

The Potential Use of Acid Treated Dried Sunflower Seed Hull as a Biosorbent for the Removal of Textile Effluent Dye from Aqueous Solution.

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ABSTRACT: *Biosorption potential of acid treated sunflower seed hull as an alternative, low-cost biosorbent in the removal of textile effluent dye from aqueous solutions was studied. Sunflower seed hull was milled and treated with 0.05M hydrochloric acid, dried and used as adsorbents for the removal of reactive textile dyes from aqueous effluent from the cotton industries. The parameters investigated were initial solution pH (2- 10), dried sunflower seed hull (DSSH dosage (2 -25 g/L), temperature (20 – 65 °C) and initial dye concentration (1.7 – 15g/L). Batch equilibrium data were modeled by Freundlich, Langmuir and Dubinin-Radushkevich (D-R) isotherms. The sorption kinetic properties were studied using pseudo first and second order, and Elovich model. The equilibrium data best fitted the Langmuir model while the sorption kinetic data were successfully described with pseudo- second order model for DSSH.*

I. INTRODUCTION

A large quantity of industries such as textile, paper, and food processing industries discharge a large amount of colored effluent into the environment. Synthetic dyes are extensively used in the textile industry because of their favorable characteristics of being easily water soluble, cheaper to produce and easier to apply with natural fibers like wool, cotton, silk and synthetic fibers like polyesters, acrylic & rayon. These synthetic dyes have complex molecular structures, which make them more stable and difficult to biodegrade. The presence of very small amounts of dyes in water (less than 1 mg dm⁻³ for some dyes) is highly visible and undesirable. Several research reports reveal that very small quantities of dyes are highly toxic and can cause acute disorders in aquatic organisms. Uptake of effluents through food chain in aquatic organisms and human beings may cause various chromosomal fractures, respiratory, mutagenic and carcinogenic problems. Therefore, wastewater containing dyes must be appropriately treated before being discharged into the water bodies. Conventional treatment processes include precipitation, sedimentation, ultra-filtration, flotation, color irradiation, ozonation, oxidization and coagulation. However the application of the above mentioned technologies is sometimes restricted due issues including; incomplete dye removal, requirement of expensive equipment and monitoring systems, high reagent or energy requirements or generation of toxic sludge and other waste products.

Adsorption, the adhesion of molecules to a surface, has been found to be an efficient and economic process to remove dyes and other contaminants from aqueous solutions. Presently, activated carbon has been the most widely used as an effective adsorbent for the removal of dyes because of its high adsorption capacity, surface area and atmospheric properties. However, there are certain disadvantages of using activated carbons namely its high usage or operating costs and regeneration issues [Akar et al., 2009]. Consequently, a considerable amount of studies have been carried out on the development of effective, low cost and easily available alternative biosorbents. Different agricultural biomass such as saw dust (Shukla et al., 2002), tree fern (Ho et al., 2005), rice hull (Chou et al., 2001), bark (Palma et al., 2003), banana peel and orange peel (Annadurai et al., 2002), coir pith (Namasivayam et al., 2001), linseed cake (Ho et al., 2005) have been previously tried for the removal of different types of dyes, but high effective and more economical biosorbent materials are still needed.

The sunflower plant is a native of North America. It was grown by the Indians for food in North Carolina before 1600 and by New England colonists for hair oil as early as 1615. Sunflower grains are botanically defined as fruits. They are composed of a thin outer shell, the pericarp, also known as “hull”, that surrounds and contains the seed, usually named “kernel” [Trotter et al., 1973]. Today, Sunflower is the fifth most important source of edible oil after soybean, rapeseed, cotton, and peanut. The total world production of 25.8 million tonnes of sunflower seed go almost exclusively to oil extraction, providing 8.2% of total world volume, estimated at around 107 million tonnes. The rising prominence of sunflower oil in world edible oil markets has stimulated an expansion in U.S. production. One million metric tons of sunflower seeds were produced in 2011 & the U.S. planted sunflower over 1.8 million acres in 2012. Sunflower seed hulls are discarded as waste during industrial process of oil extraction and thus a large amount of sunflower hulls is generated each year. Sunflower hulls have little commercial value and become a disposal problem owing to their

low bulk density, hence the utilization of such agriculture solid waste for wastewater treatment is most desirable [NASS, 2012].

The purpose of this study is to investigate the potential of the use of an agricultural waste material, such sunflower seed hull, as an alternative, cost effective biosorbent for the removal of dye from aqueous solutions. The effects of several parameters such as pH, adsorbent dosage, temperature, and initial dye concentration were investigated.

II. EXPERIMENTAL

Preparation of Dried Sunflower seed Hull (DSSH)

Sunflower seeds were obtained from a local market, de-hulled and grinded in a coffee grinder for about 10 minutes. The sunflower seed hulls were then sieved through the ASTM #20 standard sieves. The effect of acid treatment was studied. 20g of sunflowers seed hulls was then soaked in 1000 ml of (0.05M) Hydrochloric acid (HCl). Another 20g of sunflower seed Hulls was soaked in 1000ml of (0.05M) H₂SO₄. Both solutions were then left overnight. The treated material was washed several times with distilled water until the pH of the supernatant was at a pH of above 6.5. The washed Sunflower seed hull was then dried at about 100°C for about 3 hours and stored in labeled zip-lock bags until further use.

Preparation of dye effluent solution

Concentrated dye effluent was obtained from Cotton Incorporated Cary, North Carolina. The total solid concentration of the dye solution was 73.31 g/L. 100ml of a 1:5 dilution of the concentrated dye solution was prepared and 1:10 and 1:20 dilutions were prepared from this for use in the batch experiments.

Batch Adsorption Experiments

The maximum absorbance was observed at 620 nm and was used in all experiment. The concentration of dye effluent was determined from a calibration plot of absorbance at 620nm versus concentration. Batch adsorption of dye onto the adsorbent was conducted in aqueous solutions under different operating conditions viz. pH range (2-10), DSSH (0.05-0.5 g) SSH, temperature (Room temperature - 65 °C) & initial dye concentration 3-14 g/L. Batch adsorption equilibrium studies were carried out in 50 mL plastic tubes containing known concentration of dye at 25 °C. Dye solutions (20 ml each) were regularly vortex with an optimum adsorbent dosage and at optimum pH. The samples were withdrawn at preset time intervals, and the absorbances of the solution were measured using a GENESYS 5 Scanning Spectrophotometer.

The percentage of dye removal was calculated using the following equation:

$$\% \text{ dye removal} = (C_i - C_f / C_i) * 100$$

C_i is the initial dye concentration (mg/L), C_f is the final dye concentration (mg/L).

The amount of dye adsorbed onto the adsorbent at equilibrium was calculated by using the following equation:

$$q_e = ((C_i - C_e) V) / m$$

where C_e is the concentration of dye in the solution at equilibrium (mg/L), V is the volume of the solution, and m is the mass of the adsorbent (g).

The obtained experimental isotherm data were applied to different models such as Langmuir, Freundlich, & Dubinin – Radushkevich to determine the type of adsorption process. The batch adsorption kinetic studies were carried out on a solution of different initial dye concentrations with an optimum dosage at the optimum pH and at 25 °C. The adsorption kinetic data was applied to the pseudo-first-order, pseudo-second-order and Elovich model (Tsezos, M. 2001).

III. RESULTS AND DISCUSSION

Effect of initial solution pH on adsorption.

The pH of the solution is one of the most important operating parameters that affect the adsorption of dye ([Donghee Park 2010]). In this study, the effect of initial solution pH on the removal of dye using DSSH with different initial solution pH was studied and the effect of pH on adsorption capacity and % dye adsorbed are shown in figure 1. The effect of solution pH on the adsorption of dye onto HCl treated DSSH was studied by changing the pH of the solution from 2.0 – 10.0. The results indicate that the removal of dye increased with a decrease in solution pH and reached a maximum/ optimum value at pH 2.0. The pH influences surface properties of the biosorbent by way of functional group association and surface charges. Additionally, the acidity of the solution affects the competition of dye ions and hydrogen ions for the active sites on the adsorbent surface (Crini & Bardot, 2008).

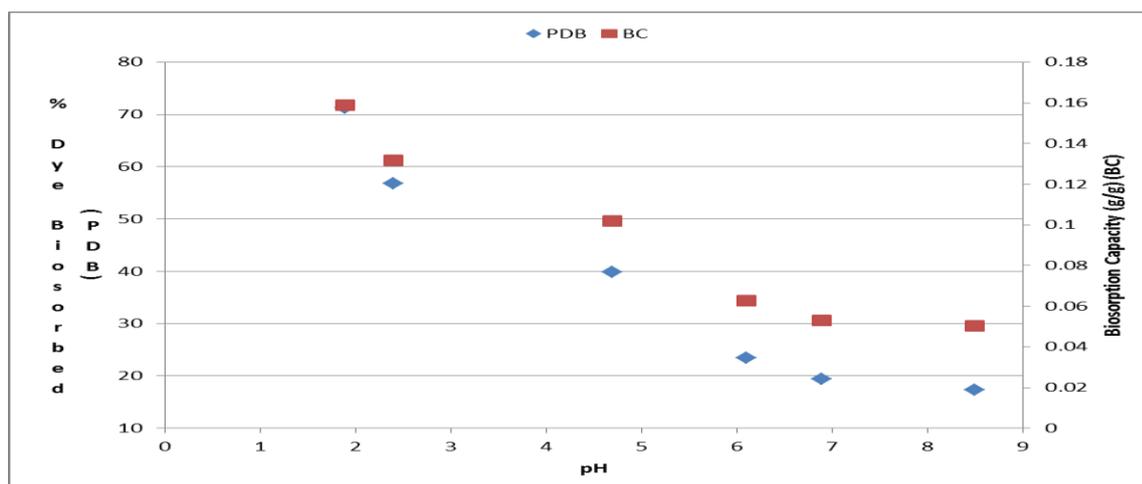


Figure 1. Effect of initial pH on adsorption of dye by DSSH

Effect of DSSH Dosage on adsorption

The effect of adsorbent dosage on the removal of dye from aqueous solution was investigated by varying the DSSH dosage ranging from 2 to 25 g/L while keeping the concentration of dye, contact time and pH constant at 2.8 g/L, 120min and 2.0 respectively. The results shown in figure 2 revealed that the removal of dye increased with an increase in DSSH dosage. This may have been as a result of the increase in number of active sites on the adsorbent surface with increasing dosage amount, resulting in an increase in dye removal. Beyond a certain amount, 20g/L, the percentage removal of dye leveled off at 90%. This may be due to a reduction in the concentration gradient of the dye molecules. [Khataee et al. 2009]

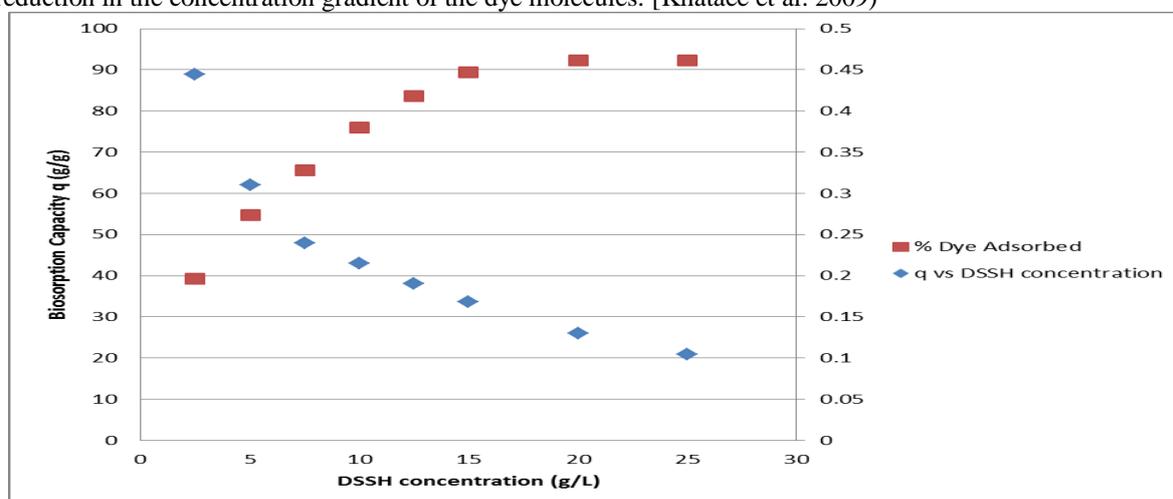


Figure 2. Effect of DSSH dosage on adsorption at 25°C and dye concentration of 3.6 g/L.

Effect of Temperature on adsorption

The effect of temperature on adsorption is shown in figure 3. The results indicate that there was an increase in biosorption with an increase in solution temperature. This may be as a result of increase rate of diffusion of adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent particles, owing to the decrease in viscosity of the solution & the change in the equilibrium capacity of the adsorbent for a particular adsorbate. Additionally, an increasing number of molecules may also acquire sufficient energy to undergo an interaction with active sites at the sunflower seed hull's surface. Furthermore, increasing the temperature may produce a swelling effect within the internal structure of the Sunflower seed hull which enables dyes to penetrate further. An increase in adsorption capacity with increasing temperatures implies the enthalpy change has positive values, indicating that the adsorption process of dye onto DSSH was endothermic, thereby suggesting the possibility of bonding between the adsorbate & adsorbent Ramanraju et al. 2014.

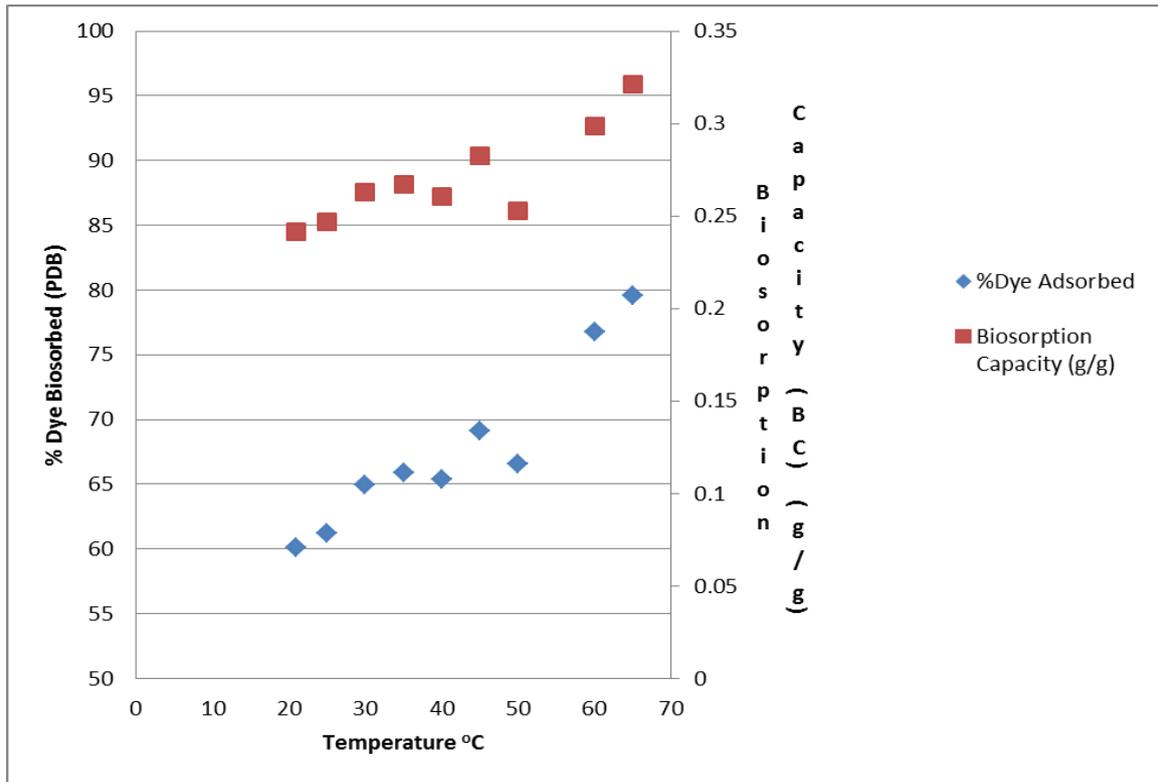


Figure 3. Effect of Temperature on the adsorption of dye by DSSH pH 2.0, DSSH 20g/L Dye concentration 8g/L.

Effect of Initial Dye Concentration

The effect of initial dye concentration (2 - 16 g/L) on the adsorption of dye by DSSH was studied as shown in figure 4. As can be seen from the figure the removal of dye decreases with an increase in dye concentration. This may be due to the saturation of the available active sites on the sunflower seed hull, beyond a certain concentration of dye. For a fixed amount of sunflower seed hull at a low dye concentration, adsorption of the dye proceeds faster due to less number of dye ions in the solution. As initial concentration increased, the number of dye ions in the solution increases against a fixed amount of available active sites, thus leading to a decrease in dye removal with an increase in initial dye concentration (Khataee et al. , 2010).

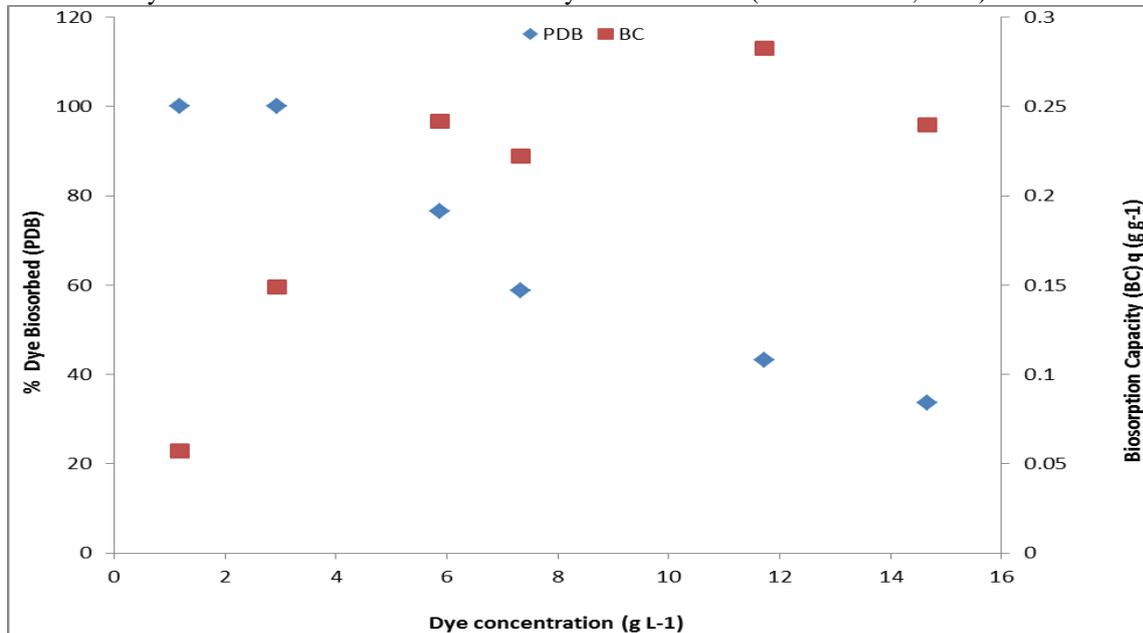


Figure 4. Effect of initial dye concentration on adsorption off dye by DSSH ; pH 2.0 T = 25°C, DSSH 20g/L.

Modelling Adsorption Isotherms

The data obtained from biosorption experiments are generally represented with equilibrium isotherms. These provide more important parameters for designing and optimizing of the biosorption systems. Different isotherm models can be used to determine the biosorption characteristics of a biosorbent. In the present study the textile wastewater dye biosorption was analyzed by three different models Langmuir, Freundlich and Dubinin–Radushkevich (D–R). The data were fitted and the calculated isotherm constants are presented in Table 1. The fundamental assumption of the Langmuir isotherm model is that biosorption takes place at specific sites within the biosorbent. Once a biosorbate occupies a binding site, no further biosorption occurs at this site. In other words Langmuir model assumes that biosorbed layer is one molecule thickness (monolayer biosorption) (Langmuir , 1918).

$$q_e = q_{max}K_L C_e / (1 + K_L C_e) \dots\dots\dots (1)$$

where q_e is the equilibrium biosorption capacity of textile wastewater dye (g/g), C_e is the equilibrium wastewater dye concentration in the solution (g/L), q_{max} is the monolayer biosorption capacity of the biosorbent (g/g), and K_L is the Langmuir constant (L/g) and is related to the free energy of biosorption. The linearized form of the Langmuir equation is given below:

$$C_e/q_e = C_e/q_{max} + (1/q_{max}K_L) \dots\dots\dots (2)$$

The effect of isotherm shape has been discussed (Hall et al., 1966) with a view to predict whether a biosorption system is favorable or unfavorable. The essential feature of the Langmuir isotherm can be expressed by means of ‘ R_L ’, a dimensionless constant referred to as separation factor or equilibrium parameter. R_L is calculated by using Equation 3.

$$R_L = 1 / (1 + K_L C_o) \dots\dots\dots (3)$$

where C_o is the initial dye concentration (g/L). The value of R_L calculated using the above equation is incorporated in Table 1. If the R_L values lie between 0 and 1, the biosorption process is considered to be favorable (Hall et al., 1966). Values of K_L and q_{max} are obtained from the intercept and slope of the linear plots at various dye concentration in Figure 5 and are represented in Table 1. The R_L values in this study were in the range 0.007- 0.036, indicating that the biosorption process is favorable.

The Freundlich isotherm is an empirical equation assuming that the adsorption process becomes on heterogeneous surfaces and adsorption capacity is related to the concentration of Azure dye at equilibrium. The Freundlich isotherm equation is generally expressed as follows (Freundlich, 1906):

$$q_e = K_F C_e^{1/n} \dots\dots\dots (4)$$

The linearized form is:

$$\ln q_e = \ln K_F + 1/n \ln C_e \dots\dots\dots (5)$$

where q_e is the equilibrium biosorption capacity on DSSH (g/g); C_e is the equilibrium dye concentration in the solution (g/L); K_F (L/g)ⁿ and n (dimensionless Freundlich isotherm constant being indicative of the extent of the biosorption and the degree of nonlinearity between solution concentration and biosorption, respectively. Values of K_F and n are obtained from the intercept and slope of the linear plots at various dye concentration in Figure 6 and are shown in Table 1. The numerical values of Freundlich constant of n was 8.62, which is a measure of the deviation from linearity of the biosorption (Malik, 2004). It is greater than unity indicating that textile effluent dye is favorably adsorbed by DSSH.

The Dubinin–Radushkevich (D–R) isotherm is more general than the Langmuir isotherm since it does not assume a homogeneous surface or constant biosorption potential (Dubinin and Radushkevich, (1947). The D–R isotherm model describes the biosorption nature of the sorbate on the biosorbent and it is used to calculate the mean free energy of biosorption. The characteristic biosorption curve is related to the porous structure of the biosorbent according to this model. The linearized form of (D–R) equation can be written as:

$$\ln q_e = \ln q_m - \beta \epsilon^2 \dots\dots\dots (6)$$

where q_m is the biosorption capacity of the biosorbent (g/g), β is a constant related to the biosorption energy, ϵ is Polanyi potential which can be presented as:

$$\epsilon = RT \ln(1 + 1/C_e) \dots\dots\dots(7)$$

where R is the universal gas constant (8.314 J/ mol/ K) and T is the temperature (K). The values of D–R isotherm constants, β and q_m are obtained from the slope and intercept of the linearized D-R plot (Fig. 7). The constant β gives an idea about the mean free energy of biosorption and E value can be computed using the following relationship

$$E = 1/(2\beta)^{0.5} \dots\dots\dots(8)$$

The magnitude of E value characterize the type of the biosorption as chemical ion exchange ($E = 8-16$ kJ/ mole) (Helfferich, 1962), or physical sorption ($E < 8$ kJ/mole) (Onyango, et al. 2004). The mean free energy of biosorption (E) was calculated to be 6.23 kJ/mole, which implies that the biosorption of textile effluent dye on DSSH may be considered as physical biosorption and q_m the theoretical saturation capacity was 0.247 g/g. According to the correlation coefficient r^2 values in Table 1 the Langmuir model was determined to be the best fit for this experiment and thus better describes the adsorption of dye onto DSSH.

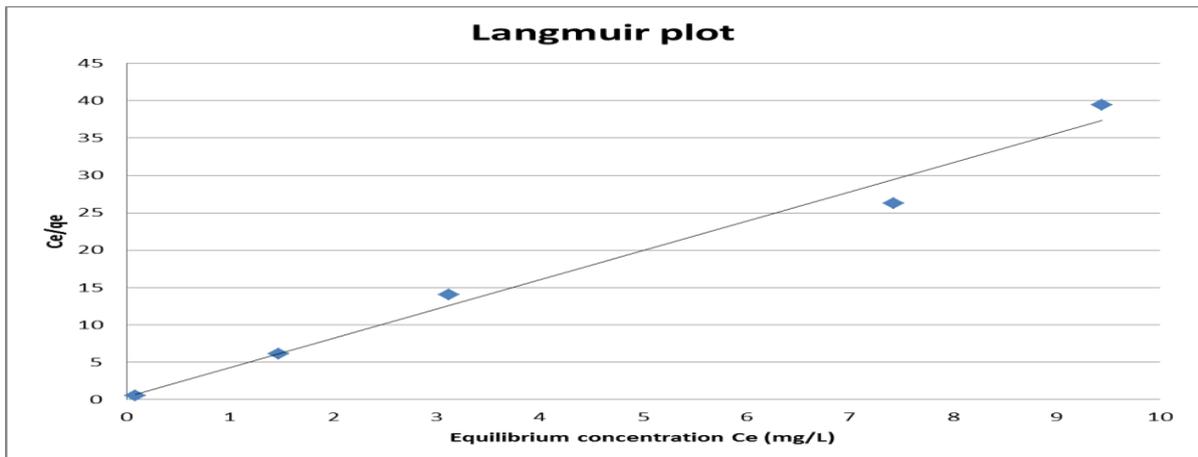


Figure 5. Langmuir plot for the biosorption of textile effluent dye by DSSH at 25 °C.

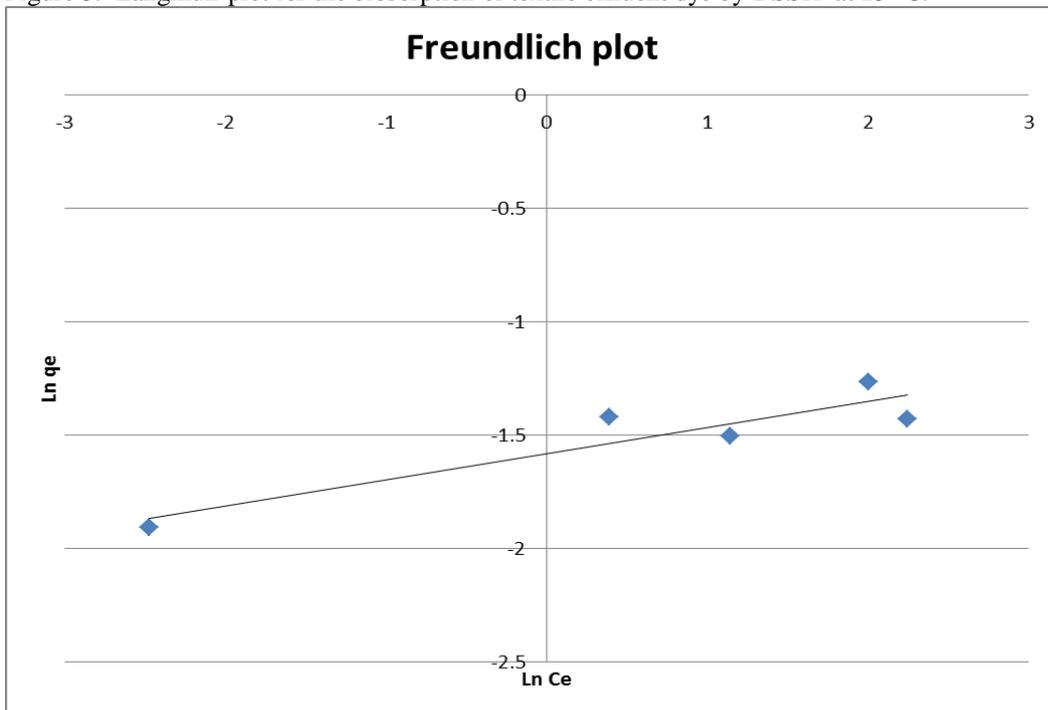


Figure 6. Freundlich plot for the biosorption of textile effluent dye by DSSH at 25 °C.

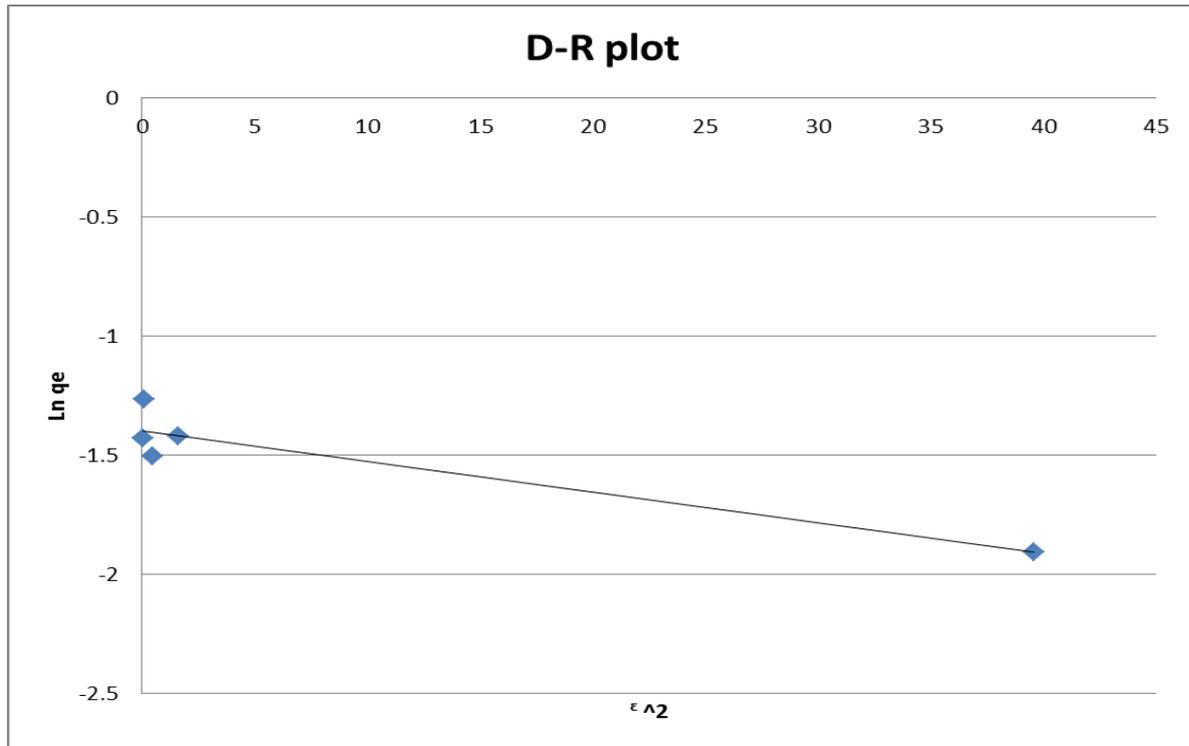


Figure 7. Dubinin-Radushkevich plot for the biosorption of textile effluent dye by DSSH at 25 °C

Table 1 Biosorption isotherm constants for the biosorption of textile effluent dye by DSSK at 25 oC

Isotherm Model	Parameter	Value	Correlation Coefficient R ²
Langmuir	Q _m (g/g)	3.91	0.983
	K _L (L/g)	0.428	
	R _L	0.007 -0.036	
Freundlich	K _F (L/g) ⁿ	0.206	0.842
	n	8.62	
Dubinin Raduskevich	q _m (g/g)	0.247	0.873
	E (Kj/mole)	6.23	

Modelling Adsorption Kinetics

Kinetics studies provide a valuable description of the reaction pathway which controls the residence time of adsorbate uptake at the solid-solution interface. The rate of adsorption characterizes whether the DSSH is a good economical operational treatment process for dye effluent. The actual rate of adsorption of dye ions can vary from a few seconds to several minutes to reach equilibrium, which is dependent on the several properties of this adsorbent. Kinetics of adsorption on the dried sunflower seed hull (DSSH) was analyzed using pseudo first-order, pseudo second-order, and Elovich Model.

The first-order rate equation can be written as follow (Kirani et al. 2006):

$$1/q_t = 1/q_1 + k_1/q_1 t \dots\dots\dots (8)$$

where q₁ and q_t are the amounts of Textile effluent dye biosorbed at equilibrium and at time t, in gg⁻¹ and k₁ is the first-order rate constant (min⁻¹) for biosorption. Values of k₁ calculated from the slopes of the plots of 1/q_t versus 1/t are given in Table 2 (figure 8). It was found that the correlation coefficients for the first-order model are lower than that of the pseudo-second-order model. This implies that the biosorption process does not follow first-order kinetics.

The pseudo-second-order kinetic model (Kirani et al. 2006) is expressed as:

$$t/q_t = 1/k_2 q_2^2 + t/q_2 \dots\dots\dots (9)$$

where q₂ is the maximum biosorption capacity (g g⁻¹) for the pseudo-second-order biosorption, q_t the amount of textile effluent dye biosorbed at equilibrium at time t (g g⁻¹) and k₂ is the equilibrium rate constant of pseudo-second-order biosorption (g g⁻¹ min⁻¹). Values of k₂ and q₂ were calculated from the plot of t/q_t against t (Fig. 9). These parameters are summarized in Table 2. The calculated q₂ values agree with experimental q values and the correlation coefficients for the pseudo-second order kinetic

plots were very high. These results suggested that the biosorption system studied follows to the pseudo-second order kinetic model. This suggests that the adsorption of dye onto the surface of DSSH is due to physicochemical interactions between the two phases (Tsezos, M. 2001).

The simplified Elovich equation is generally expressed as (Akar et al. 2011, Rajkumar et al. 2013):

$$q_t = 1/\beta \ln(\alpha\beta) + 1/\beta \ln t \dots \dots \dots (10)$$

where α is the initial biosorption rate ($gg^{-1}min^{-1}$), and the parameter β is related to the extent of surface coverage and activation energy for chemisorption(gg^{-1})

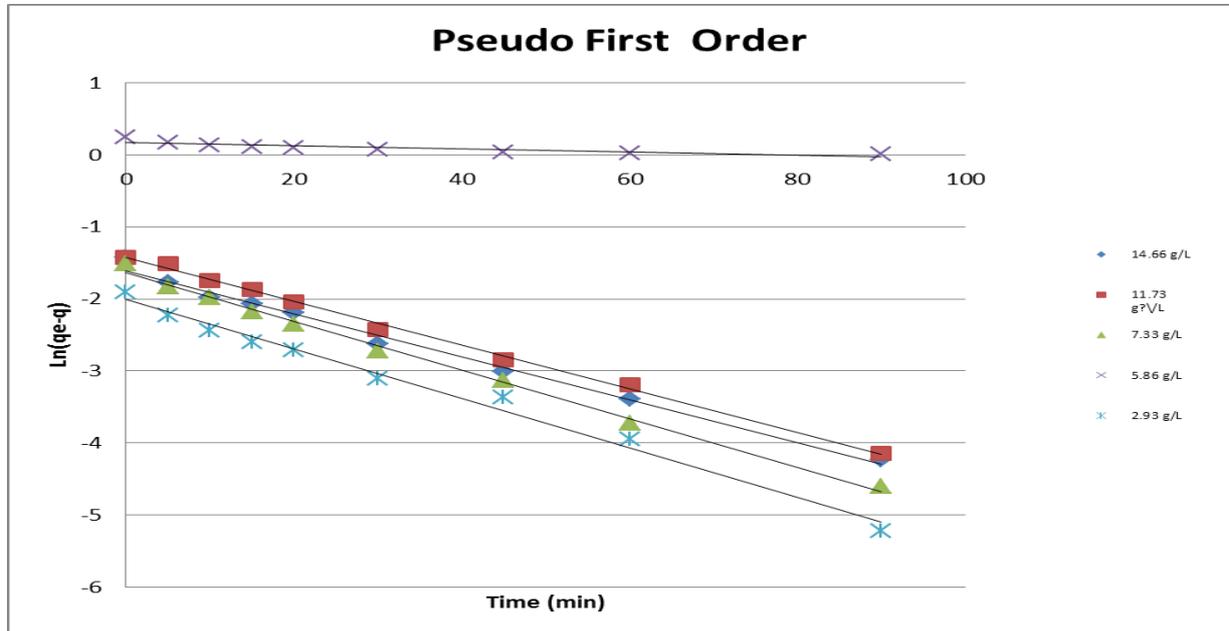


Figure 8. Pseudo-First-order kinetic plots for the biosorption of textile effluent dye onto DSSH 25 °C.

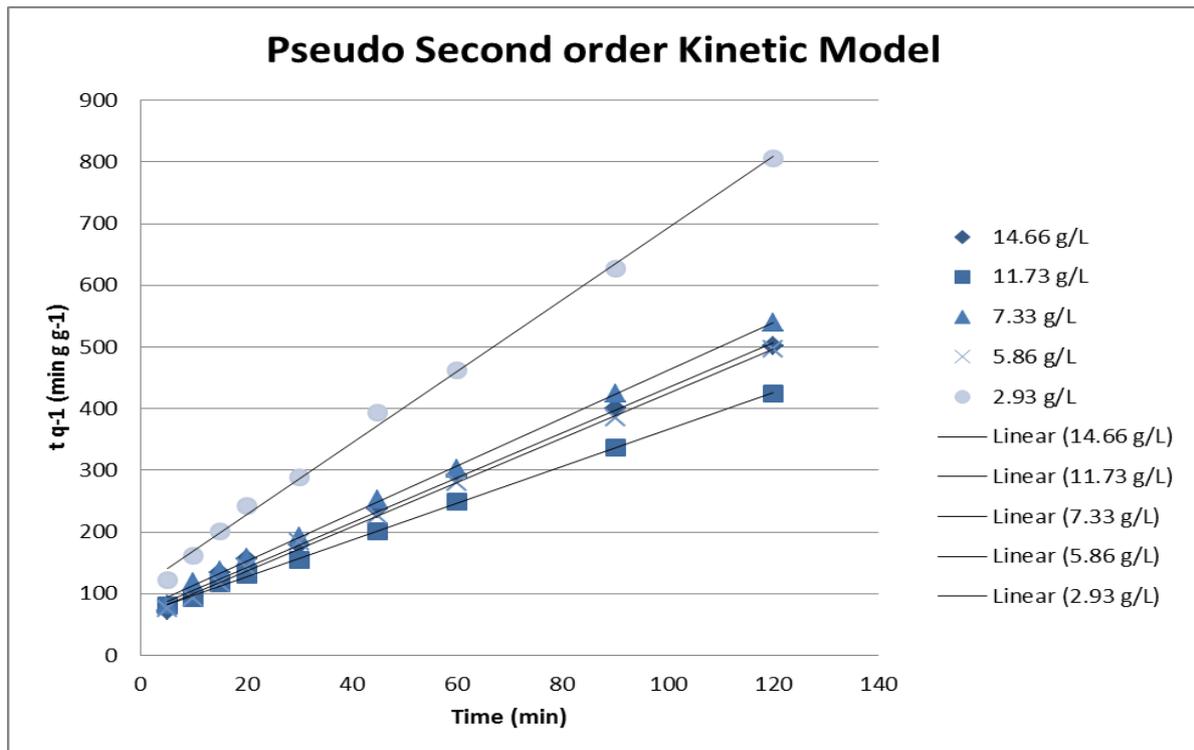


Figure 9. Pseudo-second-order kinetic plots for the biosorption of textile effluent dye onto DSSH 25 °C.

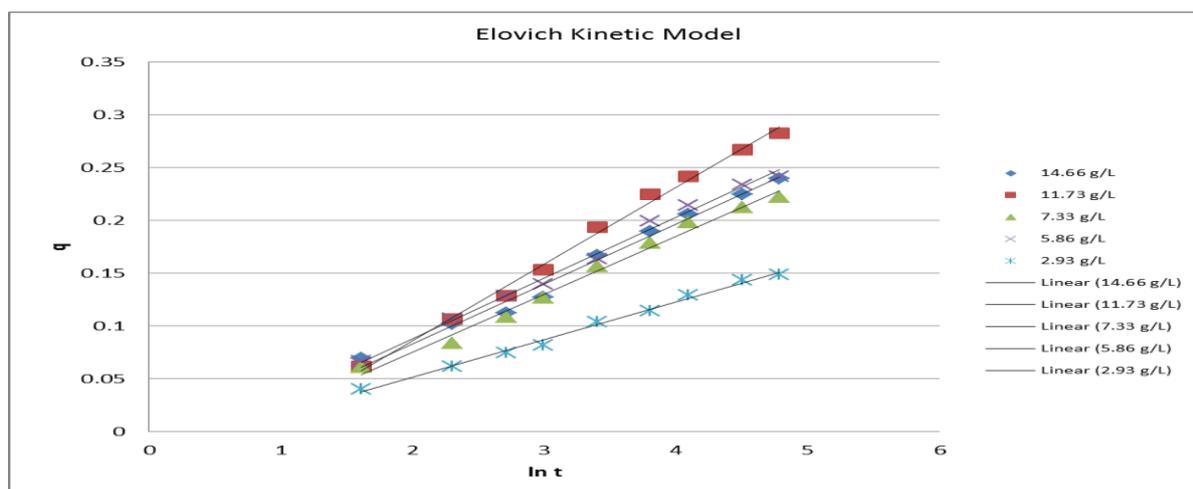


Figure 10. Elovich kinetic plots for the biosorption of textile effluent dye onto DSSH 25 °C.

Table 2. Kinetic model constants for the biosorption of textile effluent dye onto DSSH at 25 °C .

Dye Concentration (g/L)	Pseudo-first-order model			Pseudo-second-order model			Elovich model		
	k_1 (min ⁻¹)	q_e (gg ⁻¹)	R^2	k_2 (gg ⁻¹)	q_e (gg ⁻¹)	R^2	α (gg ⁻¹ min ⁻¹)	β (gg ⁻¹)	R^2
14.66	0.0298	0.200	0.990	0.190	0.275	0.996	0.0335	17.73	0.986
11.73	0.0304	0.240	0.997	0.132	0.335	0.999	0.0322	13.81	0.995
7.33	0.0337	0.195	0.996	0.199	0.258	0.999	0.0295	18.25	0.989
5.86	0.0022	1.186	0.881	0.205	0.277	0.998	0.0364	17.45	0.993
2.93	0.0343	0.134	0.889	0.301	0.172	0.997	0.0206	28.01	0.994

CONCLUSION

The potential use of dried sunflower seed hull for the biosorption of dye from aqueous solutions was successfully investigated. The optimum biosorption conditions were determined, such as pH, biosorbent dosage. Biosorption of textile effluent dye increased with a decrease in the pH of the solution. Biosorption also increased with increase in biosorbent dosage as well as increase in temperature, but decreased with increase in initial dye concentration. Biosorption process followed the pseudo second-order kinetic model and Langmuir isotherm model under the studied concentration range.

REFERENCES

- [1]. Akar, S.T., Gorgulu, A., Akar, T. & Celik, S. (2011). Decolorization of reactive Blue 49 contaminated solution by *Capsicum annum* seeds: Batch and continuous mode biosorption applications Chemical Engineering Journal 168: 125-133.
- [2]. Akar, S.T., Safa Özcan, A., Akara, T., Özcan, A., and Kaynak, Z. (2009). Biosorption of a reactive textile dye from aqueous solutions utilizing an agro-waste. Desalination, 249: 757-761.
- [3]. Annadurai, G., Juang, R.S., & Lee, D.J. (2002). Use of cellulose-based wastes for adsorption of dyes from aqueous solutions. J. hazard. Mater. B92: 263-274.
- [4]. Bailey, S.E., Olin, T.J., Bricka, M., & Adrian, D.D. (1999). A review of potentially low-cost sorbents for heavy metals. Water Res. 33: 2469-2479.
- [5]. Chern, J.M., & Wu, C.H. (2001). Desorption of dye from activated carbon beds: effects of temperature, pH and alcohol. Water Res. 35: 4159-4165.
- [6]. Chou, K.S., Tsai, J.C., & Lo, C.T., (2001). The adsorption of Congo red and vacuum pump oil by rice hull ash. Bioresour. Technol. 78: 217-219.
- [7]. Crini, G. & Badot, P.M. (2008). Application of chitosan a natural aminopolysaccharide for dye removal from aqueous solution by adsorption processes using batch studies: A review of recent literature. Progress in polymer Science, 33:399-447.
- [8]. Donghee Park, (2010). Biotechnology and Bioprocess Engineering, 15: 86-102.
- [9]. Dubinin, M.M. & Raduskhevich, L.V. (1947) Proc.Acad.Sci.U.S.S.RPhys.Chem. Sect. 55 : 331-333..
- [10]. Freundlich, H.M.F. (1906) "Über die adsorption in losungen, Z. Phys. Chem. 57: 385-470.
- [11]. Helfferich, F. (1962) Ion Exchange, McGraw-Hill, New York.
- [12]. Ho, Y.S., Chiang, T.H., Hsueh, Y.M. (2005). Removal of basic dye from aqueous solutions using tree fern as a biosorbent. Process Biochem. 40: 119-124.
- [13]. Khataee, A.R., Ayazloo, M., & Pourhassan, M. (2009). Biological decolorization of C.I. Basic Green 4 solution by *Chlorella* sp.: effect of operational parameters. Chinese J. Appl. Env. Biol. 15: 110-114.
- [14]. Khataee, A.R., Dehghan, G., Ebadi, A., Zareei, M., & Pouhassan, M. (2010). Biological treatment of a dye solution by Macroalgae Char asp. : Effect of operational parameters, intermediates identification and artificial neural network modelling. Bioresource Technology, 101: 2252-2258.

- [15]. Khattri, S.D., Singh, M.K. (1999). Color removal from dye wastewater using sugar cane dust as an adsorbent. *Adsorp. Sci. Technol.* 17: 269–282.
- [16]. Kirani, I., Akar, T., Safa Ozcan, A, Ozcan, A, & Tunali, S. (2006). Biosorption kinetics and isotherm studies of Acid Red 57 by dried *Cephalosporium aphidicola* cells from aqueous solutions. *Biochemical Engineering Journal* 31:197–203
- [17]. Langmuir, I. (1918) The adsorption of gases on plane surfaces of glass, mica and platinum, *J. Am. Chem. Soc.* 40: 1361–1403.
- [18]. Malik, P.K. (2004). Dye removal from wastewater using activated carbon developed from sawdust adsorption equilibrium and kinetics, *J. Hazard. Mater.* 113: 81–88.
- [19]. NSA. (2014). <http://www.sunflowernsa.com/stats/us-supply/>
- [20]. Namasivayam, C., Dinesh Kumar, M., Selvi, K., Begum Ashruffunissa, R., Vanathi, T., Yamuna, R.T., (2001). Waste coir pith—a potential biomass for the treatment of dyeing wastewaters. *Biomass Bioenergy* 21: 477–483.
- [21]. Nassar, M., Magdy, Y.H., (1997). Removal of different basic dyes from aqueous solutions by adsorption on palm-fruit bunch particles. *Chem. Eng. J.* 66: 223–226.
- [22]. Onyango, M.S., Kojima, Y., Aoyi, O., Bernardo, E.C., Matsuda, H. (2004). Adsorption equilibrium modeling and solution chemistry dependence of fluoride removal from water by trivalent-cation-exchanged zeolite F-9, *J. Colloids Interface Sci.* 279: 341–350.
- [23]. Ozacar, M., Sengil, A.I., (2002).. Adsorption of acid dyes from aqueous solutions by calcined alunite and granular activated carbon. *Adsorption* 8: 301–308.
- [24]. Palma, G., Freer, J., Baeza, J., (2003). Removal of metal ions by modified *Pinus radiata* bark and tannins from water solutions. *Water Res.* 37: 4974–4980.
- [25]. Pokhrel, D., Viraraghavan, T., (2004). Treatment of pulp and paper mill wastewater—a review. *Sci. Total Environ.* 333: 37–58.
- [26]. Rajkumar, P., Kumar, P.S., Kirupha, S.D., Vidhyadevi, T., Nandagopal, J. & Sivanesan, S. (2013). Adsorption of Pb(II) ions onto surface modified *Guazuma ulmifolia* seeds and Batch Adsorber Design. *Environmental Progress & Sustainable Energy* 32: 307 – 316.
- [27]. Ramanaju, B., Reddy, P. M. K., & Subrahmanyam, C. (2014) Low Cost adsorbents from agricultural wastes for removal of dyes. *Environmental Progress & Sustainable Energy* 33: 38-46.
- [28]. Shukla, A., Zhang, Y.H., Dubey, P., Margrave, J.L., Shukla, S.S., (2002). The role of sawdust in the removal of unwanted materials from water. *J. Hazardous Mater.* B95: 137–152.
- [29]. Trotter, W.K., Doty, Jr. H.O., Givan, W.D. & Lawler, J.V. (1973).. Potential for Oilseed sunflowers in the United States. US Department of Agriculture Economic Research Service AER 237.
- [30]. Tsezos, M. (2001). Biosorption of metals: the experience accumulated and the outlook for technology development. *Hydrometallurgy* 59: 241-243.