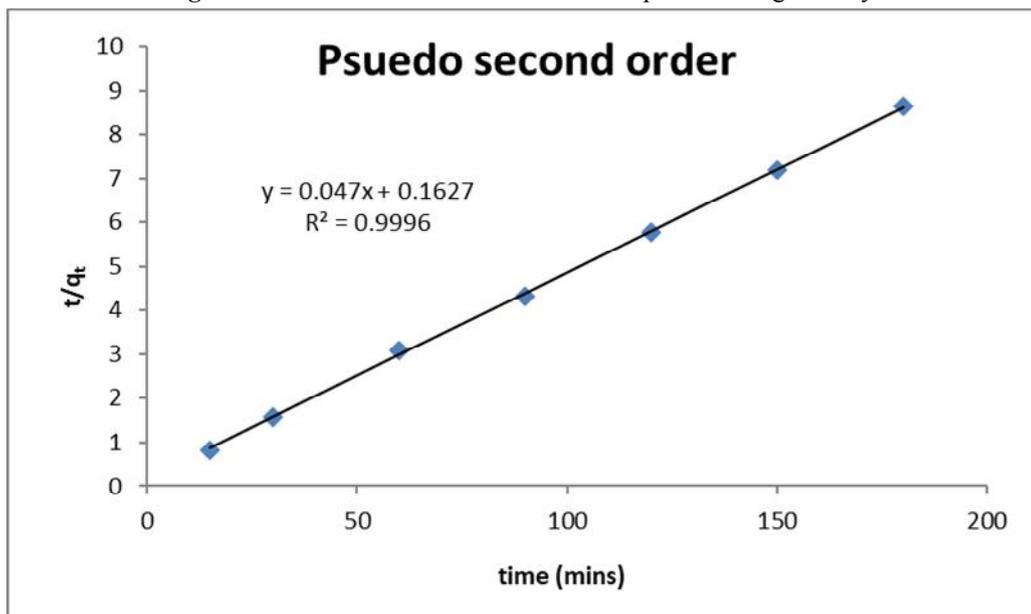
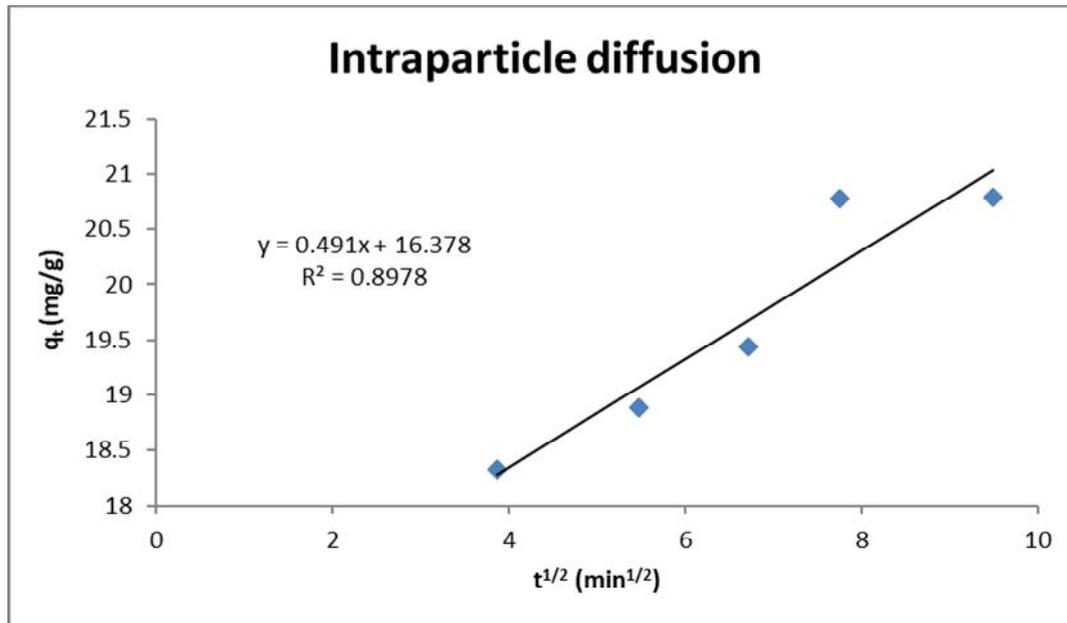


Figure 7: Psuedo second order curve for adsorption of congo red dye



**Figure 8:** Intraparticle diffusion model for adsorption of congo red dye

**Table 1:** Kinetic parameters for adsorption of congo red dye on PPHA adsorbent

Adsorption Kinetics	Constants	Units	Values
<b>Pseudo First Order</b>	$R^2$	-	0.9752
$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right)t$	$q_e$	mg.g <sup>-1</sup>	5.7862
	$K_1$	min <sup>-1</sup>	0.000911
<b>Pseudo Second Order</b>	$R^2$	-	0.9996
$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 \cdot q_e^2}$	$q_e$	mg.g <sup>-1</sup>	21.2765
	$K_2$	g.mg <sup>-1</sup> min <sup>-1</sup>	1.357 x10 <sup>-2</sup>
<b>Intraparticle diffusion</b>	$R^2$	-	0.8978
$q_t = K_{id} \cdot t^{1/2} + C$	$C$	mg.g <sup>-1</sup>	16.378
	$K_{id}$	mg.g <sup>-1</sup> min <sup>-0.5</sup>	0.491

### 3.3 Adsorption Isotherm Study

The most widely studied Langmuir equation (4), valid for monolayer chemisorption was used to test the possible adsorption mechanism on PPHA. For multilayer adsorption study Freundlich model is used and equation is shown as below (5) [14].

$$\frac{C_e}{q_e} = \frac{1}{Q_m K_L} + \frac{C_e}{Q_m} \quad (4)$$

$$\log q_e = \frac{1}{n} \log C_e + \log K_f \quad (5)$$

$K_f$ (L mg<sup>-1</sup>) and  $n$  are Freundlich constants which indicate the adsorption capacity and adsorption intensity, respectively. The graphs of Langmuir and Freundlich models are shown in figures (9) and (10) respectively. The isotherm parameters are tabulated in table 2. the  $R^2$  is more for Freundlich isotherm model suggesting multilayer adsorption process. The comparative adsorption capacities are shown in table 3.

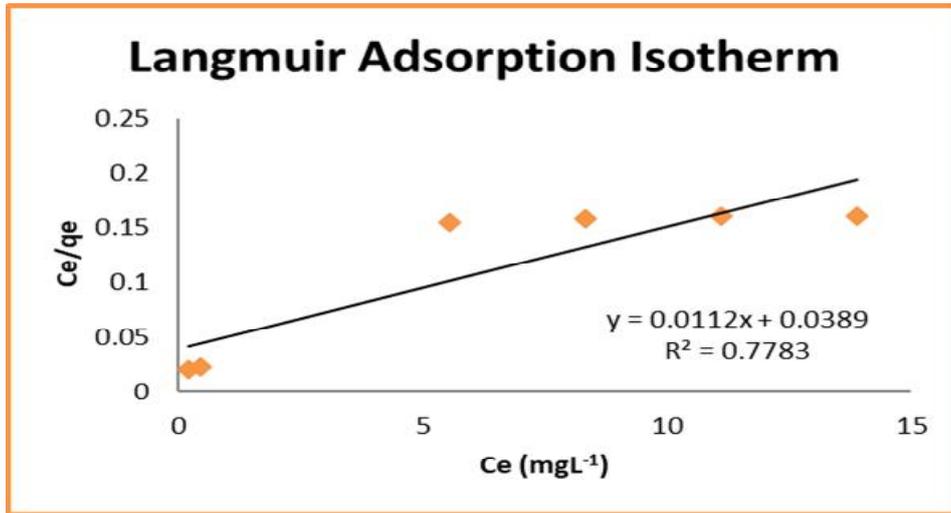


Figure 9: Langmuir model for adsorption of congo red dye on PPHA adsorbent

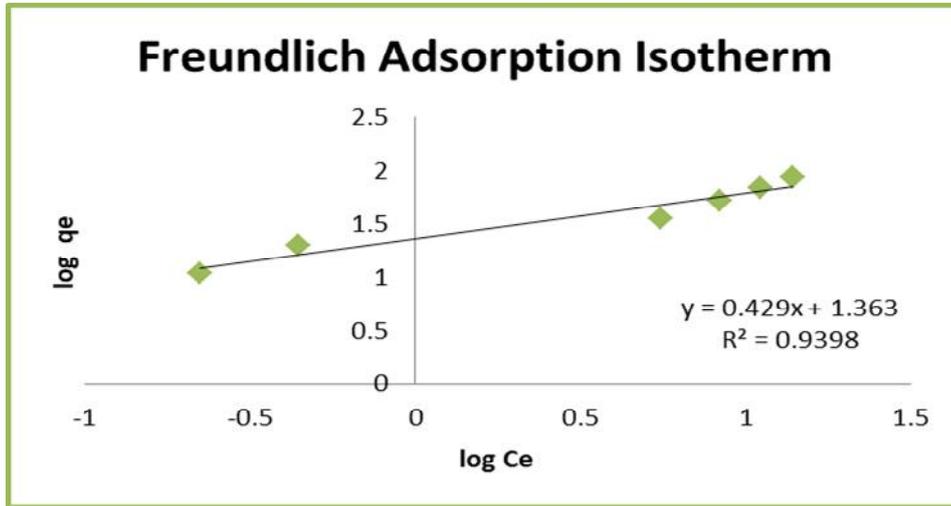


Figure 10: Freundlich model for adsorption of congo red dye on PPHA adsorbent

Table 2: Adsorption isotherm parameters for adsorption of congo red dye on PPHA adsorbent

Adsorption Isotherm	Constants	Units	Values
<b>Langmuir</b>	$R^2$	-	0.7783
$\frac{C_e}{q_e} = \frac{1}{Q_m K_L} + \frac{C_e}{Q_m}$	$Q_m$	mg. g <sup>-1</sup>	89.2857
	$k_L$	Lmg <sup>-1</sup>	0.2879
<b>Freundlich</b>	$R^2$	-	0.9398
$\log q_e = \frac{1}{n} \log C_e + \log K_f$	$K_f$	Lmg <sup>-1</sup>	23.0674
	$n$		0.429

Table 3: The comparison between bioadsorbent for congo red dye.

Material	Dyes	Adsorption Capacity $q_{max}$ [mg/g]	References
Orange peel	Congo red	14.00	[15]
Banana peel	Congo red	18.20	[15]
Jute stick powder	Congo red	35.70	[16]
Magnetic cellulose/Fe3O4/Activated carboncomposite	Congo red	66.09	[17]

<b>Chitosan/Montmorillonite</b>	Congo red	54.52	[ 18 ]
<b>Pigeon pea hulls</b>	<b>Congo red</b>	<b>89</b>	<b>This Experiment</b>

#### IV. CONCLUSION

In this study, natural carbohydrate based polymeric adsorbent of pigeon pea leaves ash was used as efficient and potential adsorbent for the adsorptive removal of congo red dye from aqueous media. For understanding the dye removal behavior, parameter affecting the congo red dye adsorption process, including contact time and dye concentration. The adsorbent was exhibited relatively fast kinetics performances based on the pigeon pea hulls ash [PPHA] functionality. The experimental data followed pseudo second order kinetics.

The equilibrium data were followed the freundlich isotherm model, confirming the multilayer coverage of congo red dye onto the PPHA adsorbent. The adsorption capacity of adsorbent towards congo red dye determined 89 mg/g from langmuir isotherm model. The results clarified that the natural adsorbent was cost-effective and exhibited much higher adsorption ability compared with the other forms of adsorbents, the current study revealed the advantages of natural adsorbent with for congo red dye adsorption from aqueous media.

Therefore, the natural polymeric pigeon pea leaves ash adsorbent can be used for the treatment of dyes from textile wastewater efficiently to clean up the contaminated water.

#### REFERENCES

- [1]. Imran Ali, Zeid A. AL-Othman, Abdulrahman Alwarthan, Molecular uptake of congo red dye from water on iron composite nano particles, *Journal of Molecular Liquids* 224 (2016) 171–176.
- [2]. Muhammad Ali Zulfikar, Henry Setiyanto Adsorption Of Congo Red From Aqueous Solution Using Powdered Eggshell . *Int.J.Chem. Tech Res.* 5 (2013).
- [3]. Jia Liua, Nan Wangb, HuiliZhangb, Jan Baeyensa, Adsorption of Congo red dye on  $Fe_xCo_{3-x}O_4$  nanoparticles, *Journal of Environmental Management* 238 (2019) 473–483.
- [4]. Himanshu Patel, R.T. Vashi, Removal of Congo Red dye from its aqueous solution using natural coagulants. *Journal of Saudi Chemical Society* 16 (2012) 131–136.
- [5]. C. Namasivayam, D. Kavitha, Removal of congo red from water by adsorption onto activated carbon prepared from coir pith, an agricultural solid waste, *Dyes Pigments* 54 (2002) 47–58.
- [6]. Peng Wang , Tingguo Yan and Lijuan Wang . Removal of congo red from aqueous solution using Magnetic Chitosan C omposite Microparticles. *BioResouces* 8[4] 6026-6043.
- [7]. Sudipta chatterjee, Hai Nguyen Tran , Ohemeng- Boahen Godfred and Seung Han Woo. Supersorption capacity of anionic dye by newer chitosan hydrogel capsules via green surfactant exchange method . *ACS Sustainable chemistry & engineering* .
- [8]. Mustafa T. Yagub, Tushar Kanti Sen, Sharmeen Afroze, H.M. Dye and its removal from aqueous solution by adsorption: A review. *Advances in Colloid and Interface Science* 209 (2014) 172–184.
- [9]. Vanitha Katheresan, Jibrail Kansedo, Sie Yon Lau, Efficiency of Various Recent Wastewater Dye Removal Methods: A Review. *Journal of Environmental Chemical Engineering* (2018),
- [10]. Yingqiu Zheng, Bei Cheng, Jiajie Fan, Jiaguo Yu, Wingkei Ho. Review on nickel-based adsorption materials for Congo red, *Journal of Hazardous Materials HAZMAT* 123559.
- [11]. M.K. Purkait, A. Maiti, S. DasGupta, S. De. Removal of congo red using activated carbon and its regeneration, *Journal of Hazardous Materials* 145[2007] 287-295.
- [12]. D.K. Venkata Ramana, Kim Min, Activated carbon produced from pigeon peas hulls waste as a low-cost agro-waste adsorbent for Cu(II) and Cd(II) removal. *Desalination and Water Treatment*.
- [13]. S. P. Sahare, S. P. Zodape, Removal of Cu(II) and Cd(II) Ions from Aqueous Solutions by Methionine Functionalized Cobalt-Magnesium Ferrite Chitosan Beads: Performance and Adsorption Mechanism. *J Polym Environ* (2022). <https://doi.org/10.1007/s10924-022-02724-7>
- [14]. S. P. Sahare, A. V. Wankhade, Sinha, A.K. *et al.* Modified Cobalt Ferrite Entrapped Chitosan Beads as a Magnetic Adsorbent for Effective Removal of Malachite Green and Copper (II) Ions from Aqueous Solutions. *J Inorg Organomet Polym* 33, 266–286 (2023). <https://doi.org/10.1007/s10904-022-02491-x>

- [15]. Annadurai, G., Juang, R., Lee, D., Use of cellulose-based wastes for adsorption of dyes from aqueous solutions, *J. Hazard. Mater.* 92(3) (2002) 263-274.
- [16]. G. C. Panda, S. K. Das, A. K. Guha, Jute stick powder as a potential biomass for the removal of congo red and rhodamine B from their aqueous solution, *J. Hazard. Mater.* 164(1) (2009) 374-379.
- [17]. H. Y. Zhu, Y. Q. Fu, R. Jiang, J. H. Jiang, L. Xiao, G. M. Zeng, S. L. Zhao, Y. Wang, Adsorption removal of congo red onto magnetic cellulose/Fe<sub>3</sub>O<sub>4</sub>/activated carbon composite: Equilibrium, kinetic and thermodynamic studies, *Chem. Eng. J.* 173(2) (2011a) 494-502.
- [18]. L. Wang, A. Wang, Adsorption characteristics of Congo red onto the chitosan/montmorillonite nanocomposite, *J. Hazard. Mater.* 147(3) (2007c) 979-985.