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Textile dye removal from aqueous solution by using peanut and pistachio shells

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Abstract: The use of peanut and pistachio shells as an adsorbent for the removal of Brillant Blue and K-RED 198, Methylene Orange, and Methylene Blue was investigated. The commonly used isotherm models were applied for data obtained from further batch studies. Dye removal capacity is as follows 65% for Brillant Blue, 73 % for KRED 198. Methylene Orange and Methylene Blue were removed poorly for peanut and pistachio shell. Freundlich isotherm model were found to be the best fitted one and based on Freundlich isotherm model adsorption capacities were 4.58 mg/g for Brillant Blue and 4.33 mg/g for K-RED 198 at peanut shells and 4.04 mg/g for Brillant Blue and 4.64 mg/g for K-RED 198 at pistachio shells. Kinetic examinations were also carried out for two dyes tested and it was found that adsorption kinetic was best described by pseudo first-order kinetic model.
Keyword: Textile dye, removal, peanut and pistachio shells, kinetic, isotherm

INTRODUCTION

Dyestuffs, chemicals and water are mostly used textile, plastic, leather and cosmetic industry. Textile is the main industry using these components and producing large quantity of coloured wastewater [1]. Approximately 100 tones dyes are discharged in rivers and lake without purification and that result in carcinogenic and toxic effect on human life and aquatic life [2]. Some of dye resits for chemical degradation in aquatic solution due to their steady-state structures [3]. Dye is very visible even at very low residuals in receiving body. It is crucial to reduce the residual concentration limits [4].

Some purification methods such as biological, oxidation, electrochemical, photochemical degradation and adsorption, coagulation/flocculation, ion exchange have been describe for removal of residual from aquatic solution [5-7]. Dye structures and concentration is very important to selection of removal methods [8]. Most of them are expensive and require high-technology [9]. However, adsorption process is technical alternative of removal the dye from wastewater due to easy design and operation, cost-efficient [10]. Economic, renewable and locally available agricultural residues such as, pine cone, grapefruit peel, canola hull, peanut hull, princess tree leaf, pistachio shells and red pine sawdust, soybean hulls, rice husk [11-14], are widely used for dye removal from aqueous solution as an adsorbent.

In this study, the adsorption capacity of peanut and pistachio shells was evaluated to remove dyes from water and also effects of pH, adsorbent dosage and contact time on the adsorption were investigated. The commonly used isotherm models were applied for data obtained from further batch studies.

MATERIAL AND METHOD

Materials

Brillant Blue and K-RED 198, Methylene orange, and Methylene Blue were chosen as a dyestuff to removal of wastewater. The deionised water was used for preparation of dye stock solution of 25 g/L. The pH value of the working solutions was adjusted to the desired values by using 0.1 M HCl or 0.1 M NaOH. All chemicals used in the present work were produced by Merck with Analytical Reagent grade. Table 1 shows the feature of the dyestuffs.

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Table 1.The feature of the dyestuffs

Materials	**Formula**	**Molecular weight**	**λ max (nm)**
Methylene blue	$C_{16}H_{18}N_3SCI$	319,85 g/mol	670
Brilliant blue	$C_{37}H_{34}N_2Na_2O_9S_3$	792,85 g/mol	628
Methylene orange (Acid Orange)	$C_{14}H_{14}N_3NaO_3S_1$	327,33 g/mol	485
K-RED 198 (reactive red 198)	$C_{27}H_{18}ClN_7Na_4O_{16}S_5$	984,21 g/mol	530

Peanut and pistachio shells were taken from dried nut factories an Osmaniye and Gaziantep city. The shells was cleaned by using deionize water and then dried out in oven at 80 ^oC. Finally, Peanut and pistachio shells was grinded by 0.5-1.2 mm and 1-1.7 mm intervals respectively.

Analytical Methods

All analyses were carried out by following American Public Health Association standard methods [15], unless mentioned otherwise. The chemicals were analytical grade (> 99%), as they were purchased from Merck GmbH (Darmstadt, Germany). pH was measured by using apparatuses with the relevant probes (LabQuest2/ Vernier, USA). Residual dyestuff concentrations were determined by the help of spectrophotometer (UV/vis spectrophotometer (T80+ Pg Ins. Ltd.).

Batch studies

The batch studies were carried out at 20 ◦C in conical flasks (1000 mL) with an orbital shaker in a constant room temperature. Stock, 25 g/L, dyes concentration was used and the selected incubation time of the flasks was ranged from 5 to 45 min. Several mL of aqueous solution was taken at different time intervals. The data to derive the isotherms and kinetic models constants were obtained by using a known amount of the shells and 100 mL aqueous solution containing dyestuff and at fixed pH values. The equation 1 was used to calculate the adsorption capacity, q ($mg.g^{-1}$).

$$q = \frac{(C_0 - C_e)}{W} \times V \qquad \text{Equation (1)}$$

Where C_0 is the initial concentration of dye, V is the volume of the solution, W represent of the mass of WS and C_e shows the residual concentration of dye at equilibrium or any time t, which defines q_e or q_t, respectively.

RESEARCH FINDINGS

Effect of pH

The sorption capacity is conducted by the pH due to pH effects on adsorbent surface and dyestuff ionization in the aquatic solution [16,17]. The effects of pH on dyestuff at 250 mL, 25 mg/L of dyestuff, and 4 g/L of adsorbent were analysed and the variety of pH values ranged between 3 and 8 are given in Fig. 1 and Fig 2. As seen figures, increase in pH values resulted slight increase in removal efficiency and this increase was negligible. On the contrary, some rechargers reported that acidic pH gave better adsorption results by using biomass adsorbent to remove reactive dyes from wastewater [18]. Maximum dye removal efficiency was obtained at neutral pH values both peanut and pistachio shells. Therefore, optimum pH value was chosen as 7.0 and the further studies carried out with neutral pH to get maximum colour removal rate during batch sorption tests.

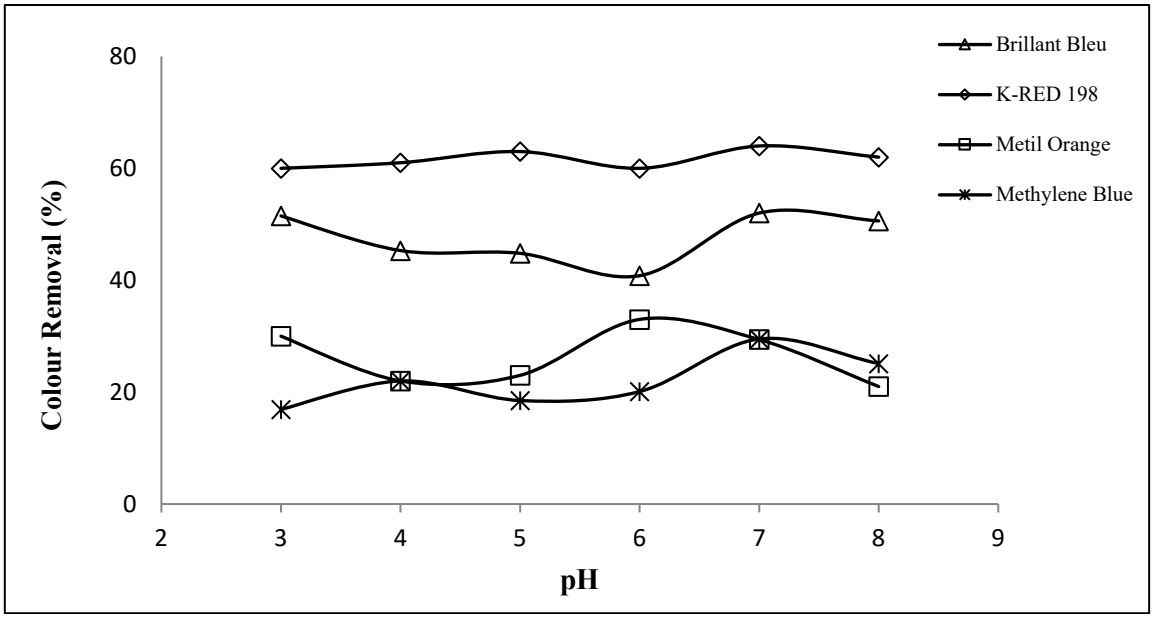

Figure 1. Effect of pH on removal of dyes for pistachio shell

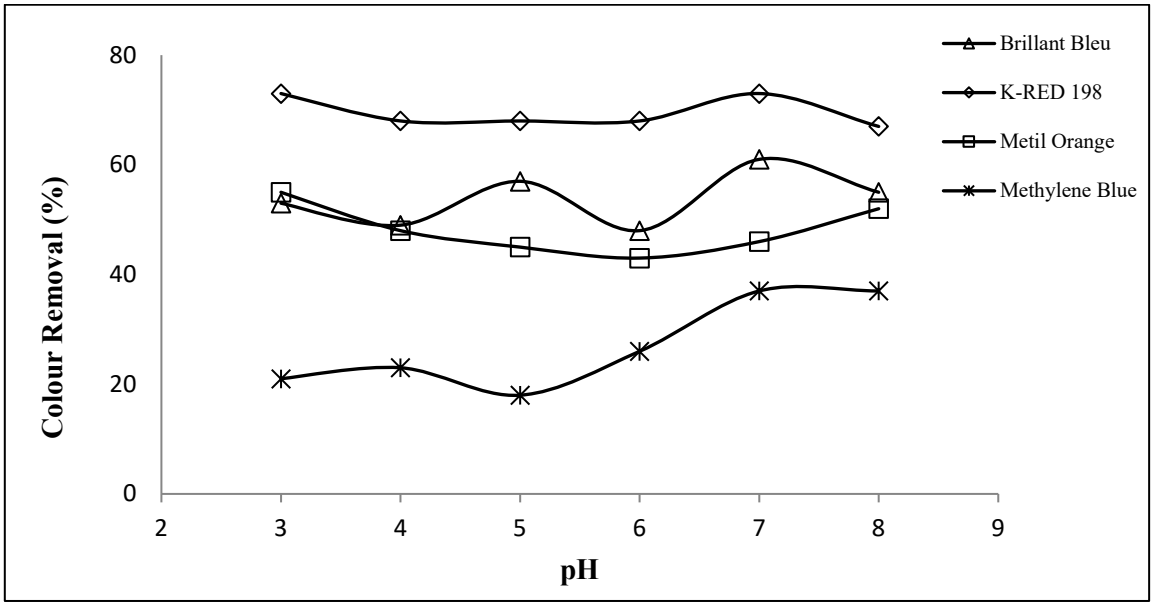

Figure 2. Effect of pH on removal of dyes for peanut shell

Effect of adsorption dosage and contact time

Adsorption dosage is an important factor for the determination of an adsorbent capacity. Figure 3 (pistachio data is not given) shows effect of peanut shells dose on removal of the dyes. The adsorbent dosages were varied between 2.0 g and 8.0 g at fixed pH and temperature of 20◦C. As seen in Fig. 3, dye adsorption rate increased with increasing the shells until 6 g. This can be explained by the fact that increase in adsorbent dosage provide higher adsorption capacity that resulted in more surface area available for dye ions will be exposed to more active sites for binding [11]. Optimum adsorbent dosage was determined as 6.0 g for peanut shells (see Fig. 3). The same figure continued for pistachio shells (data not given).

The contact time for dyes and adsorbents is also importance for the removal process. Contact time experiment helps to realize in the quantity of the dye adsorbed in different times. The equilibrium time is also one of the most important design parameters for adsorption proses. As seen Fig. 4, adsorption–desorption occurred on the shell in process of time for Methyl Orange and Methylene Blue. K-RED 198 and Brillant Blue were fast for the first time and then they gradually decreased in time until they reach equilibrium. As can be seen from Fig. 4, the most of the dye were removed in the first 45 min.

The contact time of 45 min was, therefore, selected and applied to the equilibrium experiments. The present study results are in line with Mook et al. [19] search including RB5 removal from wastewater by using palm shell.

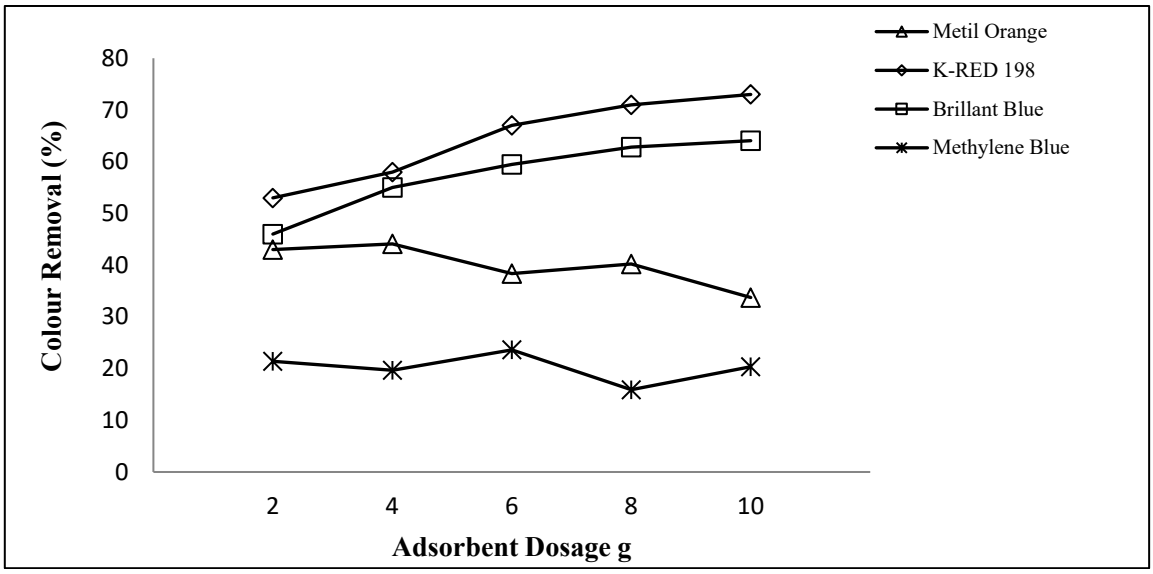

Figure 3. Effect of adsorbent dosage on removal of dyes for peanut shell

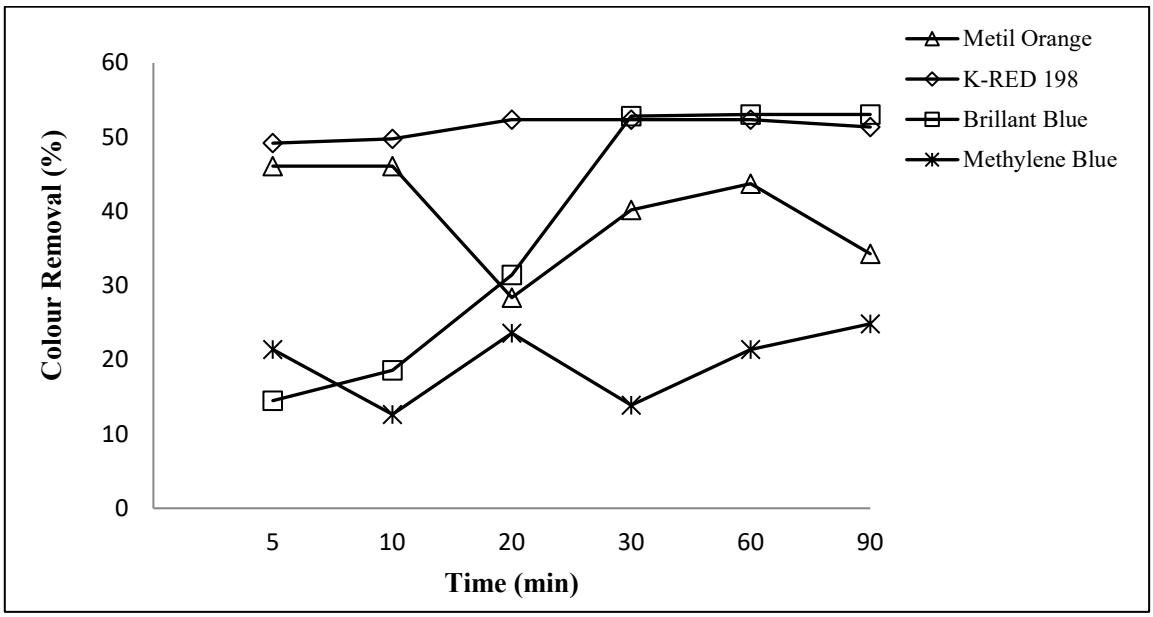

Figure 4. Effect of contact time on removal of dyes for pistachio shell

Adsorption isotherms

The equilibrium isotherm is key element to understand the interaction between a sorbate and an adsorbent. The data was applied to commonly used isotherm models; Freundlich and Langmuir. Dye removal efficiency for peanut and pistachio shells is as follows; 73.1% for K-RED 198 and 64.9% for Brilliant Blue, 73.6% for K-RED 198 and 65.84% for Brilliant Blue, respectively. The best fit isotherm was obtained by Freundlich model compared with the Langmuir model. The Freundlich isotherm is described as the multilayer adsorption of adsorbate on a heterogeneous adsorbent surface [17,20]. The isotherm model parameters are given in Table 2.

The adsorption process is acceptable when the n ranges between 1 and 10. If n is bigger than 1, chemical adsorption process occurs; n of n is lower than 1, the physical adsorption happen [1]. The value of n for both dye were found bigger than 1 and (see Table 2). These presented that chemical adsorption occurred for the removal of dyestuffs. Furthermore, high and favourable sorption occurred

on the shells for the dyestuff considering to R_L constant for Langmuir model. R_L constants are as follows; 0.206 for Brillant Blue, 0.29115 for K-RED 198 for peanut shells; 0.08136 for Brillant Blue, 0.23038 for K-RED 198 for pistachio shells;

Table 2. The isoterm model parameters of the dyestuffs

Isoterm	Parametre			
	Brillant Blue	K-RED 198	Brillant Blue	K-RED 198
Freundlich	K_F=16.1416 n=-1.93573	K_F=23.6934 n=-1.68	K_F=12.14357 n=-2.35183	K_F=67.999 n=1.0999
Langmiur	q_m=1.300052 K_L=-0.077663 R_L=0.206	q_m=1.381597 K_L=-0.0639 R_L=0.29115	q_m=1.71969 K_L=1.12313 R_L= 0.08136	q_m=0.8893 K_L=0.04948 R_L= 0.23038

Adsorption kinetic

The adsorption with natural materials is a complex process due to the heterogeneity of adsorbent surface. Adsorption rate on the solid–liquid interface is affected by the residence time [21]. Dye adsorption on adsorbent from aqueous solution includes several stage such as transport in the solution, external diffusion or boundary layer diffusion, internal diffusion or intraparticle diffusion, adsorption or desorption on the surface of the interior sites [1]. The data was applied to commonly use kinetic models; Evolvich, Fractional Powder and Pseudo First-Order. The kinetic model parameters are presented in Table 3.

Chemical reaction, mass transfer and diffusion control for adsorption process is explained by kinetic analysis. The pseudo kinetics model assumes that chemisorption of the adsorbate occurs on adsorbent. It was found that pseudo first-order kinetic model describes the shells adsorption well for all used dyestuffs. The removal of dyestuffs by the shells is complex and includes more than one mechanism. Previous adsorption research with respect to dyes with various organic adsorbent such as date stones and palm-tress waste [6] , princess tree leaf [14], pine cone [11] demonstrated that dye removal followed pseudo second-order kinetic model. The findings of the present studies are in line with previous research.

Table 3. The kinetic model parameters of the dyestuffs

Kinetik Model	Parametre			
		Brillant Blue	K-RED 198	Brillant Blue	K-RED 198
Elovich	β α R^2	1.7164 0.190336 0.9393	1.3634 0.37446 0.96	1.5852 0.317269 0.9047	1.6373 0.198656 0.927
Pseudo-first order	q_e k_{1p} R^2	5.0204 0.0653 0.9866	4.085 0.00585 0.947	6.670 0.1245 0.9297	3.261 0.031 0.9267

CONCLUSIONS AND DISCUSSION

The results of the study indicated that peanut and pistachio shells can be used as a practical, effective and low cost- efficient alternative sorbent for the removal of dyestuff. Initial adsorption studies show that Methylene Orange and Methylene Blue were removed poorly, however Brillant Blue and K-RED 198 bound to the shells. Experiment data fitted well to Freundlich isotherm model. The maximum adsorption capacities based on this model were as follows: 4.58 mg/g for Brillant Blue, and 4.33 mg/g for K-RED 198 at peanut shells, and 4.04 mg/g for Brillant Blue, and 4.64 mg/g for K-RED 198 at pistachio shells. The sorption of dyestuffs onto the shells was described well by pseudo first-order kinetic model.

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