

Dyes Removal from Wastewater Using Agricultural Waste

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ABSTRACT

Capability of Rice Husk (RH) on the removal of four types of dyes pollutant from wastewater which were methylene blue, Congo red, brilliant green and crystal violet using different design parameters by adsorption process is focus on. The design parameters studied to adsorb above four dyes using RH as an adsorbent material were initial concentration of dye, absorbance material packing height which was RH, pH of dye solution feed inlet, treatment time, feed flow rate and feed temperature, these parameters were varied from (1-100) mg/l, (10-100) cm, (1-8), (1-60) min, (5-100) ml/min and (20-55°C) respectively. Results show that the higher removal efficiency was (95.81, 93.44, 96.62 and 96.35) % for brilliant green, Congo red, crystal violet and methylene blue dyes respectively from aquatic solution and these efficiencies were decreased with increasing of initial concentration and flow rate while the removal efficiencies increased with increasing absorbance material bed height and feeding temperature. The removal efficiency was increased with increasing pH of solution for methylene blue, brilliant green and crystal violet dyes and decreased with increasing pH of solution for Congo red dye. Statistical model is achieved to find an expression combined all operating parameters with the removal efficiency for dyes used in this paper in a general equation. By this way we can possess different benefits which are: remove the toxic dyes contaminated the water, get rid of agricultural waste RH.

Key words: rice husk, dyes, aqueous solutions, adsorption and wastewater

Introduction

Extensive use of synthetic dyestuffs in a number of industrial processes such as textile, paper, plastics, food, cosmetics, and leather has brought about intractable environmental problems. Even a thimbleful of dye in water is highly visible and disgusting. The presence of various dyes also causes damage to living beings in water by reducing light penetration and inhibition of photosynthesis [1]. The textile dyeing units release large quantities of dyes in their effluents [2]. Over 70,000 tons of approximately 10,000 types of dyes and pigments are produced annually worldwide, of which, about 20–30% are wasted in industrial effluents during the textile dyeing and finishing processes [3]. In addition, the stability of most dye molecules under the condition of light, heat and chemicals leads to the fact that the dyeing effluents are difficult to degrade [4,5]. These dyes not only affect the aesthetic value of the receiving water body but also pose a major problem due to their resistance to chemical and biological degradation [6]. Many reactive azo dyes, constituting the largest dye groups decompose to potential carcinogenic aromatic amines under anaerobic conditions [7,8]. Economic, effective and

feasible methods for comprehensive treatment of dyeing industrial effluents are therefore paid much more attention, owing to the increased environmental stress and consciousness from people. Processing methods on dye removal are classified as coagulation, chemical oxidation, flocculation, hyper filtration, biological treatment and adsorption. Existing conventional technologies have suffered several drawbacks due to their high costs and low regeneration. Adsorption has been found to be superior to other techniques for treating wastewater: it is low-cost, highly efficient, simple, easy to perform and insensitive to toxic substances [9,10]. Adsorption onto activated carbon has been widely used in actual effluent treatment as a highly effective process despite its generous use in water and wastewater industries, activated carbon remains an expensive material. This has led to search for low-cost adsorbent materials with potential to replace commercial activated carbons. However, the application of this material is limited due to high cost and the difficulty in regeneration [11,12]. Therefore, studies on dye removal have been focusing on searching for abundant and low-cost adsorbents. Some agricultural wastes that have been converted to activated carbon for use in dye adsorption are olive

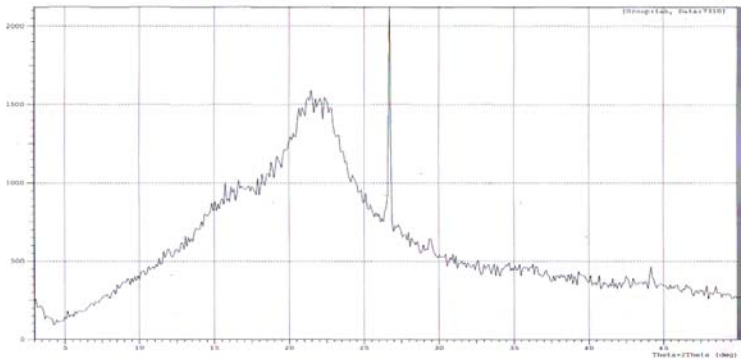
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kernels [13], *Euphorbia rigida* [14], bamboo shoot [15] and jute fiber [16] for methylene blue removal, coconut flower for reactive red adsorption [17], bamboo dust, coconut shell, groundnut shell, rice husk and straw for removal of Congo red and silk cotton hull for reactive blue removal [18]. For instance, agricultural by-products such as neem sawdust [19], palm kernel fiber [20], apple pomace [1] rice husk [21,22], tree fern [23], lemon peel [24], Bokbunja seed [25] and pineapple leaf [26] have been widely studied for dye removal. The poplar leaf powders have been reported to have the potential as a novel adsorbent for heavy metals removal [27,28]. The aim of this investigation is to study the possibility of using rice husk for removing dyes from aqueous solution, and benefit from the rice husk residue in eco-friendly method.

Materials and Methods

Table1: Characterization properties of Iraqi rice husk

Chemical Composition		XRD of Iraqi Rice Husk
Compound	Composition wt %	
SiO ₂	90.7	
Al ₂ O ₃	0.13	
Fe ₂ O ₃	0.06	
TiO ₂	0.015	
CaO	0.61	
MgO	0.25	
Na ₂ O	0.09	
K ₂ O	2.64	
P ₂ O ₅	0.73	
LOI	4.71	
S.A (m ² /g)	17.5	

Stock solutions:

In order to avoid interference with other elements in wastewater, the experiments in this study were carried out using simulated synthetic aqueous solution (SSAS) of different dyes concentrations. 1000 mg/l stock solution of dyes was prepared by dissolving known weight of four types of dyes which were methylene blue, Congo red, brilliant green and crystal violet (each one alone) in one liter of double distilled water, all solutions using in the experiments were prepared by diluting the stock solution with double distilled water to the desired concentrations for the experimental work of this investigation. The dyes concentrations were measured using spectrophotometer thermo – genesys 10 UV, USA.

Sorption unit:

Fixed bed column of continuous mode experiments were conducted in order to test four types of dyes removal by treated SSAS of above dyes each one alone at desired concentration with the various bed heights of the adsorbent media RH using different flow rates of SSAS of four types of dyes at

Rice husk (adsorbent media):

Rice husk was collected from Al-Shanafia fields for rice in the Southern of Iraq. The rice husk was washed three times with doubled distilled water. Excess distilled water was used to remove the soluble materials present in the rice husk bringing from the field, boiled to remove colour and other fine impurities may be found in the rice husk, and then dried at 105°C for 24 hours and the adsorbent thus processed was used in its original piece size. The surface area of RH was measured by BET (Brunauer – Emmett – Teller nitrogen adsorption technique). Characteristics of RH were presented in **Table 1**. When the RH was heated in an oven, most of the water had been removed from the rice husk while the second major mass loss of about 45-65% was attributed to the breakdown of cellulose constituent char, which is a carbonaceous residue.

various pH. The pH value was adjusted using 0.1 N NaOH and 0.1 N HCl solutions. A schematic representation of the sorption unit is shown in **Figure1** where the flow direction is downward by gravity. The sorption unit consists of two glass container of SSAS of dyes one for inlet and another for outlet each of (1 liter) capacity. Glass column has 2.54 cm ID and 150 cm height. The sorption column packed with adsorbent media to a height of (10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 cm) supported from the top and the bottom by glass hollow cylinder layer, each cylinder have (0.5 cm ID, 0.1 cm thickness and 1 cm long). Before starting the runs, the packed bed sorption column was rinsed by double distilled water down flow through the column. The RH is packed in the column to the desired depth, and fed to it as slurry by mixing the media RH with distilled water in order to avoid the formation of air bubbles inside the media. After the packed bed sorption column was accommodation and putting the required amount of adsorbent media, the adsorption process started by allowing the dyes SSAS of required concentration and pH down flow through the sorption column from inlet container by gravity at a precise flow rate in experiment which is

adjusted by the valve as shown in **Figure 1**. To determination the best operational conditions, the experiments were carried out at a temperature between (20 –55°C), various pH values which are (1–8) and initial feed concentrations of SSAS of different dyes which are between (1–100) mg/l each one alone and at different flow rates which are

between (5–100) ml/min for dyes initial feed concentration. Outlet samples after treatment in each experiment were collected every 10 minutes from the bottom of packed column and the unadsorbed concentration of dyes in SSAS was analyzed by spectrophotometer.

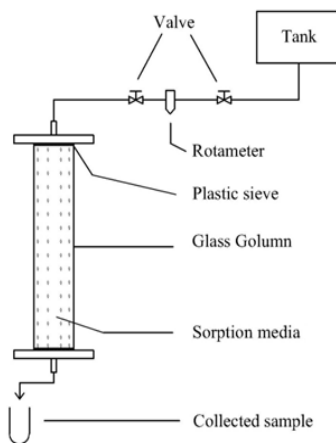


Fig. 1: The experimental setup for adsorption unit

Result and Discussion

The ability of RH to remove dyes from SSAS in fixed bed column of continuous mode at various parameters which are pH's of SSAS of dyes (pH), height bed of adsorbent media RH (h), flow rates of SSAS (F), SSAS temperature (T_{feed}) and time of treatment (t) was investigated. The experiments were achieved by varying all above parameters for different initial concentrations (C_0) of SSAS of dyes. Thus, the results obtained are explained below.

Effect of Initial Concentration:

The results showed that using adsorbent material, the percent removal of dyes was decreased when the initial concentration (C_0) of SSAS of dyes was increased at constant other variables as shown in **Figure 2**. This can be explained by the fact that the initial concentration of dyes had a restricted effect on dyes removal capacity; simultaneously the adsorbent media had a limited number of active sites, which would have become saturated at a certain concentration. This was lead to the increase in the number of dyes molecules competing for the available functions groups on the surface of adsorbent material. Since the solution of lower concentration has a small amount of dyes than the solution of higher concentration of it, so the percent removal was decreased with increasing initial concentration of dyes. For adsorbent media, higher percent removal were (95.81, 93.44, 96.62 and 96.35) % for brilliant green, Congo red, crystal violet and methylene blue dyes respectively at initial dyes concentration of 1 mg/l, so adsorbent

material was found to be efficient to dyes removal from SSAS and wastewater.

Effect of pH:

The results showed that using adsorbent material, the percent removal of Congo red was decreased when the pH of SSAS was increased at constant other variables, while the percent removal of methylene blue, brilliant green and crystal violet dyes were increased when the pH of SSAS was increased at constant other variables as shown in **Figure 3**. It is well recognized that the pH of the aqueous solution is an important parameter in affecting adsorption of heavy metal ions [29]. High adsorption of Congo red at low pH can be explained in both terms; the species of Congo red and the adsorbent surface. For this case, at low pH, i.e. acidic conditions, the surface of the adsorbent (RH) becomes highly protonated and favours adsorb of above group of Congo red dye in the anionic form. With increasing the pH of SSAS, the degree of protonation of the RH surface reduces gradually and hence adsorption is decreased [30].

Furthermore, as pH increases there is competition between hydroxide ion (OH^-) and species of Congo red, the former being the dominant species at higher pH values. The net positive surface potential of sorbent media decreases, resulting in a reduction the electrostatic attraction between the (*sorbent*) Congo red species and the (*sorbate*) adsorbent material surface (RH), with a consequent reduced sorption capacity which ultimately leads to decrease in percentage adsorption of Congo red dye [11]. In the other hand, the adsorption of methylene

blue, brilliant green and crystal violet dyes (each one alone) can be explained by ion-exchange mechanism of sorption in which the important role is played by functional groups that have cation exchange properties. For this case at lower pH values, dyes removal was inhibited, possibly as a result of the competition between hydrogen and dyes molecules on the sorption sites, with an apparent preponderance of hydrogen ions, which restricts the approach of metal cations as in consequence of the repulsive force. As the pH increased, the ligand functional groups in adsorbent media (RH) would be exposed, increasing the negative charge density on the adsorbent material surface, increasing the attraction of dyes molecules with positive charge and allowing the sorption onto adsorbent material surface.

Effect of Adsorbent Media Bed Height:

The results elucidated that when the adsorbent media bed height was increased, the percent removal of dyes was increased too at constant other variables as shown in **Figure 4**. The increased of bed height (*h*) meaning increased in the amount of adsorbent media RH, thus increasing the surface area of adsorbent material, hence increased the number of active sites in the adsorbent material surface i.e. increased the availability of binding sites for adsorption and consequently increase dyes removal capacity on RH. This lead to increase the ability of adsorbent media to adsorb greater amount of dyes from SSAS at different initial concentrations and ultimately the percent removal of dyes increased.

Effect of Flow Rate:

The results illustrated that when the flow rate of SSAS of dyes was increased, the percent removal of dyes was decreased at constant other variables as shown in **Figure 5**. This may be due to the fact that when the flow of SSAS of dyes increasing, the velocity of solution in the column packed with the adsorbent media RH was increasing too, so the solution spend shorter time than that spend in the column while at low flow rate, the SSAS of dyes resides in the column for a longer time, and therefore undergoes more treatment with the adsorbent media,

Conclusion:

Conclusions point demonstrate as below:

1. RH showed a good ability to remove four types of dyes which are methylene blue, Congo red, brilliant green and crystal violet from SSAS using fixed bed adsorption unit. So, it could be recommended for removal of dyes from wastewater in Iraq instead of other material because it is valid, cheaper, economical, easy and simplicity for using, and has a high ability to adsorb dyes, can be used

thus the adsorbent media uptake low amount of dyes from SSAS of dyes for high flow rate, therefore the percent removal of dyes was decreased when the flow rate was increased.

Effect of Feed Temperature:

The results demonstrated that when the temperature of feed which was SSAS of dyes was increased, the percent removal of dyes was increased too at constant other variables as shown in **Figure 6**. The effect of temperature is fairly common and increasing the mobility of the acidic ion. Furthermore, increasing temperatures may produce a swelling effect within the internal structure of the adsorbent media enabling dyes ions to penetrate further. It was indicated that dyes adsorption capacity increased with increasing feed temperature from 5 to 55°C. This effect may be due to the fact that at higher temperature an increase in active sites occurs due to bond rupture.

Effect of Treatment Time:

The results demonstrated that when the treatment time of SSAS of dyes increased the percent removal of dyes increased at constant other variables as shown in **Figure 7**. This may be due to the fact that when the time of treatment of SSAS of dyes increasing and the velocity of SSAS in the column packed with the adsorbent material was remaining constant, the solution spend longer time than that spend it when the time of treatment decreased, so the adsorbent material uptake more amount of dyes from SSAS, therefore the percent removal of dyes from SSAS was increased.

Statistical Model:

A statistical model was carried out on the experimental results obtained from this study. Regression Analysis and π Theorem was adopted to maintain a relation between the percent removal of dyes and the feed temperature, flow rate, pressure, pH of feed solution, initial concentration of dyes, adsorbent media RH bed height, treatment time and column diameter. These relations are shown in equations below.

several times by costly regeneration method and can be used finally in another benefit uses.

2. Maximum removal of dyes was (95.81, 93.44, 96.62 and 96.35) % for brilliant green, Congo red, crystal violet and methylene blue dyes respectively at initial dyes concentration of 1 mg/l.

3. The percentage removal of dyes was increased with decreeing flow rate of SSAS, and initial concentration of dyes while the percentage removal was increasing with increasing of treatment time and the height of adsorbent material RH. The percentage removal was increased with increasing

the pH of SSAS of methylene blue, brilliant green and crystal violet dyes while decreased with increasing the pH of , Congo red dyes

Table 2: Statistical equations

Dye	Equation	R^2
Brilliant Green	$\%R = 1.6831 \times 10^{-3} \left(\frac{T_f \cdot P \cdot h_b \cdot C_{P_{sol}} \cdot t}{F \cdot d \cdot C_o \cdot g} \right)^{0.127} (pH)^{0.044}$	0.993
Congo Red	$\%R = 3.2477 \times 10^{-3} \left(\frac{T_f \cdot P \cdot h_b \cdot C_{P_{sol}} \cdot t}{F \cdot d \cdot C_o \cdot g} \right)^{0.115} \left(\frac{1}{pH} \right)^{0.062}$	0.985
Crystal Violent	$\%R = 6.2079 \times 10^{-5} \left(\frac{T_f \cdot P \cdot h_b \cdot C_{P_{sol}} \cdot t}{F \cdot d \cdot C_o \cdot g} \right)^{0.195} (pH)^{0.025}$	0.991
Methylene Blue	$\%R = 4.7779 \times 10^{-4} \left(\frac{T_f \cdot P \cdot h_b \cdot C_{P_{sol}} \cdot t}{F \cdot d \cdot C_o \cdot g} \right)^{0.154} (pH)^{0.013}$	0.989

where
 $\%R$ Percent Removal of Dye from SSAS
 T_f Feed Temperature, (K)
 P Pressure, (Pa)
 h_b Adsorbent Material Bed Height, (m)
 C_{P_s} Heat Capacity of Aqueous Solution, (J/g. K)
 F Aqueous Solution Flow Rate, (m³/s)
 d Internal Diameter of Sorption Column, (m)
 C_o Initial Concentration of Dyes, (g/m³)
 t Treatment Time, (s)
 g Acceleration of Gravity, (m/s²)

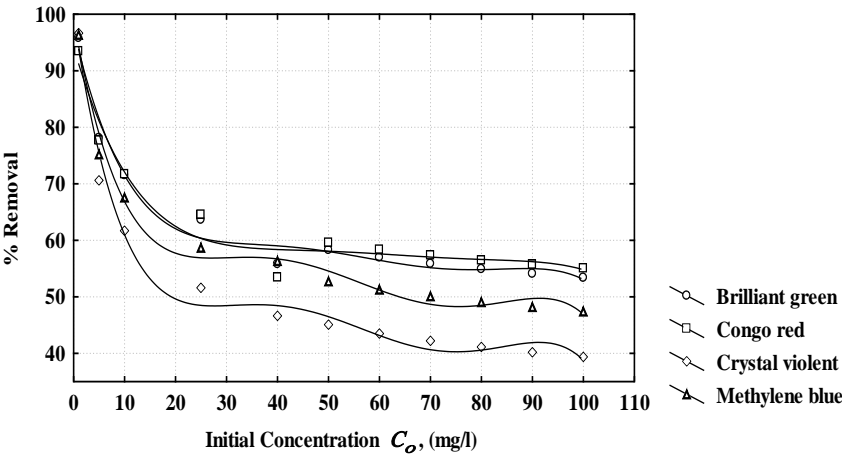


Fig. 2: Effect of initial concentration (C_o) on the percent removal of dyes @ $T_f=55^\circ\text{C}$, $h_b = 1$ m, $pH=1$, $t=60$ min. and $F=5$ ml/min.

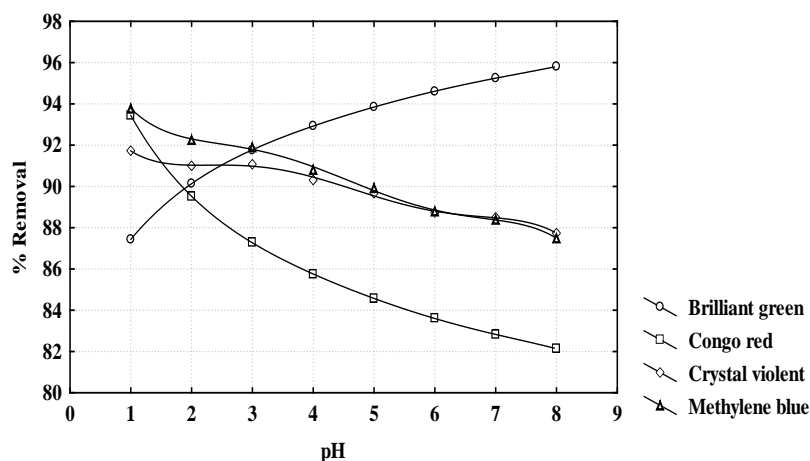


Fig. 3: Effect of pH on the percent removal of dyes @ $C_o = 1 \text{ mg/l}$, $T_f = 55^\circ\text{C}$, $h_b = 1 \text{ m}$, $t = 60 \text{ min.}$ and $F = 5 \text{ ml/min.}$

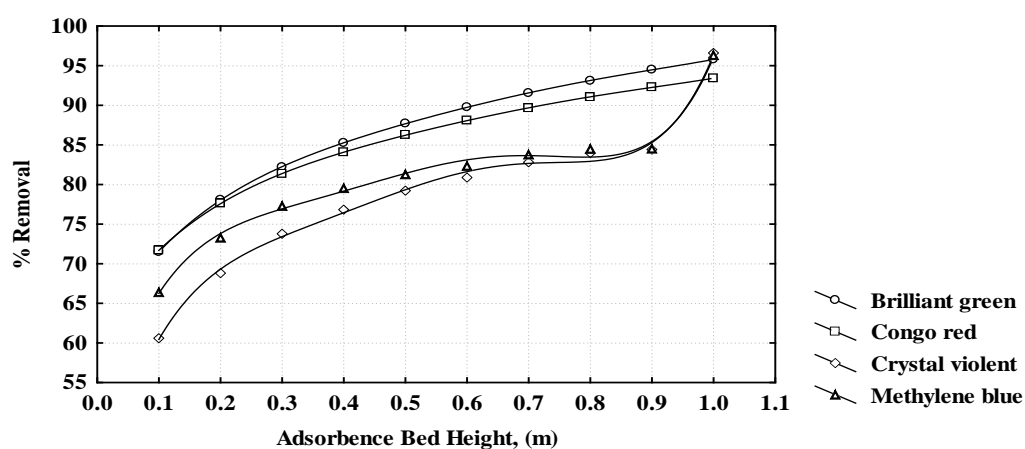


Fig. 4: Effect of adsorbent media bed height (h_b) on the percent removal dyes @ $C_o = 1 \text{ mg/l}$, $pH = 1$, $T_f = 55^\circ\text{C}$, $t = 60 \text{ min.}$ and $F = 5 \text{ ml/min.}$

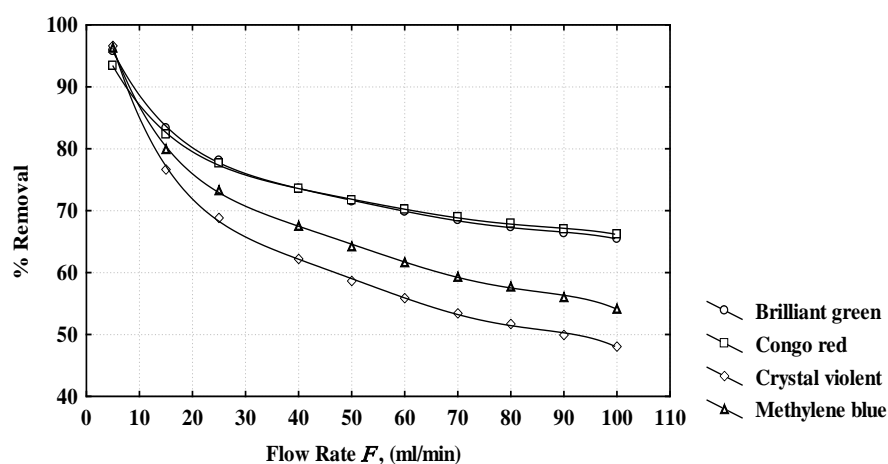


Fig. 5: Effect of aqueous solution flow rate (F) on the percent removal of dyes @ $C_o = 1 \text{ mg/l}$, $pH = 1$, $T_f = 55^\circ\text{C}$, $h_b = 1 \text{ m}$ and $t = 60 \text{ min.}$

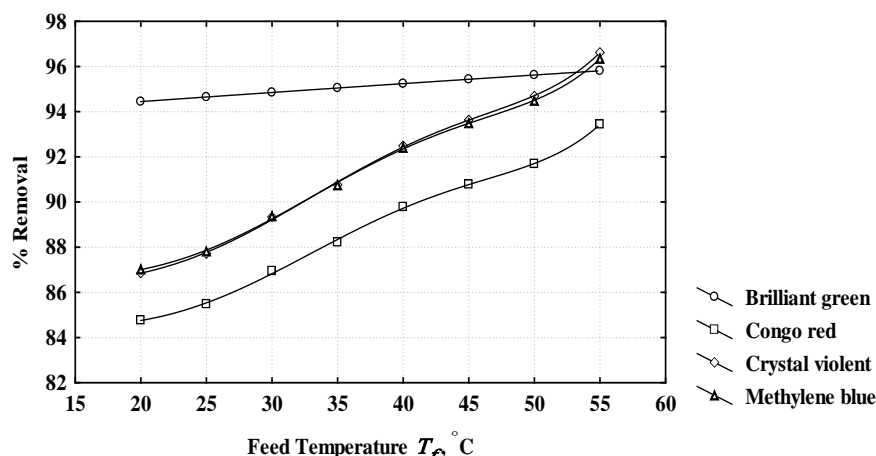


Fig. 6: Effect of feed temperature (T_f) on the percent removal of dyes @ $C_o = 1$ mg/l, $pH=1$, $h_b = 1$ m, $t=60$ min. and $F=5$ ml/min.

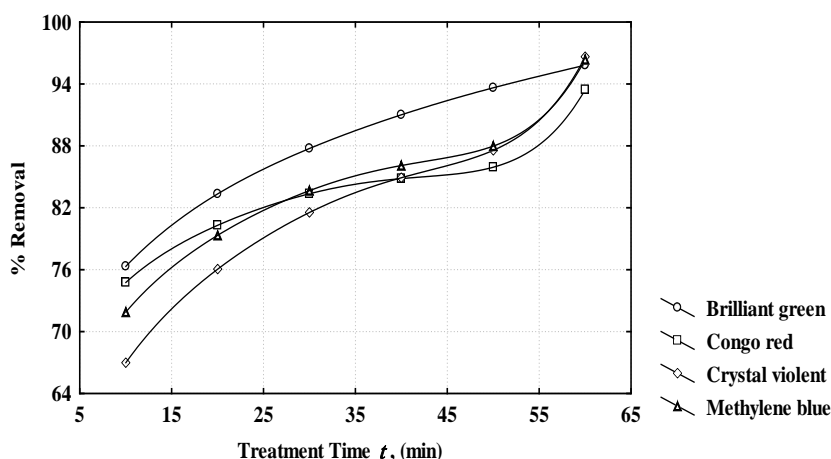


Fig. 7: Effect of treatment time (t) on the percent removal of dyes @ $C_o = 1$ mg/l, $T_f=55^\circ\text{C}$, $pH=1$, $h_b = 1$ m, and $F=5$ ml/min.

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