NC STATE UNIVERSITY
COLLEGE OF Textiles NC STATE UNIVERSITY
JTATM
Journal of Textile and Apparel, Technology and Management

Volume 7, Issue 3, Spring2012

Potential Application of Orange Peel (OP) as an Eco-friendly Adsorbent for Textile Dyeing Effluents

A.G. El-Said[a]
A.M. Gamal [b]
Chemistry Department, Faculty of Science
Al-Azhar University (Girls), Egypt

Heba F. Mansour[c]
Textile printing, Dyeing & Finishing Department
Faculty of Applied Arts
Helwan University, Egypt

[a]asrargoma@yahoo.com [b]Super_3mr@yahoo.com
[c]heba1fm@yahoo.co.uk

ABSTRACT

The use of low-cost and eco-friendly adsorbents has been investigated as ideal alternatives to the current expensive methods for removing dyes from waste water. Orange peel (OP) was used as a low cost natural waste adsorbent for the removal of textile effluents. The effectiveness of (OP) in adsorbing ;C.I. Direct Red 79 (DR 79) and C.I. Direct Yellow 27 (DY 27) from their dye baths has been studied as a function of pH, solid/liquid ratio, agitation time and initial dye concentration. The sorption isotherms were analyzed using Langmuir and Frendlich models. The results indicated that acidic solutions supported the adsorption of the studied dyes within (OP). Adsorption kinetic models were analyzed using the pseudo-first, second order equation and intraparticle diffusion equation. The results showed that the order equation fitted the experimental data very well. By the way, the effect of adsorbent surface was analyzed by scanning electron microscope (SEM), whereas the SEM images showed reasonable agreement with adsorption measurements.

Keywords: environmental technology, clean chemistry, textile dyes, direct dyes, green adsorbents.

1. Introduction:

Textile industries produce huge amounts of polluted effluents that are normally discharged to surface water bodies and ground water aquifers. These wastes cause many damages to the ecological system of the receiving surface water, creating a lot of disturbance to the ground water resources (Georgiou, D. et. al. 2002; Tsui, L.S. et. al. 2003). Dyes are classified as follows: anionic / direct, acidic and reactive, cationic / basic, and non-ionic dispersed dyes, whereas over 80% of which are constituted of the aromatic azo type. (Hameed, B.H. & El-Khaiary, M.I.2008)

Moreover, 50,000 tones of dyes containing hazardous substances which can damage the aquatic and vegetal life, are discharged annually via effluents into environment (Brown, D.198).Toxicity of various dyes especially benzidine based dyes are well known because of their mutagenicity and carcinogenicity Gregory, AR. Et.al. 1991) It is rather difficult to treat dye effluents because hot and strongly colored textile dyeing wastewater is notoriously known to contain a large amount of suspended solids ,high COD(chemical oxygen demand) concentration and with a highly fluctuating pH. Hence there is a need to remove dyes from dyeing wastewater before it mixes with water bodies. (Alparslan, S, 2003)

From the aesthetic point of view, the removal of color from waste effluents has become environmentally important (Araceli, R. et. al. 2009; Tamez Uddin, M.D. et. al.2009) and the governments awareness have been under severe pressure to stop such effluents to the public watercourses, unless treated properly. The USEPA (environmental proportion Agency) has classified textile wastes into four groups, 1- dispersible, 2- hard-to-treat, 3- high-volume, and 4- hazardous and toxic wastes (Tsui, L.S. et. al. 2003. The most widely methods for removing dyes from wastewater systems include physicochemical, and biological methods ,such as flocculation, coagulation, precipitation, adsoption, membrane filtration, electrochemical techniques, ozonation and fungal decolorization. (Sotelo, J.L. et. al. 2002; Chen, G. et. al. 2003)

Amongst the numerous techniques of pollutant removal, adsorption is an effective and useful process, but only that of adsorption is considered to be superior in comparison with the other techniques of waste water treatment in terms of low cost, easy availability, simplicity of design, high efficiency, ease of operation, biodegradability and the ability to treat dyes in more concentrated form. (Saad, S. A. et. al. 2007)

Nowadays, the remediation of several pollution problems is a target of the scientific researchers. Technical ways of solving environmental concerns and menaces are available a long time ago, but making them cheaper and sustainable is still a challenge, especially when searching for natural raw materials as a possible source that could provide a successful low cost solution. (Demirbas,A. 2008; Pavan, F.A. et. al. 2008; Alenor, S. et. al. 2009; Sanchez-Martin, J. et. al. 2010)

Orange peel principally consists of cellulose, pectin, hemicellulose, lignin, chlorophyll pigments and other low molecular weight hydro-carbons (Liang, S. et. al. 2010). These components contain various functional groups, such as carboxyl and hydroxyl groups which make the orange peel to be a potential adsorbent material for removing metal ions from aqueous solutions (Arami, A. et. al. 2005; Doulati Ardejani, F. et. al. 2007; Feng, N.C. et. al. 2009; Liang, S. et. al. 2009; Perez Marin, A.B. et. al. 2009). Depending on this phenomenon, this work was aimed on studying the potential adsorption of orange peel as a natural waste material that could provide a successful eco-friendly low cost solution for removing Direct Red 79, (DR 79) and C.I. Direct Yellow 27 (DY 27) from the textile dyeing effluents. The effective parameters of pH, solid / liquid ratio, time and initial dye concentration were investigated. Adsorption isotherms and kinetics rate investigated the different models were used to evaluate the experimental data and to elucidate the possible adsorption mechanism. (SEM) showed the effect of adsorbent.

2. Materials and Methods

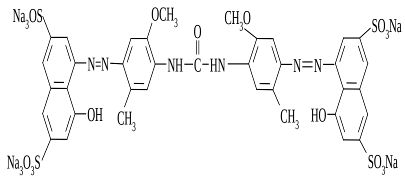
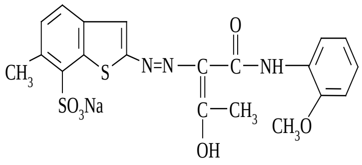
2-1. Preparation of Orange peel adsorbents

Orange peels were selected and washed with water several times to remove ash and other contaminants, followed by double distilled water (DDW) washing. The washed peels were left to dry at ambient temperature for 36 hrs, then crushed and sieved to small particles (3.35 mm sieve).

2-2. Dyeing solutions

C.I. Direct Red 79 (DR 79) and C.I. Direct Yellow 27 (DY 27) were purchased from Ciba Ltd. and were used without any further purification. Table (1), show the properties and structure of that dyes, respectively.

Table. Main characteristics and structures of dyes used

Dye	**Structure**	**Class**	**C.I. name**	**MW ($gmol^{-1}$)**	**Molecular formula**	**λ_{max} nm**
Direct Red 79	 (a)	Anionic	Direct Red 79 (DR 79)	1047	$C_{37}H_{28}N_6Na_4O_{17}S_4$	510
Direct yellow 27	 (b)	Anionic	Direct yellow 217 (DY27)	650.62	$C_{24}H_{20}N_4Na_2O_9S_3$	397

Working solutions (1000 mg/L) prepared for both dyes. The pH adjustments of the solutions were made by adding few drops of 0.1 M of H_2SO_4 or NaOH

2-3. Measurements

2-3-1. Adsorption Studies

A series of batch experiments were conducted to study the adsorption mechanism, adsorption isotherm and kinetics:

The prologue investigations were carried out in batches in different conditions such as different pH's, concentrations, contact time, the amount of solid adsorbent used for adsorption , etc.. .. The dye concentration ranging from (20-100) mg/L was studied to check the adsorption propensity. 50 ml of the prepared dyes solutions of known concentration was poured to a known amount of adsorbent. The mixture was continuously shaken; the equilibrium was established after 60 min for the two dyes. The dye removal was determined spectrophotometrically by monitoring absorbance changes at maximum wavelength (λ_{max}) (510nm) for DR 79 and (397nm) for Dy 27 using Perkin Elimer-Lamda spectropho-tometer model 201. The percentage of removal and equilibrium adsorption uptake q_e mg/g was calculated using equations 1 and 2 as follows:

$$\text{Removal \%} = 100\,(C_0 - C_e) / C_0 \qquad \textbf{Eq. 1}$$

$$q_e = (C_0 - C_e)\, V / m \qquad \textbf{Eq. 2}$$

Where $\mathbf{C_o}$ is the initial sorbate concentration ratio mg/L $\mathbf{C_e}$ is the equilibrium sorbate concentration mg/L **V** is the volume of solution L, and **m** is the mass (mg) of the adsorption.

2-3-2. Kinetics studies

Kinetic experiments were conducted with a 50ml in stoppered conical flasks at ambient temperature. The experiment was conducted with 50 ml dye solution at the initial concentration 20 mg/L and solid (OP) 40 mg/50ml.

The mixture was shaken continuously and samples were taken at predetermined time intervals (10-60 min). The mixture and the dye solution was analyzed at λ_{max} 510 nm and λ_{max} 397 nm for DR 79 and Dy 27 respectively.

2-3-3. Desorption studies

Desorptoin studies were carried out to elucidate the mechanism and to recover the adsorbate. 50 milliliters of 20 mg/L dye, contact with 40mg orange peel (OP) for the equilibrium time (60 min). After centrifugation, the supernatant dye solution was discarded and the adsorbent was separated then allowed to agitate with 100 ml of double distilled water at different pH's values (2.0-8.0) for the predetermined equilibrium time of adsorption. The desorbed dye solution was separated by centrifugation and estimated as before.

3. Results and discussion

3-1. Characterization of the OP

FTIR (Perkin – Elmer spectrophotometer spectrum one) in the range 500-4000cm^{-1} was studied. As shown in Figure 1, the peaks positions exhibited at 3420 are due to O–H and N–H stretching, while the band at 2924 represents the cH_2 asymmetric. The band at 1733 reflects the stretched carbonyl group of the unionized carboxyl group. The band at 1060 corresponded to C–OH represents the stretching of alcoholic group and carboxylic acids. SEM micrographs of the (OP) were illustrated in Figure 2. It was noted that the irregular and porous surfaces could be observed, resulted in, the presentation of an adequate morphology for dye adsorption within the (OP).

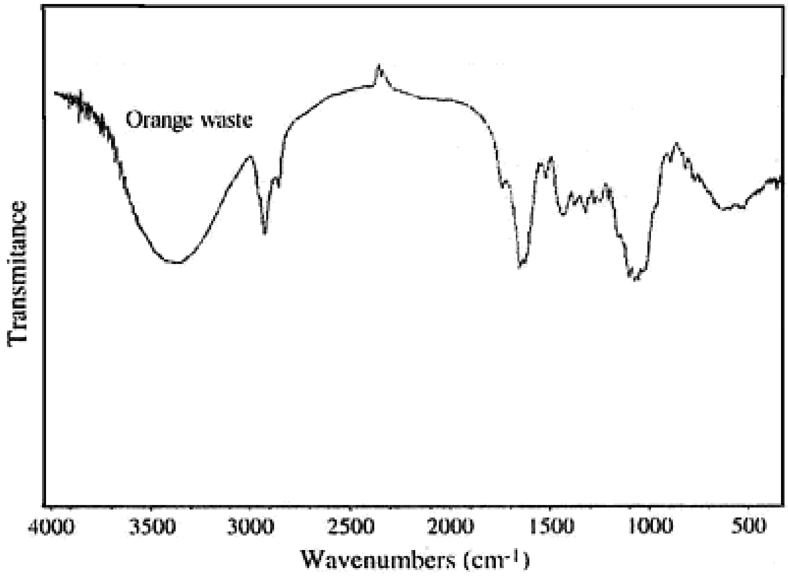
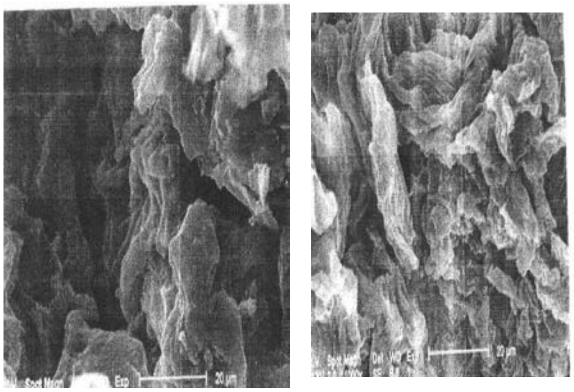


Figure 1. FTIR spectra of the orange waste

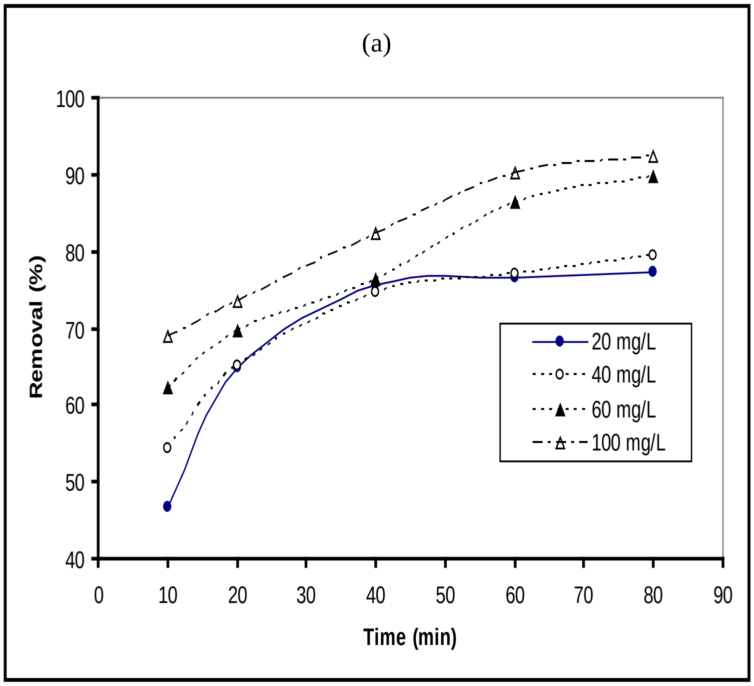


(a) (b)

Figure 2. SEM image (a) Raw OP (b) after adsorption process on DR 79

3-2. Effect of contact time and initial dye concentrations

The effect of contact time on the adsorption of DR79 and Dy 27 onto OP adsorbent was shown in Figure 3. The results indicated that the dye uptake from water was concentration dependent and increased with the initial concentration of both dyes. The equilibrium time was found to be at 60 min with a dye concentration ranging from (20-100 mg/L).The dye uptake increased rapidly in the initial stages of conduct time, then became almost constant denoting the attainment of equilibrium. This phenomenon might be initially due to the all active sites on the adsorbent surface were vacant and the solution concentration was high. After that period, a few surface active sites were available, so only a verge low increase in the dye uptake was observed [Tamez Uddin, M.D. et. al 2009).



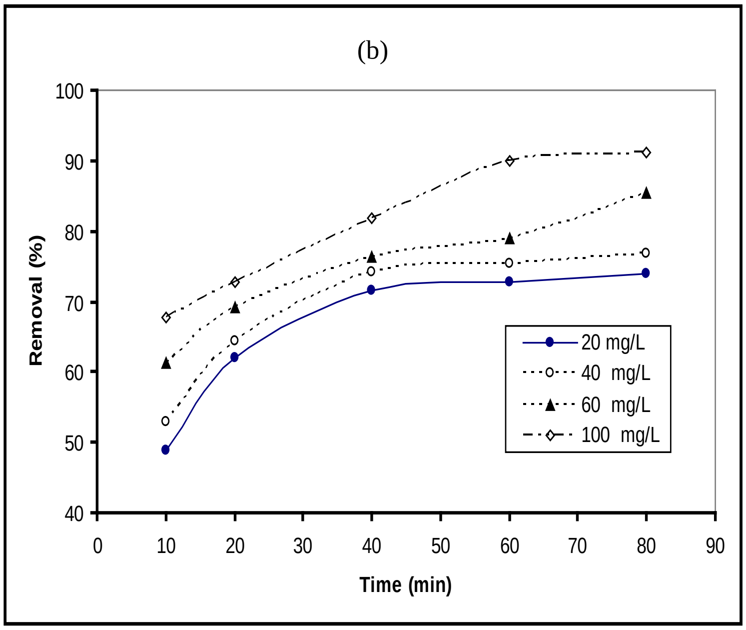


Figure 3. **Effect of time and initial dye concentration on adsorption of the selected dyes on 0P condition, pH 3, T 25°C. ms = 40mg/50ml *(a)* DR79 and (*b*) Dy 27**

3-3. Effect of pH

Figure 4 illustrated the experimental results as a percentage of dye removal versus pH. It was noted that, the pH values have an important role in the adsorption process (Janos, P. et. al 2009). When varying the pH between 2.0 and 8.0 with 20 mg/L of dye with a fixed amount of adsorbent 40 mg/50ml. Dyes are dissociated to polar groups (RSO_3^-) and (OP) has more charge which could be also affected the pH of solutions. Therefore at various pH values, the electrostatic attraction as well as the organic property and structure dye molecules and OP could play a very important role in dye adsorption. As the pH of the system increases, the number of negatively charged sites will increased. The negatively charged site on the adsorbent doesn't favor the adsorption of anionic dyes due to the electrostatic repulsion, whereas a maximum sorption of DR 79 and Dy 27 was occurred at acidic pH=3.0 $\pm$ 0.5. Lower adsorption of DR 79 and Dy 27 in alkaline pH values is due to the presence of excess [OH^-] ions which are destabilizing anionic dyes and are competing with the dye anions of the adsorption sites (Namusivayam, C. & Kavitha, D. 2002). (There is no a definite structure between dye and OP).

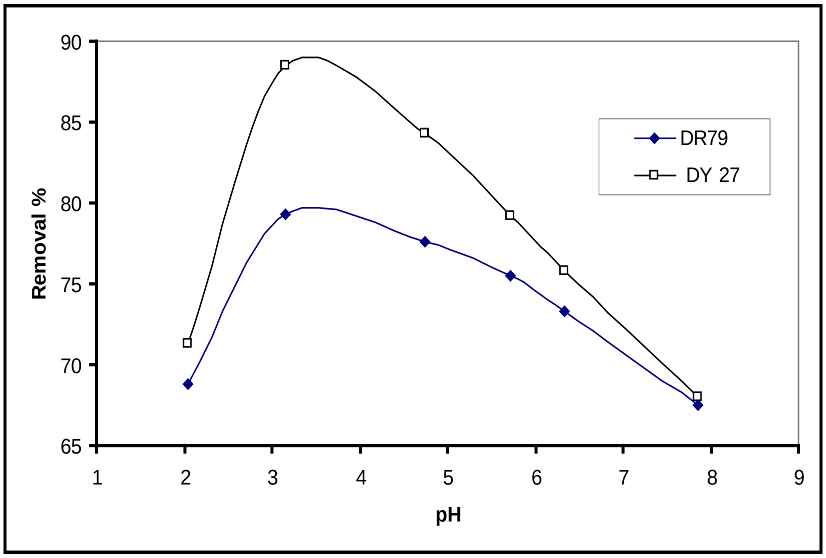


Figure 4. **Effect of pH on adsorption of dyes on OP conditions C_o=60 mg/L, T 25°C, ms40mg/50ml, contact time 60 min.**

3-4. Effect of solid/liquid ratio

Solid/liquid (abbreviated as S/L) is the ratio of the mass of absorbent/ volume of dye solution is an important parameter affecting the efficiency of the dye ions adsorption. Figure 5 illustrated the effect of S/L ratio on the dye adsorption by OP.

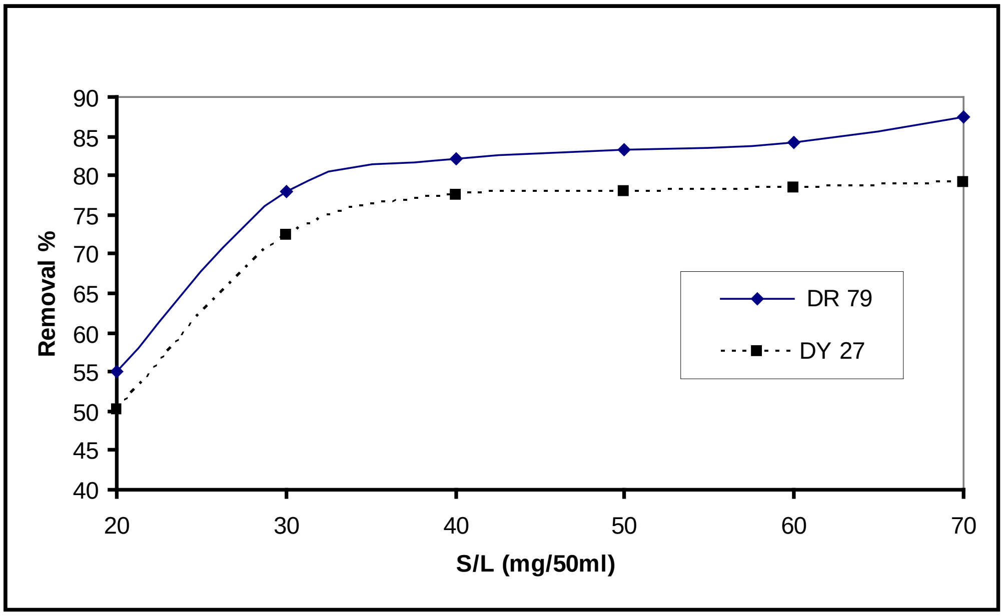


Figure 5. **Effect of adsorbent dose on the adsorption of dyes on OP conditions C_o=60 mg/L, pH 3, T 25°C, and contact time 60 min.**

Obviously, the adsorption efficiency increased as the S/L ratio increased, with a less increase when S/L ratio surpassed 40mg/50 ml. When S/L ratio is small, the active sites for binding adsorbate on the adsorbent surface are less. So the adsorption efficiency is low, whereas the S/L ratio increased in the increment of adsorption efficiency until saturation. (Liang, S.et.al. 2009). By the way, considering the cost, the optimum S/L ratio of 80 mg/50 ml was chosen in this study

3-5. Adsorption dynamics

The adsorption kinetics was investigated for better understanding of the dynamics of adsorption of dye ions onto OP adsorbent. The observed rapid kinetics has significant practical importance as it could be used for the scale-up to a larger system.

Various models such as pseudo-first and second kinetic equations and intra-particle diffusion equation are used to examine the controlling mechanism of adsorption process, such as chemical reaction, diffusion control and mass transfer (Liu, Y. & Liu, Y.J. 2008; Özacar, M. et. al. 2008; Sengil, I.A. & Özacar, M. 2009).

The pseudo-first-order kinetic model known as the Lagergern equation was represented as shown in equation 3. (Lagergern, S.1898).

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} \qquad \textbf{Eq. (3)}$$

Where $\mathbf{q_t}$ and $\mathbf{q_e}$ are the amounts of ion adsorbed at time (t) and at equilibrium (mg/g), respectively, and $\mathbf{k_1}$ is the rate constant of pseudo-first-order adsorption process (min^{-1}). The values of the k_1 are presented in Table 2.

Table 2. The kinetic parameters for the adsorption of dyes on OP adsorption

Dye	Pseudo-first order		Pseudo-second order		Intrapartide diffusion	
	$K_1(min^{-1})10^2$	R^2	K_2(mg/g.min)10^3	R^2	$\mathbf{k_{int}}$ (mg/g. min) 10^2	R^2
DR 79	3.300	0.980	4.700	0.998	3.7	0.992
DY 27	4.100	0.989	5.300	0.991	3.2	0.9882

The pseudo-second – order kinetic model - was represented in equation 4. (HO, Y.S. & McKay, G. 1998).

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_t} t \qquad \textbf{Eq. (4)}$$

Where $\mathbf{k_2}$ is the equilibrium rate constant of pseudo-second-order adsorption (mg/g.min) .

The intra-particle diffusion model was also tested, whereas its initial rate of diffusion was represented as equation 5. (Annaduri, G. et. al. 2002).

$$\mathbf{q_t = k_{int}\, t^{\,1/2}. + C} \qquad \textbf{Eq. (5)}$$

Where $\mathbf{k_{int}}$ is the intra-particle diffusion rate constant (mg/g. min) which can be investigate from the relation between $\mathbf{q_t}$ versus $(t)^{1/2}$.

The application of the three previous models has been carried out and the adsorption kinetics of dyes were studied, whereas the rates of sorption were found to conform to pseudo-second order kinetics with good correlation ($R^2 \geq 0.99$) as shown in Table 2.

3-6. Adsorption isotherms

Adsorption isotherms are basic requirements for the design of adsorption systems. These data provide information about the capacity of the adsorbent or the amount required for removing a unit mass of pollutant under the system concentrations. Two most common isotherm equations namely, Langmuir and Freundlich have been tested in the present study to analyze the equilibrium data of solute between adsorbent and solution. Based on the assumption that all adsorption sites are equivalent and adsorption in active sites is independent of whether the adjacent is occupied, the linear form of Langmuir adsorption can be expressed as shown in equation 6. (Langmuir, I. 1918).

$$\frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{C_e}{Q_o} \qquad \textbf{Eq. (6)}$$

Where $\mathbf{C_e}$ is the equilibrium concentration **mg/L,** $\mathbf{q_e}$ is the mono-layer adsorption capacity of adsorbent (mg/g) and $\mathbf{Q_o}$, b are Langmuir constants related to adsorption capacity and energy of adsorption, respectively.

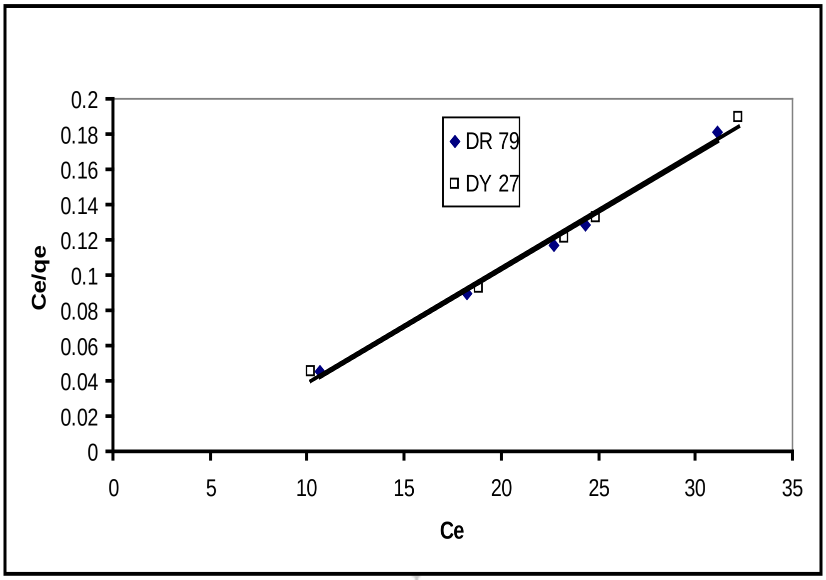


Figure 6. Langmuir isotherm on the adsorption of dyes on OP, conditions. pH 3, T 25°C, ms 40mg/50ml contact time 60 min.

The linear plots of $\mathbf{C_e/q_e}$ versus $\mathbf{C_e}$ shows that the adsorption obeys Langmuir isotherm model as illustrated in Figure 6. $\mathbf{Q_o}$ and b were determined from the slope and intercepted of the plot as presented in Table 3. The essential characteristics of Langmuir isotherm can be expressed in terms of dimensional less constant separation factor for equilibrium parameters, whereas $\mathbf{R_L}$ was defined as shown in equation 7:

$$R_L = \frac{1}{1+bC_{\max}} \qquad \textbf{Eq. (7)}$$

Where $\mathbf{C_{max,}}$ is the highest initial dye concentration in the dye solution (mg/L)

Through the mathematical calculation, the parameter $\mathbf{R_L}$ values indicates the shape of isotherm to be irreversible (R_L=0), favorable ($0<R_L<1$), linear (R_L=1), or unfavorable (R_L>1) Frendlich isotherm model was also used to explain the observed phenomenon, and presented as shown in equation 8.

$$\log q_e = \log k_f + 1/n \ \log C_e \qquad \textbf{Eq. (8)}$$

Where $\mathbf{k_f}$ and **n** [where **is n?**] are the Frendlich adsorption constants, which can be determined by the linear plot of **log** $\mathbf{q_e}$ versus log $\mathbf{C_e}$**,** as shown in Figure 7.

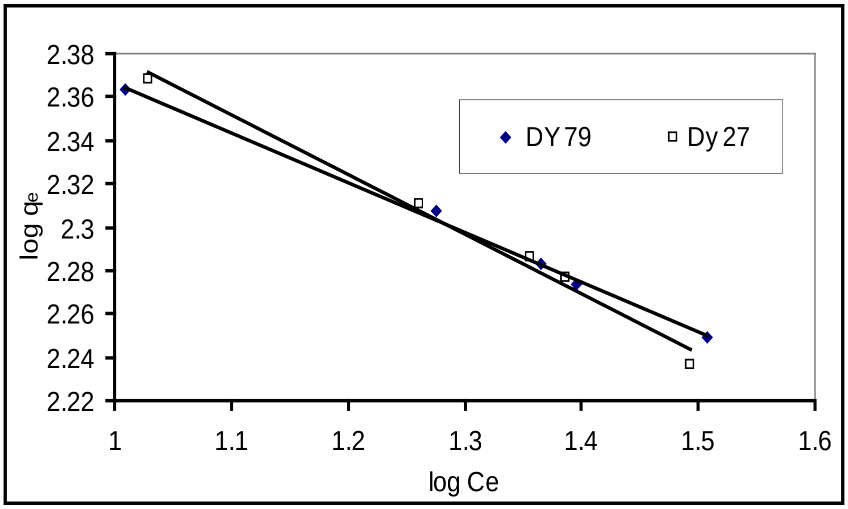


Figure7. Frendlich isotherm on the adsorption of dyes on OP, conditions pH 3, T 25C, ms 40mg/50ml, contact time 60 min.

Table 3. A comparison of Langmuir and Freundlich Constants for absorption of dyes on (OP)

Dye	Langmuir model			Freundlich model		
	Q_o	b	R^2	K_f	1/n	R^2
DR 79	151.50	0.236	0.990	451.860	0.270	0.987
DY 27	153.85	0.247	0.994	395.370	0.230	0.997

A sit can be seen in table 3, which indicates the adsorption of dyes onto OP that obeyed both Langmuir and Frendlich isotherms.

3-7. Desorption studies

Desorption studies help to elucidate the mechanism and recovery of the adsorbate and adsorbent. The regeneration of the adsorbent may lead the treatment process to be economical. At dye concentration of 20 mg/L, as the desorbing pH value was increased from 2.0-8.0 the percent of desorpton increased from 20 at pH 2 to 82.5 at pH 8 for DR 79 and from 17.5 at pH 2 to 64.5 at pH 8 for Dy 27 as shown in figure 8.

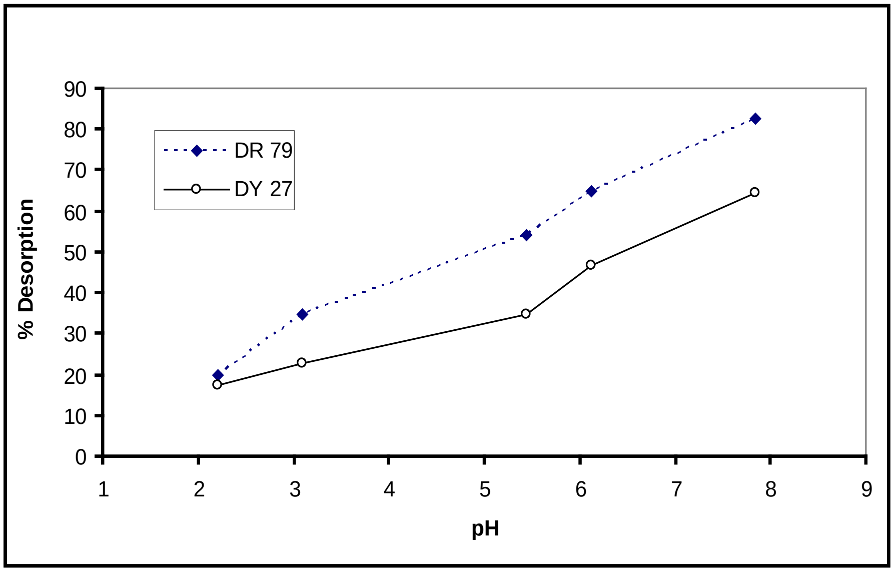


Figure 8. Effect of pH on desorption of dyes on OP

By increasing the pH value of the system, the number of the negatively charged sites on the adsorption favors increased, decreasing the desorption of anion dyes due to the electrostatic repulsion (Arami, M. et. al. 2006).

Conclusion

Concerning the environmental awareness and the economical point of view, this research was carried out to detect one of the natural waste materials to be an adsorbent for the color textile effluents. Orange Peel (OP), which discarded as a waste material from fruit stall possessed a considerable potential for the removal of anionic dyes from colored textile effluents. The pH value had a great influence on the adsorption efficiency, whereas at low pH value the adsorption efficiency was relatively high. Scanning electron micrographs (SEM) exhibited that, OP had a considerable numbers of pores where, there was a good possibility for DR 79 and Dy 27 dyes to be trapped and adsorbed into these pores. The most important factor to design and run an industrial adsorption plant is the knowledge of adsorption kinetics and isotherms. Hence, the experimental results were analyzed by using the Langmuir and Freundlich equations. The kinetics of adsorption was studied by using pseudo-first, second –order equation and intra-particle diffusion equation. It is found that pseudo-second-orders equation provided the best correlation coefficient. Desorption studies were conducted and elucidated that the recovery at the adsorbate and adsorbent might be possible in alkaline solution.

References

1. Alenor, S.; Carene, B.; Emmanuel, E.; Lambert, J.; Ehrhard’t, J.J.; & Gaspard, S., (2009). Adsorption studies of methylene blue and phenol onto vietiver roots activated carbon prepared by chemical activation. Journal of Hazardous Material, 165 (1-3), 1029-1039
2. Alparslan, S. (2003), Color removal from textile waste water by sequential anaerobic- aerobic treatment system. Master degree thesis of Natural and

Applied Sciences, Dokuz Eylul University, İZMİR, Turkey. http://www.fbe.deu.edu.tr/ALL_FILES/Tez_Arsivi/2003/YL-t1595.pdf

3. Annaduri, G.; Juang, R.S. & Lee, D. J., (2002).Use of cellulose based wastes for adsorption of dyes from aqueous solutions. Journal of Hazardous Material, 92 (3), 263-274.
4. Araceli, R.; Juan, G.; Gabriel, O. & Maria, M., (2009). Adsorption of anionic and cationic dyes on activated carbon from aqueous solutions: Equilibrium and kinetics. Journal of Hazardous Material, 172 (2-3), 1311-1320.
5. Arami, A.; Yousefi Limaee, N.,;Mahmoodi, N. M. & Tabrizi, N.S., (2005).Removal of dyes from colored textile waste water by orange peel adsorbent. Equilibrium and kinetic studies. Journal of Colloid and Interface Science, 228 (2), 371-376.
6. Arami, M.; Limall , N.Y.; Mahmood , N.M. & Tabrizi, N.S., (2006). Equilibrium and kinetic studies for adsorption of direct and acid dyes from aqueous solution by soymeal hul. Journal of Hazardous Material, 135 (1-3),171-179.
7. Beltran-Heredia, J.; Sanchez-Martin, J.; Delgado- Regalado, A. &. Jurado-Bustos, C., (2009). Removal of Alizarin Violet 3R (anthraquinonic dye) from aqueous solution by natural coagulants. Journal of Hazardous Material, 170 (1), 43-50.
8. Brown, D. (1987), Effects of colorants in the aquatic environment. Ecotoxicology and Environmental Safety, 13 (2), 139-147.
9. Chen, G.; Lei, L.; Hu. X. & Lock, P., (2003). Kinetic Study into the wet air oxidation of printing and dyeing waste water. Separation and Purification Technology, 31 (1), 71-76.
10. Demirbas,A., (2008). Heavy metal adsorption onto agro-based waste materials a review. Journal of Hazardous Material, 157 (2-3), 220-229.
11. Doulati Ardejani, F.; Badii, KH., Yousefi limaee, N.; Mahmoodi, N.M.; Arami, M., Shafaei, S.Z. & Mirhabibi, A.R., (2007). Numerical modeling and laboratory studies on the removal of Direct Red 23 and direct Red 80 dyes from textile effluents using orange peel a low – cost adsorbent. Dyes and Pigments, 73 (2), 178-185.
12. Feng, N.C.; Guo, X.Y. & Liang, S., (2009). Adsorption study of Copper (II) by chemically modified orange peel. Journal of Hazardous Material, 164 (2-3), 1286-1292.
13. Freundlich, H.M.F., (1906).Uber die adsorption in losungen. Zeitschrift für Physikalische Chemie, 57 (A), 385-470.
14. Georgiou, D.; Melidis, P.; Aivasidis, A., & Gimouho-poulos, K., (2002). Degradation of azo-reactive dyes by ultraviolet radiation in the presence of hydrogen peroxide. Dyes and pigments, 52, (2), 69-78.
15. Gregory, AR.; Elliot, S. & Kluge, P, (1991). Ames testing of direct black 3B parallel carcinogenicity. Journal of Applied Toxicology,1, 308-13
16. Hameed, B.H. & El-Khaiary, M.I., (2008). Sorption kinetics and isotherm studies of a cationic dye using agricultural waste: Broad bean peels. Journal of Hazardous Materials,154 (1-3), 639-648
17. HO, Y.S. & McKay, G., (1998). The kinetics of sorption of basic dyes from aqueous solution by sphagnum moss peat. Canadian Journal of Chemical Engineering, 76 (4), 822-827.
18. Janos, P.; Coskum, S.; Pilarova, V. & Rejnek, J., (2009). Removal of basic (methylene blue) and acid (e.g acid orange dyes from water by sorption on chemically treated wood shavings. Bioresource Technology, 100 (3), 1450-1453.
19. Lagergern, S., (1898). About the theory of so-called adsorption of soluble substance. Kunglia Svenska Vetenskapsakademiens Handlingar, 24 (4), 1-39.

20. Langmuir, I., (1918).The adsorption of gases on plane surface of glass mica and platinum. Journal of American chemical society, 40 (9), 1361-1403.
21. Liang, S.; Guo, X.Y.; Feng, N.C. & Tian, Q.H., (2009). Adsorption of Cu^{+2} and Cd^{+2} from aqueous solution by mercapto acetic acid modified orange peel. Colloids Surf B Biointerfaces, 73 (1), 10-14
22. Liang, S.; Guo, X.; Feng, N. & Tian, Q., (2010). Isotherms, kinetics and thermodynamic studies of adsorption of Cu^{+2} from aqueous solutions by Mg^{+2}/k^{+} type orange peel adsorbents. Journal of Hazardous Material, 174 (1-3), 756-762.
23. Liu, Y. & Liu, Y.J., (2008). Biosorption isotherm kinetics and thermo-dynamics. Separation and *Purification Technology*, 61 (3), 229-242.
24. Namusivayam, C. & Kavitha, D., (2002). Removal of Congo red from water by adsorption onto activated carbon prepared from cori pith, an agricultural solid waste. Dyes and pigments, 54 (1), 47-58.
25. Özacar, M.; Sengil, I.A. & Turkmenier, H., (2008). Equilibrium and kinetic data, and adsorption mechanism for adsorption of lead on to valonia tannin resin. Chemical engineering journal, 143 (1-3), 32-42.
26. Pavan, F.A.; Mazzocato, A.C.& Gushiken, Y., (2008). Removal of methylene blue dye from aqueous solution by adsorption using yellow passion fruit peel as adsorbent. Bioresource Technology, 99 (8), 3162-3165.
27. Perez Marin, A.B.; Ortuno, J.F.; Aguilar, M.I.; Meseguer, V. F.; Saez, J. & Liorens, M., (2009). Use of chemical modification to determine the binding of Cd(II) Zn(II) and Cr(III) ions by orange waste. Biochemical Engineering Journal, in press
28. Saad, S. A ; Daud, S. ; Kasim, F.H. & Saleh, M.N. (2007), Dyes removal from aquous solution by using chemical treated empty fruit bunch at various pH. The International Conference of Sustainable Materials ICoSM http://dspace.unimap.edu.my/dspace/bitstream/123456789/1175/1/Dyes%20Removal%20from%20Aqueous%20Solution
29. Sanchez Martin, J.; Gonzatez Velasco, M.; Beltran Heredia, J.; Gragera Carvajae, J.& Salguero Fernandez, J., (2010). Novel tannin based adsorbent in removing cationic dye (Methylene blue) from aqueous solution, Kinetics and equilibrium studies. Journal of Hazardous Material, 174 (1-3), 9-16.
30. Sengil, I.A. & Özacar, M., (2009). Competitive bisorption of Pb^{+2}, Cu^{+2} ions from aqueous solutions onto valonia tannin resin. Journal of Hazardous Material, 166 (2-3), 1488-1494.
31. Sotelo, J.L.; Ovejero, G.; Deigado Martinez J.A., (2002). Adsorption of lindane from water on GAC: effect of carbon loading on kinetic behavior. Chemical Engineering Journal, 87 (1), 111-120.
32. Tamez Uddin, M.D.; Akhtarul Islam, S.; Mahmoud Rukanuzzaman M.D., (2009). Adsorptive removal of methylene blue by tea waste. Journal of Hazardous Material, 164 (1), 53-60.
33. Tsui, L.S.; Roy, WR. & Gole, M.A., (2003). Removal of dissolved textile dyes from waste water by a compost sorbent. Coloration Technology, 119 (1), 14-8.
34. Weber, T.W. & Chakravorte, R.K., (1974). Pore and Solid diffusion models for fixed absorbers. AIChE Journal, 20 (2), 228.
35. Zhang, J.H.; Yan, X.; Dan-Zhao, Z.; Yu-lin, S. & Hong-Wen, G., (2010). Preparation of dye waste-barium sulfate hybrid adsorbent and application in organic waste water treatment. Journal of Hazardous Material, 175 (1-3), 179-186.