Removal of Cresol Red by Adsorption Using Wastepaper

Mohamad Salman¹, Muslum Demir², Kuok Ho Daniel Tang³, Linh Thi Thuy Cao⁴, Seng Bunrith⁵, Tse-Wei Chen⁶, Noura M. Darwish⁷, Bandar M. AlMunqedhi⁸, Tony Hadibarata⁹*

¹Perak State Agricultural Development Corporation, 30250 Perak, Ipoh, Malaysia. 
²Department of Chemical Engineering, Osmaniye Korkut Ata University, Osmaniye 80000, Turkey. 
³Environmental Science Program, Division of Science and Technology, BNU-HKBU United International College, 2000 Jintong Road, Tangjiawan, Zhuhai GD 519087, China. 
⁴Program of Biotechnology, Graduate School of Integrated Sciences for Life, Hiroshima University, 1-3-1, Kagamiyama, Higashihiroshima, Hiroshima 739-8530, Japan. 
⁵Faculty of Hydrology and Water Resource Engineering, Institute of Technology Cambodia, PO BOX 86, Russian Federation Bvld, Phnom Penh, Cambodia. 
⁶Department of Materials, Imperial College London, London, SW7 2AZ, United Kingdom. 
⁷College of Science, Ai Shams University, Cairo, Egypt. 
⁸Department of Botany and Microbiology, College of Science, King Saud University, P.O. 2455, Riyadh 11451, Saudi Arabia. 
⁹Environmental Engineering Program, Curtin University Malaysia, CDT250, Miri, Malaysia 

*Correspondence: hadibarata@curtin.edu.my

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ABSTRACT: The utilization of less expensive and more effective adsorbents derived from a variety of basic materials has been investigated. The research aimed to investigate the feasibility of employing waste paper as the adsorbent to remove the cresol red (CR) dye from wastewater through adsorption mechanism. Langmuir, Jovanovic, and Freundlich model were observed for isotherms models, while pseudo-first-order and pseudo-second-order were examined for kinetic models. The results indicated that increasing the adsorbent dose and contact time gave no significant effect to adsorption capacity while adsorption capacity increased with the increasing of pH until it reached a maximum at pH 8, and raising the starting dye concentration leads in a significant increase in adsorption capacity (16.7 mg/g). When the experimental adsorption isotherms and kinetic were fitted using the Freundlich models and pseudo-second-order model, it was discovered that those models were more accurately represented by the data, as indicated by a high correlation coefficient (R²) of 0.974 and 0.963.

KEYWORDS: Recycling waste papers; decolourization; weight; adsorption; cresol red dye

1. Introduction

Aquatic pollution has become a serious ecological issue all over the world, and it is generally produced by the addition of chemical substances in exact concentrations, whether from natural or man-made sources [1-3]. The dyeing process are one of the key sources of wastewater generation. Various synthetic dyes were bonded with a substance that will lend color to them, and due to their aromatic structures, it make them biochemically stable. Wastewater from numerous industrial processes, such as dyestuff, textiles, plastics, and printing, contains several kinds of synthetic dyes, which are chemicals that will bring color to the material [4,5]. Because
of its massive production and extensive usage, it might be viewed as a substantial source of environmental contamination as well as a serious health problem. Discharging even a modest amount of colorful wastewater can influence the appearance of receiving streams, but it can also disrupt aquatic life and food webs due to dyes' carcinogenic and mutagenic effects [6,7]. Dye removal from wastewater can be treated via conventional methods as flocculation, filtration, and adsorption. Adsorption technique is one of the most successful and least expensive technologies for generating high-quality water [8-11], and it is regularly utilized. The usage of expensive adsorbents, on the other hand, has been highlighted as a potential limiting factor [12, 13]. The utilization of less expensive and more effective adsorbents derived from a variety of basic materials, ranging from trash to dye removal, has been demonstrated [14]. Low-cost adsorbents for the removal of colors from waste water have been investigated by researchers, including agricultural waste [15]. This great affinity for dyes is owing to the presence of cellulose in these affordable adsorbents, which is present in modest concentrations in these adsorbents. Everyday, a substantial volume of paper waste in a variety of forms is generated. A huge percentage of this cellulosic material is burned to create heat, with just a small portion of it being recycled for use in the pulp and paper sectors. Put together with the sorption ability of cellulosic material, waste paper represents a potentially green supply that might be exploited as a low-cost dye removal adsorbent in a range of applications [16]. The objective of the study was to investigate the ability of waste paper for the adsorption of CR.

2. Materials and Methods

2.1. Dye and adsorbent

The CR dye was utilized in this experiment were from the laboratory stock supplied by Sigma Aldrich (USA). The characteristic of CR dye is summarized in Table 1. Waste paper (A4 paper, newspapers and manila card) was used as adsorbent in this experiment. All waste paper was soaked in water for 3-5 min in order to easily blended, then form into small balls of 1cm in size. The waste paper was dried at room temperature for 24 h prior to use.

<table>
<thead>
<tr>
<th>Item</th>
<th>Dye</th>
</tr>
</thead>
<tbody>
<tr>
<td>Structure</td>
<td>![Structure Diagram]</td>
</tr>
<tr>
<td>Chemical name</td>
<td>Cresol Red</td>
</tr>
<tr>
<td>Chemical formula</td>
<td>C11H17NaO5S</td>
</tr>
<tr>
<td>Appearance</td>
<td>Brown powder</td>
</tr>
<tr>
<td>Molecular mass</td>
<td>382.43 g/mol</td>
</tr>
<tr>
<td>Melting point</td>
<td>250°C</td>
</tr>
<tr>
<td>Absorption, λmax</td>
<td>425nm</td>
</tr>
<tr>
<td>Water solubility</td>
<td>Soluble in water and ethanol</td>
</tr>
</tbody>
</table>

2.2. Batch study

The studies were conducted in (300) mL Erlenmeyer flasks containing 2g of the adsorbent and 50mL of CR solutions. Various experimental parameters were summarized in Table 2. After the experiment, the waste paper were separated by using filter papers and the adsorption
process was analyzed by UV-visible spectrophotometer (UV-160 A Shimadzu) at 367 nm. The following equation was used to calculate the adsorption capacity of the adsorbent [16]:

\[
\text{Adsorption capacity } \left( \frac{mg}{g} \right) = \frac{C_0 - C_t}{M} \times V
\]

**Table 2: Investigated factors in the CR adsorption**

<table>
<thead>
<tr>
<th>Factors</th>
<th>pH</th>
<th>Adsorbent mass (g)</th>
<th>CR Concentration (mg/L)</th>
<th>Contact Time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Effect of pH</td>
<td>4–8</td>
<td>1</td>
<td>240</td>
<td>1</td>
</tr>
<tr>
<td>Effect of adsorbent mass</td>
<td>7</td>
<td>1 - 2.5</td>
<td>240</td>
<td>1</td>
</tr>
<tr>
<td>Effect of CR concentration</td>
<td>7</td>
<td>1</td>
<td>10 - 50</td>
<td>1 - 5</td>
</tr>
<tr>
<td>Effect of contact time</td>
<td>7</td>
<td>1</td>
<td>240</td>
<td>1</td>
</tr>
</tbody>
</table>

2.3. Adsorption isotherms and kinetic studies

Adsorption is typically represented using an isotherm, which describes the distribution of adsorbed molecules between the liquid and solid phases when the adsorption process reaches equilibrium [17]. Adsorption isotherm and kinetics models are mathematical equations used to determine the efficiency of adsorbents that interact with dye solutions by maximising their surface properties, adsorption capacity, and effectiveness as an adsorption system. Additionally, using kinetics models, the effect of contact time in the range of 1 to 5 h on the rate of dye removal was determined. Additionally, three common adsorption models were chosen for this study: Langmuir, Jovanovic, and Freundlich isotherms, while pseudo-first-order and pseudo-second-order kinetics were examined. The equation of the isotherm and kinetic model was shown in Table 3.

**Table 3. Isotherm and kinetic model equation**

<table>
<thead>
<tr>
<th>Model</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isotherm model:</td>
<td></td>
</tr>
<tr>
<td>Langmuir</td>
<td>( \frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} )</td>
</tr>
<tr>
<td>Freundlich</td>
<td>( \log q_e = \log K_F + \frac{1}{n} \log C_e )</td>
</tr>
<tr>
<td>Jovanovic</td>
<td>( \ln q_e = \ln q_m - K_J C_e )</td>
</tr>
<tr>
<td>Kinetic model:</td>
<td></td>
</tr>
<tr>
<td>Pseudo-first-order</td>
<td>( \ln(q_e - q_t) = \ln q_e - K_F t )</td>
</tr>
<tr>
<td>Pseudo-second-order</td>
<td>( t = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} )</td>
</tr>
</tbody>
</table>

3. Results and Discussion

3.1. Adsorption capacity

The effects of pH on the adsorption capacity is shown in Figure 1A. The adsorption capacity was gradually increased with the increasing pH until it reached a maximum value at pH 8, and low pH was shown to be unfavorable. At pH values of 8, the highest adsorption capacity (16.7 mg/g) from solution were detected, respectively. Due to the fact that the cellulose in the paper
has a negative surface charge over a wide pH range, a significant electrostatic attraction exists between the adsorbent and CR, resulting in adsorption [17]. When the pH of a solution is elevated, the positive charge at the solution interface increases, resulting in the appearance of a positively charged adsorbent surface [16]. Figure 1B illustrates the removal of CR by waste paper at various adsorbent masses (1-2.5 g). The results indicated that increasing the adsorbent mass gave no significant effect to adsorption capacity (in the range of 10.3-11.7 mg/g). The stagnant of adsorption capacity is due to no significant increase in adsorbent surface area and availability of more adsorption site area. As a result, the amount of dye that adsorbs stable [18].

The effects of dye concentration on the CR removal by paper waste are depicted in Figure 1C. The results indicate that raising the starting dye concentration from (10 to 40) mg/L leads in a significant increase in adsorption capacity (6.10 mg/g to 16.7 mg/g ). Increased dye concentration has a minor effect due to the saturation of vacant sites on the adsorbent surface at higher dye concentrations [19]. In other words, as the pollutant content in the aquatic environment decreases, the adsorbate molecules have a greater chance of reacting with the accessible active sites on paper waste, increasing the adsorption rate [20]. The adsorption capacity of waste paper on CR removal at different contact times (1-5 h) is shown in Figure 1D. The results indicated that contact time gave no significant effect on adsorption capacity. The highest adsorption capacity for CR was calculated to be 12.7 mg/g after a 5-h contact time, while the lowest adsorption capacity was 10.1 mg/g after a 3-h contact time. This demonstrated that when the equilibrium state was attained, the maximal availability of the adsorbents connected to the dye particles at the binding sites was steady [9].

![Figure 1](image_url)

**Figure 1.** Adsorption capacity of waste paper on various factors: pH (A), adsorbent mass (B), CR concentration (C), contact time (D).

3.2. Adsorption isotherm and kinetics

The isotherm parameters for CR adsorption on waste paper adsorbent are shown in Figures 2. The results indicate that while both the Freundlich equations suit the experimental equilibrium data for adsorption isotherms, the Freundlich isotherm model provides a more reasonable fit than the Langmuir and Jovanovic isotherm model. This can be demonstrated by examining the coefficients of determination for three models, specifically the $R^2$ straight line. The Freundlich
isotherms for CR adsorption had R² values of 0.9736, which were close to 1 compared to the Langmuir and Jovanovic isotherms. When the 1/n value is less than one, it indicates a function of the absorbent material's strength; when the value approaches zero, it becomes heterogeneous; and when the value exceeds one, it indicates a cooperative adsorption process [21]. Freundlich isotherms of waste paper for CR exceeded one, indicating cooperative adsorption. Separation factor (RL) is smaller than 1, indicating that the adsorption is favorable. The best fitted adsorption isotherm will differ from previous research because the composition of adsorbents reacting with different dyes will affect the outcome. This is also consistent with Freundlich isotherm equilibrium findings, which suggest multilayer coverage of CR on the surface of paper waste [19]. Additionally, it is assumed that the energy adsorbed on the adsorbent is not uniform [21,22].

The linear plot was displayed against a graph of ln (qe-qt) for pseudo-first-order, and against a graph of t/qt against t for pseudo-second-order. The pseudo-first-order and pseudo-second-order kinetics parameters were derived by fitting the presented curve to a straight line equation. Pseudo-second order was shown to be a better fit for waste paper than Pseudo-first order. Pseudo-second-order (R²) values were respectively 0.963 and 0.432, however pseudo-first-order values were only 0.432 (Table 4). Thus, it can be concluded that pseudo-second-order adsorption kinetics is the best fit for the removal of CR using waste paper as an adsorbent.

<table>
<thead>
<tr>
<th>Adsorption Kinetics</th>
<th>Adsorption constant</th>
<th>Cresol Red</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pseudo-1st Order</td>
<td>qe calculated</td>
<td>1.18341</td>
</tr>
<tr>
<td></td>
<td>k₁</td>
<td>0.0095</td>
</tr>
<tr>
<td></td>
<td>R²</td>
<td>0.432</td>
</tr>
<tr>
<td>Pseudo-2nd Order</td>
<td>qe calculated</td>
<td>12.70648</td>
</tr>
<tr>
<td></td>
<td>k₂</td>
<td>0.149791</td>
</tr>
<tr>
<td></td>
<td>R²</td>
<td>0.963</td>
</tr>
</tbody>
</table>

4. Conclusions
Waste paper possessed the potential to act as an adsorbent for CR. Numerous factors affecting the outcome, such as pH, dosage, initial concentration and contact time were investigated. The highest adsorption capacity of waste paper was 6.7 mg/g. The Freundlich isotherm model and pseudo-second-order model adequately described the adsorption results, with $R^2$ values of 0.9736 and 0.963.

**Abbreviation**

- $M$ : mass of adsorbent (g)
- $V$ : dye solution volume (mL)
- $C_0$ : concentration of the dye solution (mg/L)
- $C_t$ : dye solution concentration after adsorption process (mg/L)
- $C_e$ : concentration of adsorbate at equilibrium (mg/g)
- $q_e$ : equilibrium quantity of the adsorbate
- $q_m$ : maximum adsorption capacity (mg/g)
- $q_t$ : maximum uptake of adsorbate from plot ln $q_e$ versus $C_e$
- $K_L$ : Langmuir rate constant (mg/g)
- $K_F$ : Adsorption capacity (L/mg),
- $1/n$ : adsorption intensity
- $K_J$ : Jovanovic constant
- $k_1$ : pseudo-first-order rate constant
- $k_2$ : pseudo-second-order rate constant
- $t$ : contact time with adsorbent (min)
- $RL$ : separation factor

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**Competing Interest**

There is no competing interest to declare.

**References**


