



# Modeling of adsorption isotherms of dyes onto various adsorbents: A Short Review

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## Abstract

The frequent contamination of water resources with dyes has been attracted enormous environmental researchers around the world. This paper presents a short review of adsorption isotherms of dyes from aqueous solutions by various adsorbents such as agricultural solid wastes and activated carbons. Several isotherm models are described. The present short review reveals that the equilibrium data fitted Langmuir isotherm in majority of cases and has successful application in many adsorption processes of monolayer adsorption. Most of the reported studies are performed in the batch process; this gives a platform for the designing of the continuous flow systems with industrial applications.

*Keywords:* dyes, adsorption, modelling, isotherms.

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## 1. Introduction

Dyes represent one of the problematic groups; they are emitted into wastewater from various industrial branches, mainly from the dye manufacturing and textile finishing and also from food coloring, cosmetics, paper and carpet industries. It is estimated that more than 100,000 commercially available dyes with over  $7 \times 10^5$  tonnes of dyestuff produced annually [1–3]. The colour is the first contaminant to be recognized in wastewater. The presence of even very small amounts of dyes in water less than 1ppm for some dyes is highly visible and undesirable [4, 5].

The presence of dyes in water bodies causes environmental damage to aquatic organisms by blocking sunlight, retarding photosynthetic activity and disturbing the re-oxygenation capacity, which creates anaerobic condition that limits aquatic plan growth [6]. In addition, contaminated surface water and groundwater would make the water bodies unsuitable for other use [7] and can cause carcinogenic [8, 9] and mutagenic effects [10, 11]. The presence of dyes in effluents is a major concern due to their adverse effects to many forms of life. The discharge of dyes in the environment is a matter of concern for both toxicological and esthetical reasons [12].

Some treatment technologies are used in the removal of dyes from aqueous media such as electrochemical treatment, coagulation, precipitation, solvent extraction, membrane filtration and advanced oxidation process [13, 14]. However, these methods have several disadvantages such as high-energy consumption, incomplete ion removal, and production of toxic sludge and other waste products that require further treatment and disposal [6]. However, the adsorption is considered to be one of the most popular, efficient and comparable low cost process due to its simplicity [15].

The aim of this short review paper was to describe the modelling of adsorption isotherms of dyes from aqueous solutions by various adsorbents. The objective is not an exhaustive review of all the types of adsorbents used, but to focus onto agricultural solid wastes and activated carbons. The reader is strongly encouraged to refer to the original research papers for information on experimental conditions.

## 2. Adsorption isotherms and models

In general, an adsorption isotherm is an invaluable curve describing the phenomenon governing the retention of a substance from the aqueous porous media or aquatic environments to a solid-phase at a constant temperature and pH [16, 17]. Adsorption equilibrium is established when an adsorbate containing phase has been contacted with the adsorbent for sufficient time, with its adsorbate concentration in the bulk solution is in a dynamic balance with the interface concentration [18].

Typically, the mathematical correlation, which constitutes an important role towards the modeling analysis, operational design and applicable practice of the adsorption systems, is usually depicted by graphically expressing the solid-phase against its residual concentration [19].

Over the years, a wide variety of equilibrium isotherm models such as Langmuir, Freundlich, Brunauer–Emmett–Teller, Redlich–Peterson, Dubinin–Radushkevich, Temkin, Toth, Koble–Corrigan, Sips, Khan, Hill, Flory–Huggins and Radke–Prausnitz isotherm, have been formulated in terms of three fundamental approaches [20]. Kinetic consideration is the first approach to be referred. Hereby, adsorption equilibrium is defined being a state of dynamic equilibrium, with both adsorption and desorption rates are equal [21]. Whereas, thermodynamics, being a base of the second approach,

can provide a framework of deriving numerous forms of adsorption isotherm models, and potential theory, as the third approach, usually conveys the main idea in the generation of characteristic curve [22]. However, an interesting trend in the isotherm modeling is the derivation in more than one approach, thus directing to the difference in the physical interpretation of the model parameters [23].

### 3. Agricultural solid wastes as adsorbents

On searching for economical and available starting materials; different low cost adsorbents were used for the removal of dyes. Some researchers explored the ability of agricultural wastes solid as adsorbents to eliminate the dyes through various equilibrium studies.

Among them, Doulati Ardejani et al. (2008) [24] studied the adsorption of Direct Red 80 dye from aqueous solution on almond shells as an eco-friendly and low-cost adsorbent. Equilibrium data were attempted by various adsorption isotherms including Langmuir, Freundlich and Brunauer-Emmett-Teller (BET) models. It was found that the adsorption process by mixture type of almond shells follows the Langmuir non-linear isotherm. Furthermore, the experimental data by internal and external almond shells could be well described by the BET and Freundlich isotherm models, respectively. Senthil Kumar et al. (2010) [25] prepared cashew nut shell as the adsorbent for the removal of Congo red dye from an aqueous solution. The equilibrium data have been analyzed using Langmuir, Freundlich, Redlich–Peterson, Koble–Corrigan, Sips, Toth, Temkin and Dubinin–Radushkevich isotherms. The experimental data yielded excellent fits within the following isotherms order: Redlich–Peterson > Toth > Koble–Corrigan > Sips > Freundlich > Langmuir > Temkin > Dubinin–Radushkevich, based on its correlation coefficient values. Vucurovic'et al. (2012) [26] used sugar beet pulp as an adsorbent for removal of Methylene Blue. Freundlich and Langmuir isotherm models were found to be suitable for description of Methylene Blue adsorption on Sugar Beet Pulp. The Sugar Beet Pulp was found to have a Langmuir monolayer adsorption capacity of 714.29 mg g<sup>-1</sup> at pH 8 and 25 °C. Guechi and Oualid Hamdaoui (2013) [27] investigated biosorption of Malachite Green from aqueous solutions using the *Typha angustifolia* leaves. Equilibrium data were fitted to the Langmuir, Freundlich, Redlich–Peterson and Sips isotherm models using non-linear regression technique. The results showed that the experimental equilibrium data were best represented by the Redlich–Peterson and Sips isotherms, but the Redlich–Peterson model was better. Inyinbor et al. (2016) [28] prepared a highly efficient low cost adsorbent from *Raphia hookerie* fruit epicarp for adsorption of Rhodamine B dye. The equilibrium adsorption data were fitted using four isotherms tested models. Freundlich isotherm best described the uptake of Rhodamine B dye onto *Raphia hookerie* with the maximum monolayer adsorption capacity was 666.67 mg g<sup>-1</sup>. Abdi and Nasiri (2017) [29] investigated the removal of Fast Green FCF dye from aqueous solutions using Flower Gel in a batch adsorption process. Various isotherms including

Langmuir, Freundlich and Tempkin were applied. The results showed that the equilibrium experimental data were fitted well to the Langmuir isotherm and the maximum adsorption capacity for this adsorbent was  $58.82 \text{ mg g}^{-1}$ . Benkaddour et al. (2018) [30] used the watermelon seeds treated with hexane for the removal of reactive yellow 145 from aqueous solutions. The Langmuir, Freundlich, Temkin, Elovich and Dubinin- Radushkevich models were studied. It was proved that the experimental data fitted well to the Freundlich model, which signifies that the phenomenon of adsorption is done in multilayers on heterogeneous surfaces. Boumaza et al. (2018) [31] studied the biosorption potential of *Typha angustifolia* biomaterial waste for the removal of Methylene Blue. The Freundlich, Langmuir and Temkin isotherms are employed. The equilibrium data are adequately represented by the Langmuir isotherm with the maximal monolayer biosorption capacity of *Typha angustifolia* is found to be  $106.757 \text{ mg g}^{-1}$  at  $25 \text{ }^\circ\text{C}$ . Sánchez Orozco et al. (2018) [32] investigated the potential of *Typha latifolia* L. stem and leaf powder without any modification to eliminate Methylene Blue from aqueous solutions. Equilibrium isotherms were used for data analysis. The experimental data fitted well to the Langmuir model with a maximum adsorption capacity of  $126.6 \text{ mg g}^{-1}$ . Renita et al. (2019) [33] used de-oiled biomass (*Sargassum myriocystum*) as biosorbent for the removal of acid Fuchsin dye from wastewater. The linear regression analysis was done for equilibrium data and the Langmuir model showed good fit. Langmuir monolayer capacity of biosorbent for acid Fuchsin dye was  $9.9 \text{ mg g}^{-1}$ . Table 1 shows selected agricultural solid wastes as adsorbents used for dyes removal from aqueous solutions.

**Table 1.** Selected agricultural solid wastes adsorbents used for dyes removal from aqueous solutions

Dye	Adsorbent	Adsorption capacity ( $\text{mg g}^{-1}$ )	Reference
Methylene Blue	Sugar Beet Pulp	714.29	[26]
Rhodamine B	Raphia hookerie fruit epicarp	666.67	[28]
Fast Green FCF	Flower Gel	58.82	[29]
Methylene Blue	<i>Typha angustifolia</i>	106.757	[31]
Methylene Blue	<i>Typha latifolia</i>	126.6	[32]
Acid Fuchsin	de-oiled biomass ( <i>Sargassum myriocystum</i> )	9.9	[33]

#### 4. Activated carbons

Among the variety of adsorbents, activated carbon has been proven to be effective in the removal of pollutants from water [34]. Thus, research on the production of activated carbon from a renewable, low-cost indigenous agricultural waste has gained attention worldwide because of its low cost and highly abundant characteristics [35].

Mark Daniel et al. (2013) [36] studied the adsorption of Eriochrome Black T (EBT) from aqueous solution using rice hullbased activated carbon. The equilibrium data was evaluated using Langmuir,

Freundlich, Temkin and Dubinin–Radushkevich isotherm. The Freundlich model best describes the uptake of EBT dye, which implies that the adsorption of EBT dye onto rice hull activated carbon is heterogeneous. Maneerung et al. (2016) [37] used activated carbon prepared from carbon residue via physical activation as an adsorbent for adsorption of Rhodamine B. The equilibrium data were fitted into different adsorption isotherms and found to fit well with Langmuir model with a maximum monolayer adsorption capability of 189.83 mg g<sup>-1</sup>. Ait Ahsaine et al. (2018) [38] used high surface area activated carbon prepared from Almond shell agricultural biomass using potassium hydroxide as activating agent as an adsorbent for adsorption of Methylene Blue and Cristal Violet dyes. Isotherm data were modeled using Langmuir and Freundlich models. Langmuir isotherm model presented the best fit to experimental data suggesting homogeneous distribution of adsorption sites. The adsorbent demonstrated high monolayer adsorption capacity of 833.33 and 625 mg g<sup>-1</sup> for Methylene Blue and Crystal Violet, respectively. Bhomick et al. (2018) [39] described the synthesis of activated biocarbon from *Pinus kesiya* cone by ZnCl<sub>2</sub> activation and its efficacy in the removal of Alizarin Red S (ARS) dye. The adsorption isotherm was well defined by Langmuir model with a maximum adsorption capacity of 118.06 mg g<sup>-1</sup>. Boudechiche et al. (2019) [40] studied the adsorption of two cationic textile dyes namely Basic Yellow 28 (BY28) and Basic Red 46 (BR46) from synthetic water using a new activated carbon. The results indicate that the Langmuir model was the most appropriate for fitting the equilibrium data. The maximum adsorption capacities were found to be 424 and 307 mg g<sup>-1</sup> for BY28 and BR46 respectively at 20 °C and pH ~ 8. Daoud et al. (2019) [41] used the activated carbons prepared from *Phoenix dactylifera* rachis (PRAC) and *Ziziphus jujuba* stones (JSAC) using chemical activation by H<sub>3</sub>PO<sub>4</sub> for removal a commercial reactive dye BEZAKTIV Red S-Max (BRSM). The experimental equilibrium data were studied using Langmuir, Freundlich and Temkin models, and it was found that the Langmuir model described well the BRSM adsorption, showing a maximum adsorption capacity of BRSM onto PRAC and JSAC of 196.08 and 37.04 mg g<sup>-1</sup>, respectively. Table 2 shows selected activated carbon from agricultural solid wastes as adsorbents used for dyes removal from aqueous solutions.

Makrygianni *et al.* presented that various low-cost adsorbents derived from agricultural wastes have been investigated intensively for dye removal from contaminated wastewater [42]. Locally available agricultural wastes are easily converted to charcoals which can be used as activated carbons. Therefore, removal of dye contaminants from wastewaters using agricultural based activated carbon has offered promising results with maximum efficiency in the field of adsorption technology because they show outstanding removal capabilities for various class of dyes and could be used in place of commercial activated carbon [42-45].

**Table 2.** Selected activated carbons used for dyes removal from aqueous solutions

Dye	Adsorbent	Adsorption capacity (mg g <sup>-1</sup> )	Reference
Rhodamine B	Activated carbon prepared from carbon residue	189.83	[37]
Methylene Blue	Carbon prepared from Almond shell	833.33	[38]
Cristal Violet		625	
Alizarin Red S	Activated biocarbon from Pinus kesiya cone	118.06	[39]
Yellow 28	New activated carbon	424	[40]
Basic Red 46		307	
BEZAKTIV Red S-Max	<i>Phoenix dactylifera</i> rachis	196.08	[41]
	<i>Ziziphus jujuba</i> stones	37.04	

## Conclusion

This short review is devoted to the adsorption of dyes from aqueous solutions, which are chemical compounds that have been detected in the aquatic environment and belong to some of the most popular emerging pollutants that may cause serious environmental and human health problems.

The modelling of adsorption isotherms of dyes from aqueous solutions by various adsorbents has been reviewed. There are some conclusions from this short review as following:

- The current short review highlights the enormous potential of agricultural solid wastes to be used as low-cost adsorbent or as precursors for the synthesis of activated carbons for the adsorption of dyes.
- Literature also reveals that the equilibrium data fitted Langmuir isotherm in majority of cases and has successful application in many adsorption processes of monolayer adsorption.

Most of the reported studies are performed in the batch process; this gives a platform for the designing of the continuous flow systems with industrial applications.

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