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Study of Bio Sorbents for the Treatment of Simulated Dyes Waste Water

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Author's contribution

The sole author designed, analyzed and interpreted and prepared the manuscript.

Article Information

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Original Research Article

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ABSTRACT

Water pollution is one of the burning issues of today's world; it is the primary cause of different diseases in living beings. Textile effluent is the primary source of water pollution. Marine lifespan, environment and our ecosystem are affected severely by the dumping of dyes from industries into the water. The objective of this research is adsorption, thermodynamics and kinetic studies of two different organic dyes onto abundantly available inexpensive adsorbents like *Phoenix dactylifera* (date pits), *tea waste* (tea leaves), *Zea covering* (corn husk) and *Prunus persica* (peach seeds) for the elimination of acidic (Congo red) and basic (Malachite Green oxalate) dyes from solutions. Selected adsorbents have high surface reactivity and adsorption capability to eliminate the mentioned dyes from the wastewater system.

Keywords: Phoenix dactylifera; tea waste; zea covering; Prunus persica; Congo red dye; malachite green oxalate dye; adsorption models; adsorption kinetics and SEM.

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1. INTRODUCTION

Many dyes used in the textile industry cause environmental and health problems It is well known that malachite green oxalate and congo red, are incredibly toxic dyes, considered as the primary pollutants. Colours are not biodegradable and tend to accumulate in living organisms causing illnesses and disorders [1]. Therefore, removal of dyes from water is currently one of the most critical environmental issue being investigated. Treatment processes of malachite green oxalate and congo red dye removal from seawater through the process of adsorption have recently been studied [2]. However, it has become a challenge for researchers to seek cheaper and more efficient adsorbents for an elimination of dyes.

Tea leaves, corn husk, date pits and peach seeds are the most widely consumed products throughout the world for its beneficial effects on health, such as antioxidant, anti-carcinogenic, antimicrobial activities [3]. The objective of the present recent is to eliminate malachite green oxalate dye and congo red dye from water. Mentioned natural adsorbents were instigated to be reliant on contact time, dye concentration and amount of adsorbent by using spectrophotometric technique before and after adsorption of dye. Maximum adsorption of date pits observed in 20 min with percentage removal of 96.3 %, maximum adsorption of tea leaves observed in 30 min with 94.23%, extreme adsorption of peach seed powder found in 40 min with percentage removal of 95.48% and the maximum adsorption of corn husk observed in 40 min with 94.40%. The investigational data fitted well to pseudo-second-order kinetics model and have a regression coefficient value of 0.999 approximately [4]. Values of percentage removal and K_D for all the adsorbents and dyes systems were also examined at temperatures from 298K to 318K. The adsorption isotherms like Langmuir and Freundlich were employed, and the values of constants were calculated to estimate the adsorption characteristics [5]. Thermodynamic parameters like ΔG°, ΔH° and ΔS° were also calculated and it was observed that adsorption is spontaneous and endothermic [6]. The surface morphology of adsorbate and adsorbent was resolute by SEM technique of Jeol Japan with model number JSM 6380A. K_D (the adsorptiondesorption coefficient) values are determined over a range of concentrations at a constant temperature [7].

2. EXPERIMENTAL SECTION

2.1 Preparation of Malachite Green Oxalate and Congo Red Dye Solutions

Dye solution of congo red was prepared by using double distilled water. The absorbance of respective concentrations of dye was measured by UV-Visible spectrophotometer of Jeol Japan with model number EX-54175JMU showed a maximum peak in diluted concentration of dye around 498 nm. Molar extinction coefficient of congo red is approximately 45000 $M^{-1}cm^{-1}$. Similarly, Malachite green oxalate dye showed a peak in the diluted concentration of dye around at wavelength 621 nm and its molar extension coefficient is $1x10^5$ M⁻¹cm⁻¹ [8].

2.2 Preparation of Natural Adsorbents

Peach, corn, tea and date wastes were collected from Nazimabad suburb of Karachi, Pakistan, washed with distilled water, ground and sieved into powder of sizes 0.146-0.342 mm, 0.1546- 0.4623 mm and 0.0365-0.2876 mm, 0.265-0.435 mm, respectively dried in an oven at 390 K for 2 days, after complete drying all adsorbents were stored in desiccator for further use [9].

2.3 Optimization of Adsorbent Dosage

The number of adsorbents varied from 0.1g to 1.2g. All the flasks were placed in shaking incubator for 30 min, and the temperature was adjusted. The analyte of each flask was filtered by using filter paper and an absorbance of both the dyes were analyzed by using spectrophotometer at their particular wavelengths. The optimum dose of all the adsorbents were obtained by calculating % removal values and distribution coefficient values [10].

2.4 Optimization of pH

The pH of Point Zero Charge (pH_{PZC}) was determined by adopting pH drift method for the efficient removal of dyes solution. The 0.005M NaCl solution was prepared and initial pH was adjusted by adding either 0.1M HCl or 0.1M NaOH in such a manner that 3 flasks have acidic pH (2, 4, and 6) and other 3 flasks have basic pH (8, 10, 12). The solutions were agitated with 0.05g of adsorbents and pH was recorded. pH of flasks was noted after 24 and 48 hours.

2.5 Ionic Strength (KCl)

Different concentrations of KCl (0.01–0.05 M) were added to investigate the effect of ionic strength for the adsorptive removal of dyes. The increase in ionic strength causes an increase in the adsorption of congo red and malachite green oxalate dye [11].

2.6 Determination of Shaking Time

For optimum shaking time, 30ml of dye solution was taken in shaking flask and the optimized

Optimization of Amount for the Elimination of Congo Red Dye by Using Tea leaves powder Amount(g) Equilibrium Conc.x10⁶ (M) We All 2008 CONCICE ASSESS EXABLE ASSESS EXABLE A 0.1 2.933 2.933 93.139 1.761 0.2 1.842 77.452 1.751 0.3 9.111 78.690 1.822 0.4 4.066 90.488 0.612 0.5 7.601 82.224 0.912 0.6 9.602 77.546 0.961 0.7 2.977 93.035 0.255 0.8 2.466 94.230 0.185 **Optimization of Amount for the Elimination of Congo Red Dye by Using Date pits powder Amount(g) Equilibrium Conc.x10⁷ (M) % Removal K_D** 0.1 0.213 67.123 128 0.2 6.888 6.888 6.888 89.383 20.666 0.3 0.153 76.369 30.666 0.4 0.106 0.106 83.561 16 0.5 3.333 94.863 4 0.6 2.444 96.232 2.444 0.7 6.444 6.444 6.444 6.444 6.523 0.8 7.555 88.356 5.666 0.9 4.222 93.493 2.814 **Optimization of Amount for the Removal of MGO Dye by using Corn Husk powder Amount(g) Equilibrium Conc.x106 (M) % Removal KD** 0.1 1.712 **1.712 1.712 1.712 1.712 1.71** 89.579 10.275 0.3 1.141 1.141 93.052 2.283 0.5 9.200 94.401 1.104 0.7 1.423 91.336 1.220 0.9 1.920 88.312 1.280 1.2 1.631 90.069 0.815 **Optimization of Amount for the Removal of MGO Dye by Using Peach seeds shell powder Amount(g) Equilibrium Conc.x10⁶ (M) Example 2 We Removal K**_D 0.1 0.210 89.605 4.905 0.3 0.152 90.134 5.081 0.5 8.193 94.697 1.638 0.7 7.051 95.436 1.007 0.9 8.193 94.697 0.910 1.2 6.984 95.480 0.582

Table 1. Analysis of amount

amount of adsorbents were added in all flasks. The shaking time was varied from 10 to 50 min for both dyes. After a specific interval of time content of each flask was filtered, and the absorbance of the filtrate was recorded using UV-visible Spectrophotometer. The optimum shaking time of adsorbent was determined by finding distribution coefficient (K_D) and percentage removal values [12].

Table 2. Analysis of time

Table 3. Analysis of temperature

% Removal of CR dye by using tea leaves at different temperatures					
Dye	Ci(M)	% REMOVAL			
	(10^5)	303K	308K	313K	318K
CR dye	0.1	79.96071	90.56	84.67	79.96
	0.3	88.14383	95.9	98.54	90.53
	0.5	99.45455	93.8	82	65.45
	0.7	71.20448	44.14	96.5	97.47
	0.01	77.37643	81.36	83.4	87.45
	0.003	93.83562	80.46	93.49	72.26

Table 4. Langmuir isotherms

Table 5. Freunlich isotherms

Table 6. Adsorption kinetics

Table 7. Thermodynamic parameters

Optimization of amount

Fig. 1. Optimization of amount for elimination of Congo red dye by using used tea leaves powder

Fig. 2. Optimization of amount for elimination of Congo red dye by using date pits powder

Fig. 3. Optimization of amount for elimination of Malachite green oxalate dye by using Corn Husk powder

Fig. 4. Optimization of amount for elimination of MGO dye by using Peach Seed powder

OPTIMIZATION OF TIME

Fig. 6. Optimization of time for elimination of Congo red dye by using Date pits powder

Fig. 7. Optimization of time for elimination of Malachite green oxalate dye by using Corn husk powder

Fig. 8. Optimization of time for elimination of Malachite green oxalate dye by using Peach seed powder

ADSORPTION KINETICS

Fig. 10. Kinetics of tea leaves by Pseudo -second order

Fig. 12. Kinetics of corn husk by Pseudo -second order

Set 1: Tea waste, Set 2: corn husk, Set 3: peach seeds Set 4: date pits

Fig. 13. Optimization of pH

Fig. 14. Optimization of pH of adsorbents

Fig. 15. Optimization of ionic strength

SEM images of tea leaves before and after adsorption

SEM images of corn husk before and after adsorption

SEM image of peach seed before and after adsorption

SEM image of Date pits before and after adsorption

Fig. 16. SEM images of adsorbents

3. RESULTS AND DISCUSSION

Adsorption of carcinogenic dyes Congo Red (CR) was carried out by tea leaves powder and date pits powder. Adsorption of MGO dye was carried out by peach seeds powder and corn husk powder. Different experiments were performed in the adjusted circumstances of adsorbent's amount in Table (1), adsorbents stay time in Table (2) and adsorbents were analyzed at different temperatures in Table (3). Concentrations of dyes before and after adsorption were recorded by ultraviolet visible spectrophotometer. The structure of natural adsorbents were analyzed by SEM technique.

3.1 Examination of Effects of Adsorption Parameters on the Adsorption

3.1.1 Effect of adsorbent's amount

The optimum amount of adsorbent was taken as 0.4g for tea leaves in Fig. (1), 0.6g for date pits in Fig. (2), 0.5 g for corn husk in Fig. (3) and 0.5g for peach seeds powder in Fig. (4). By further increasing of amount of natural bio sorbents did not show any effective removal of dyes as shown in Table (1).

3.1.2 Effect of p H

The zero point charge (Ppzc) of tea waste, corn husk, peach seeds and date pits were determined. Adsorption of cation is favored at pH >7, while the adsorption of anion is favored at pH <7. At pH 2.0 a significantly high-electrostatic attraction exists between the positively charged surface of the adsorbent and anionic dye. As the pH of the system increases, the number of negatively charged sites increases and the number of positively charged sites decreases. A negatively charged surface site on the adsorbent does not favor the adsorption of dye anions due to the electrostatic repulsion. Also, lower adsorption of dyes at alkaline pH is due to the presence of excess ions competing with the dye anions for the adsorption sites. Nevertheless, significant adsorption of anionic dye on the adsorbent still occurred above due to the fact that a chemical interaction between the dyes and tea waste, corn husk, peach seeds and date pits.

3.1.3 Effect of Ionic strength

Different concentrations of KCl (0.01–0.05 M) were added to investigate the effect of ionic strength on adsorptive removal of dyes. The increase in ionic strength causes increase in the adsorption of congo red and malachite green oxalate. Salt addition increases the aggregation of dye molecules and decreases the solubility. An increase in aggregation promotes the adsorption of dyes molecules. Another possibility is that increase in ionic strength increases the positive charge of the adsorbent on the surface thus increases the electrostatic attraction between dyes and adsorbents. Thus increase in ionic strength was found to have an increase in adsorption of both dyes.

3.1.4 Effect of stay time

For tea leaves - congo red system, maximum adsorption was obtained at 35 minutes in Fig. (5), for date pits – congo red system, maximum adsorption capacity was obtained at 20 minutes in Fig. (6), for corn husk- malachite green oxalate system, maximum adsorption capacity was acquired at 30 minutes in Fig. (7) and for peach seeds – malachite green oxalate system, maximum adsorption capacity was achieved at 15 minutes, as shown in Fig. (8).

3.2 Adsorption Isotherms

3.2.1 Langmuir adsorption isotherm

This isotherm shows monolayer adsorption on a consistent surface. Monolayer adsorption must be merely defined by Langmuir adsorption isotherm. Well-known Langmuir equation is as follows:

$$
C_e/X/m = 1/KV_m + C_e/V_m
$$

Here, equilibrium concentration is C_e (mol/dm³), amount adsorbed at equilibrium is X/m (mol/g), intercept is Vm (mol/g) and slope is K (dm³/mol). The adsorption of Congo Red (CR) and malachite green oxalate (MGO) were examined at different temperatures.

3.2.2 The freundlich adsorption isotherm

This isotherm is specified by the following equation:

$Log X/m = log K + 1/n log C_e$

Values of "K" and "n" were calculated from the intercepts and slopes of their relevant graphs and were written in tables. Increase in values of constant (K) with the increase in temperature for congo red dye and malachite green oxalate dye showed that adsorption of both dyes are favorable at higher temperatures [13]. The values of "n" lies in between -1 to10, which showed advantageous effect of the adsorption process. Values of R^2 proved that Freundlich isotherm, which showed formation of multilayer on the surface of adsorbent as shown in Table (5).

3.2.3 Influence of thermodynamic parameter

Thermodynamic parameters of adsorption progression were used to accomplish the process of spontaneity. Change in Gibb's free energy measures the spontaneity. Its negative value proves the reaction is spontaneous.

∆H^o, ∆S^o and ∆G^o were premeditated by the following equations:

 ΔG^0 = ΔH^0 -T ΔS^0

Ln K_D = $\Delta S^0/R$ - $\Delta H^0/RT$

 ΔG^0 = -RT LnK_D

Here R, is the gas constant, absolute temperature is T, K_D is distribution constant. ΔH^0 and ∆S⁰ were obtained from slopes and intercepts of "In K_D " versus 1/T [14].

Negative values of Δ*G*° confirmed feasibility of method and spontaneity of adsorption with a maximum adsorption of dyes as shown in Table (7).

3.3 Kinetics of Adsorption

Linear graph of "t/qt" on y-axis and "t" on x-axis for different concentrations of CR dye and MGO dye were plotted which correspond that adsorption procedure followed pseudo-second order kinetic. Here qe and qt are the amount of the dye adsorbed on the adsorbent (mol/g) at equilibrium and t is time in minutes, k_2 is the adsorption of second order rate adsorption constant (mol/g.min). The correlation coefficients for the second order models are near to 0.999 shows the linearity with high degree of correlation coefficient as shown in Table (6) [15].

 $\ln(q_e - q_t) = \ln q_e - k_1 t$

$$
\frac{t}{q_t}=\frac{1}{k_2q_e^2}+\frac{t}{q_e}
$$

3.4 SEM Interpretations of Natural Particles

Top characterization techniques is SEM. The scanning electron micrograph specifies that the particles are quite homogenous in nature and the size ranging from 50 - 120nm for natural bio sorbents. After the adsorption of tea leaves, date pits, corn husk and peach seed powder, the diameter of all the natural adsorbents were decreased because the dye coated onto their surfaces.

4. CONCLUSION

For the elimination of chemical toxins from water only adsorption is the familiar, effective and cheap method that yields high-quality results. The present research emphasizes on the removal of contaminants by using adsorption process with the collection natural

Firdous; CSIJ, 21(3): 1-16, 2017; Article no.CSIJ.38363

adsorbents. The characterization of natural adsorbents were analyzed by SEM. Malachite green oxalate dye adsorption was calculated and analyzed by using corn husk and peach seeds powder. Similarly adsorption of Congo red dye was analyzed by using waste tea leaves and date pits powder. Investigational data presented adsorption followed the pseudo second-order kinetics. Experimental data was form fitted well in Freundlich and Langmuir isotherms. The negative value of ∆G[°] proved the spontaneity of adsorption of waste tea leaves powder, date pits powder and corn husk powder. The positive ΔG° value of peach seeds powder confirmed nonspontaneity of the adsorption. It was concluded that this specific method could be employed on industrial scale for waste minimization. All natural adsorbents proposed a lot of auspicious benefits in the forthcoming era. Treatment of dyes using fresh seeds powder was a highly economic and simple method than other methods meanwhile it has an excellent capability of eliminating color. Hence, it is applicable for industrial pollutants for improving the worth of wastewater of fabric
industries and numerous others. industries and numerous others. Furthermore effort for obtaining other constraints of dye waste using the mentioned method can be conceded out to develop the adsorption proficiency.

COMPETING INTERESTS

Author has declared that no competing interests exist.

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Firdous; CSIJ, 21(3): 1-16, 2017; Article no.CSIJ.38363

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