APPLICATION OF SPENT TEA LEAVES AS AN EFFICIENT LOW COST BIOSORBENT FOR REMOVAL OF ANIONIC SURFACTANTS FROM AQUEOUS SOLUTIONS

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In this research, biomaterial wastes such as spent black tea leaves (SBTL) spent green tea leaves (SGTL) as well as sawdust (SD) obtained from Narra wood were used to remove sodium dodecyl sulfate (SDS) from aqueous solutions. The effect of pH, temperature, amount of adsorbent and initial concentration of SDS has been examined. The result indicated that the SDS can be significantly adsorbed by the used biosorbents at their natural pH values. Equilibrium and kinetics studies were carried out for the adsorbents to assess the adsorption equilibrium model that they followed. The correlation coefficients were determined by linear regression analysis, and compared. The removal efficiency, maximum adsorption capacity and cost were the prime parameters for the selection of the adsorbents in this study. Among the examined adsorbents and considering all parameters, SBTL showed the higher performance for SDS removal.

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Introduction

Surfactants are one of the major components in the formulation of various industrial and household products. There are four classes (cationic, anionic, amphoteric and non-ionic) based on the ionic charge (if present) of the hydrophilic portion of the surfactant in an aqueous solution [1]. Many industrial effluents such as cosmetic and detergent industries, laundry and car washing services contain mixtures of surfactants.[2-5]

These applications of the surfactant, increasing its discharge in the wastewater, produce foam and enter into the underground water resources and constituting an ecological risk for aquatic organism. They also create many health hazards like dermatitis and harmful for the aquatic flora and fauna.[6-8] According to the Council of European Surfactants Producers Statistics the total quantity of surfactants (without soaps) consumed in Western Europe in 2002 was more than 2.5 million tons.[9] Nowadays, the role of surfactants and surfactant detergents a factor of surface and ground-water pollution is comparable to that of oil pollution of the world oceans [10]. So, the water treatment process is necessary in order to remove surfactant from industrial and domestic wastes to reduce its concentration. Some processes have already been employed for this purpose, such as aerobic and anaerobic degradation, biodegradation and sorption technique. [11-19]

Adsorption of anionic surfactant has been examined onto numerous adsorbent like activated carbon, silica gel, clay, soil, kaolinite, sand stone, granite sand, ozonation, TiO_2 photocatalytic treatment, Fenton oxidation, wet air oxidation and electrochemical treatment.[20-35] Among the various treatments for surfactant degradation, ozonization and photocatalytic methods are the most costly methods and adsorption seems to be the most efficient and cost effective.[10] In this study, we have selected three low cost, environmental friendly waste materials such as spent green tea leaves (SGTL), spent black tea leaves (SBTL) and wood sawdust (SD) as adsorbent for removal of SDS surfactant. Several experiments have been carried out to optimize the adsorption process.

Experimental

Materials and method

SDS ($M=288.38$ g mol^{-1}) surfactant solutions were prepared with deionized water. All chemical reagents used were analytical grade. Chemical structure of sodium dodecyl sulfate was shown in Figure 1.

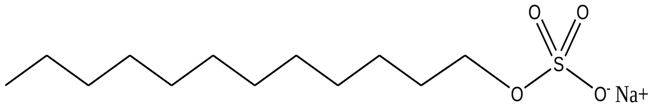

Figure 1. Molecular structure of SDS

Sawdust obtained from Narra wood (SD), spent green tea leaves (SGTL) and spent black tea leaves (SBTL) were collected from local carpentry and tea shop. The sawdust was first sieved to 35-50 mesh and washed with tap water and then washed with distilled water. SBTL and SGTL the same sawdust washed first with tap water and then with distilled water to avoid the presence of any foreigner materials. The washed materials thereafter were dried at 50 ^{0}C for 12 h and kept at room temperature. SDS (85% purity) was purchased from Merck company, and used as purchased. All the reagents *viz*., methylene blue (MB), chloroform, NaOH, HCl, and borax were of AR grade. Stock solution of SDS (100 mg L^{-1}) was prepared in distilled water. SDS test and standard solutions with required concentrations

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were prepared by diluting the stock solution appropriately. A high precision electronic balance (Sartorius) was used for weighing purpose. A pH meter (Metrohm, model 827) with a combined double junction glass electrode was utilized for pH measurement.

Measurement procedures

SDS determination was carried out using methylene blue as per standard method.[36] It forms a complex pair ion with cationic dye of MB. The complex after its formation was extracted into chloroform. The complex was formed anionic part of SDS and cationic part of MB. The color intensity of the chloroform layer gave a measure of the SDS concentration and analysed spectrophotometrically (λ_{max}=620 nm).

A calibration curve (graph of absorbance vs. concentration, known as Lambert-Beer's Law plot) was used to quantify unadsorbed SDS (Fig. 2).

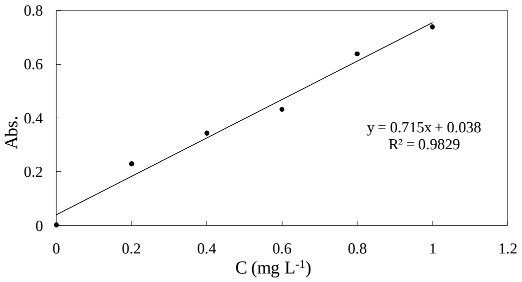

Figure 2. Calibration curve prepared for analysis of SDS

A spectrophotometer (Perkin Elmer Junior) was used for all absorbance measurements. The following equations were utilized to calculate the percentage of adsorption and the amount of adsorbed SDS (φ, in %), respectively:[37]

$$\varphi = \left(\frac{C_0 – C_e}{C}\right) \times 100 \qquad (1)$$

$$q = V\left(\frac{C_0 - C_e}{m}\right) \qquad (2)$$

where C_0 is initial SDS concentration (mg L^{-1}), C_t is the left out SDS concentration in bulk solution at time t (mg L^{-1}), V is the volume of SDS solution (L), m is adsorbent mass (g), and q is the amount of SDS adsorbed onto unit amount of the adsorbent (mg g^{-1}) at equilibrium.

Results and discussion

Effect of pH

In this investigation, fixed volumes of SDS solutions (50 mL) with initial concentration of 10 mg L^{-1} were mixed with constant amount of selected adsorbents (0.50 g). The mixtures were shaken in a mechanical shaker with 170 rpm speed at room temperature for duration of 2 h at different pHs (2-12). The results obtained have been shown in Figure 3.

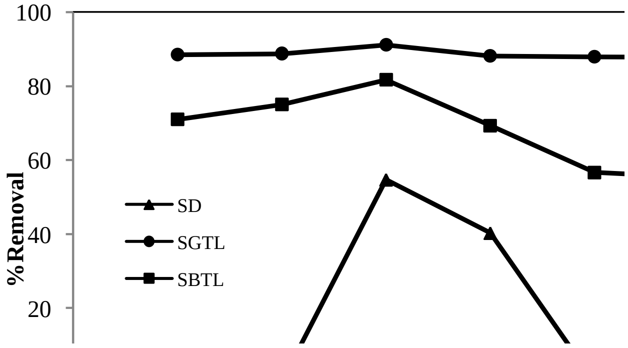

Figure 3. The effect of initial pH SDS solution on adsorption efficiency

As the results show, maximum sorption is occurred at the natural pH of selected adsorbents (pH=6-7). Among the used adsorbents, SD showed highest sensitivity to pH for SDS uptake. It seems alkaline pH media is unfavorable for adsorption of SDS. It might be due to the presence of excess OH^- ions on the surface of adsorbents that compete with the anionic surfactant (SDS) for adsorption sites. At low pH might also destroy the active sites on the surface of adsorbents which resulted to decrease in SDS removal.

Effect of dosage

In this study different weights of adsorbents (0.10-0.50 g) were contacted with 50 mL SDS solutions with known concentration (10 mg L^{-1}). The results obtained have been shown in Figure 4.

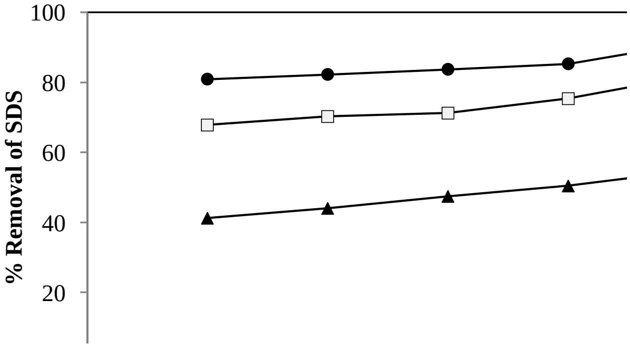

Figure 4. Effect of adsorbent dosage on removal of SDS

According to our results the percentage removal of increased with the increase in weight of adsorbents. This may be due to the increase in availability of surface active sites resulting from the increased weight of the adsorbent. However, SGTL indicated higher sorption capacity than the SD and SBTL biosorbents.

Effect of initial concentration

For performing this experiment 0.50 g of adsorbents were contacted with 50 mL of SDS solution with various concentrations (10-100 mg L^{-1}) at pH 6-7 for 2 h shaking at room temperature. The results obtained are shown in Figure 5. As the results indicate, SGTL showed the superior adsorptive behaviour compared to SD and SBTL and SD showed the least sorption capacity. However, with increasing the initial SDS concentration, removal percentages are decreased for all of the used adsorbents.

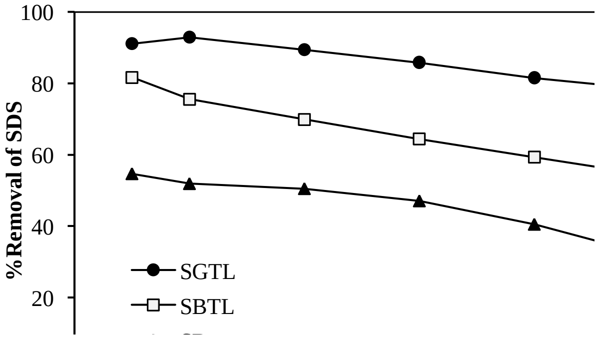

Figure 5. Effect of initial concentration of SDS on sorption by SD, SGTL and SBTL adsorbents.

Effect of contact time

In this investigation fixed amounts of adsorbents (0.50 g) were contacted with 50 mL of 10 mg L^{-1} SDS solution at natural pH values for different exposure times (15-150 minutes) accompanied by shaking at room temperature. The results obtained are shown in Figure 6. As the results exhibit, with increasing contact time up to 120 min, removal percentages of SDS were increased for three adsorbents and the equilibrium of adsorption was reached after 2 h. After 2 hours, some decrease due to desorption was observed.

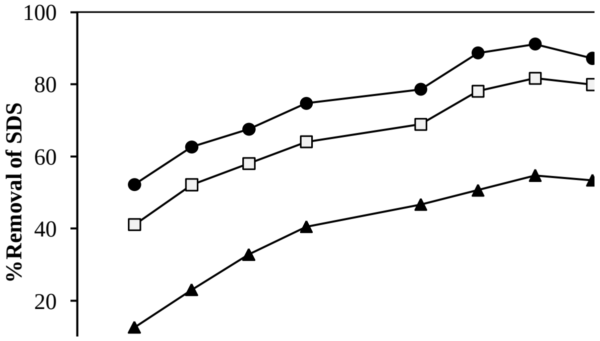

Figure 6. Effect of contact time on removal of SDS using SD, SGTL and SBTL adsorbents

Adsorption kinetic

Kinetics of adsorption is one of the important characteristics in explaining the efficiency of an adsorption process and potential application of an adsorbent. In order to inspect the mechanism of solute adsorption onto the selected adsorbents, pseudo-first and second order reaction kinetic models were applied and a comparison of the best fit adsorption mechanism was prepared. The pseudo-first order Lagergren rate equation is the one most widely utilized for the adsorption of a solute from a liquid solution and is represented as: [38]

$$\lg(q_e - q_t) = \lg q_e - \frac{K_1}{2.303} \times t \qquad (3)$$

where; q_t and q_e ($mg.g^{-1}$) are the amount of SDS adsorbed per unit mass of adsorbent at time t and at equilibrium respectively, and K_1 is equilibrium rate constant of pseudo-first-order adsorption. Therefore a linear trace is carried out between log (q_e-q_t) and t, provided the adsorption follows first order kinetics. For determining of reaction mechanism and potential application of an adsorbent, kinetic study is very useful. The equilibrium kinetic data were further analysed employing pseudo-second-order kinetic model suggested by McKay et al.[39] The differential equation is the following:

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2 \qquad (4)$$

where k_2 is rate constant for pseudo-second-order adsorption (g mg^{-1} min^{-1}). For the boundary conditions t=0 to t=1 & q_t=0, q_t=q_t integrated form of equation is as follows:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + K_2 t \qquad (5)$$

The linear form of equation can be expressed as follows:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \qquad (6)$$

The plots of t/q_t versus *t* should give straight lines where slopes and intercepts are $1/q_e$ and $1/K_2q_e^2$, respectively. The values of the rate constant K_2 and adsorption capacity q_e are calculated from these parameters and are summarised in Table 1. Based on regression analysis (R^2>0.95) it could be concluded that adsorption of SDS onto SD, SGTL and SBTL followed the pseudo-second-order kinetics model which suggesting a chemisorption mechanism.[40]

Adsorption isotherms

Isotherms provide an estimate of adsorption capacity and also useful information about applicability of a candidate adsorbent for adsorption of an undesired contaminant. In this work Langmuir and Freundlich models were employed for treatment of equilibrium adsorption data. Langmuir model is represented by the following equation:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_1 C_e} \qquad (7)$$

where C_e is the equilibrium concentration of SDS solution (mg L^{-1}), q is the amount adsorbed by adsorbent (mg g^{-1}), q_m is the maximum amount adsorbed, K_L a Langmuir's constant signifying energy of adsorption.

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Table 1 Adsorption kinetic parameters of SDS onto SD, SGTL and SBTL adsorbents

	Pseudo first order			**Pseudo second order**			
Adsorbent	**K_1 (min^{-1})**	**q_e ($mg.g^{-1}$)**	**R^2**	**K_2 ($g.mg^{-1}.min^{-1}$)**	**q_e ($mg.g^{-1}$)**	**R^2**	**q_{exp} ($mg.g^{-1}$)**
SD	0.022	0.579	0.8946	0.017	0.816	0.9553	0.546
SGTL	0.016	0.432	0.6830	0.068	0.960	0.9870	0.911
SBTL	0.025	0.721	0.9306	0.049	0.909	0.9868	0.816

Table 2 Adsorption isotherm constants for the adsorption of SDS onto SD, SGTL and SBTL adsorbents

	Freundlich isotherm parameters			**Langmuir isotherm parameters**			
Adsorbent	**n**	**K_F**	**R^2**	**K_L ($L\ mg^{-1}$)**	**q_m ($mg.g^{-1}$)**	**R^2**	**R_L**
SD	1.44	0.21	0.9511	0.019	6.71	0.9967	0.344
SGTL	1.58	1.24	0.9629	0.191	8.62	0.9930	0.049
SBTL	1.66	0.58	0.9953	0.088	5.71	0.9881	0.102

The values of K_L and q_m were calculated from the slope and intercept of the linear plot. The Langmuir model deals with monolayer adsorption and constant adsorption energy. The widely used empirical Freundlich equation based on adsorption on a heterogeneous surface is represented by the following equations:

$$q_e = K_F C_e^{1/n} \tag{8}$$

$$\lg q_e = \lg K_F + \frac{1}{n}\lg C_e \tag{9}$$

where, q_e is equilibrium adsorption capacity (mg L^{-1}), C_e is the equilibrium or residual concentration (mg L^{-1}) of SDS dye in solution, and K_F and $1/n$ are empirical parameters indicating adsorption capacity of adsorbent and intensity as well as expression of favorable or un favorable adsorption process, respectively. $1/n$ is a dimensionless constant. Its values for a linear, favorable and unfavorable adsorption are 1, $1/n<1$ and $1/n>1$, respectively. The values of Freundlich parameters are easily calculated from the slope and intercept of the linear plot of log q_e against log C_e. The Freundlich equation deals with physicochemical adsorption on heterogeneous surfaces. For a good adsorbent n is usually between 1 and 10. The adsorption isotherms using both Langmuir and Freundlich equations (linear forms) obtained for removal of SDS have been shown in Figs. 7 and 8, respectively.

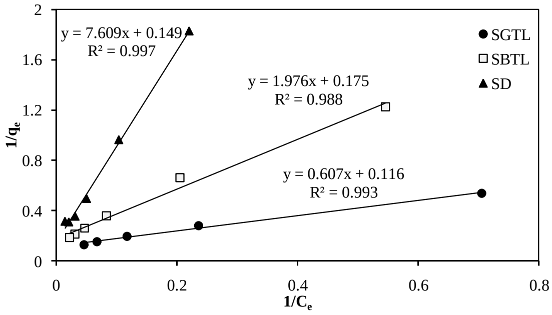

Figure 7. Langmuir isotherm obtained for adsorption of SDS

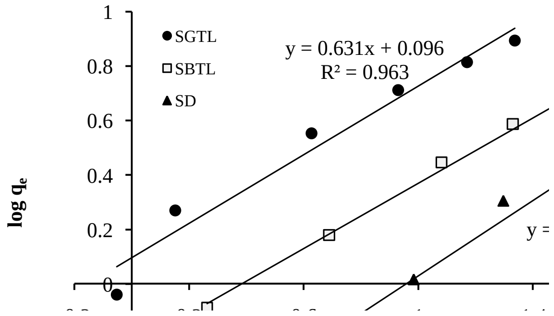

Figure 8. Freundlich isotherm obtained for adsorption of SDS

The calculated results of the Langmuir and Freundlich isotherm parameters are summarised in Table 2. In the case of SBTL, the correlation coefficient value R^2 obtained shows that the equilibrium data fitted better with the Freundlich model as compared to Langmuir equation under the concentration range studied.

According to the results, the equilibrium data fitted better with the Langmuir model as compared to Freundlich equation under the concentration range studied for SD and SGTL. The essential characteristics of the Langmuir isotherm and the favorable nature of adsorption can also be expressed in terms of a dimensionless constant separation factor (R_L), which is defined by the following equation: [41]

$$R_L = \frac{1}{1 + K_L C_0} \tag{10}$$

where; K_L (L mg^{-1}) is the Langmuir constant and C_o is the highest SDS concentration in solution (mg L^{-1}). The values of R_L indicates the type of isotherm to be irreversible ($R_L=0$), favorable ($0<R_L<1$), linear ($R_L=1$) or unfavourable ($R_L>1$).

Effect of temperature and thermodynamic study

The effect of temperature on the adsorption of SDS on SD, SGTL and SBTL was investigated at four temperatures: 298, 308, 323 and 343 K. The adsorption efficiency had a little increase by raising the temperature. This is due to the fact that at high temperature, the diffusion rate of the SDS molecules and their kinetic energy increases through the external boundary layer and internal sites of the adsorbent.

The data obtained at different temperatures can be used to evaluate the thermodynamic parameters. The standard Gibbs free energy change (ΔG°) is the fundamental parameter of spontaneity of a process and can be expressed as:

$$\Delta G^{\circ} = -RT \ln K_C \tag{11}$$

where K_c is the adsorption distribution coefficient, R is the universal gas constant (8.314 J mol^{-1} K^{-1}) and *T* is the absolute temperature (K). The standard enthalpy change (ΔH°) and the standard entropy change (ΔS°) were computed from *van't Hoff* equation (Eq. 12).

A plot of $\ln K_c$ versus 1/T should be straight line. The slope and intercept of the plot gives the values of ΔH° and ΔS° while ΔG° was calculated using fundamental free Gibbs energy equation.[42]

$$\ln K_C = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{RT} \tag{12}$$

The values associated with the thermodynamic parameters are listed in Table 3. The negative values obtained for ΔG° at all investigated temperatures clearly indicate the feasibility of the process and spontaneous nature of the adsorption. Positive values of ΔH° indicate the endothermic nature of the process. As the results shown, the positive values of ΔS° for all adsorbents confirms the favourable condition for adsorption of anionic surfactant from aqueous solution.

Table 3 Thermodynamic parameters for adsorption of SDS on SD, SGTL and SBTL

Adsorbent	**T (K)**	**ΔG°, kJ mol^{-1}**	**ΔH°, kJ mol^{-1}**	**ΔS°, J mol^{-1} K^{-1}**
SD	288	-0.1		
	298	-0.4		
	308	-0.7	11.77	41.12
	318	-1.3		
SGTL	288	-4.5		
	298	-5.8		
	308	-7.2	35.17	137.67
	318	-8.7		
SBTL	288	-3.2		
	298	-3.7		
	308	-4.5	19.24	77.43
	318	-5.5		

Column study (Breakthrough curves)

Sorption isotherms which are obtained from batch study do not give accurate scale-up data for industrial treatment systems since sorption in a column is not normally in a state of equilibrium.

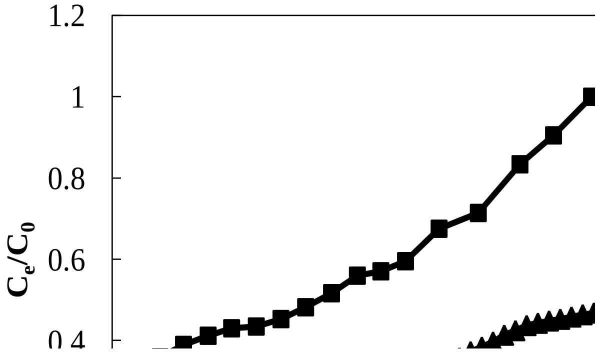

Figure 9. Breakthrough curve obtained for removal of SDS using SGTL and SBTL

Consequently, there is a need to perform flow tests using columns to evaluate the performance of adsorbent. The design of packed bed adsorbent in continuous systems, concentration vs. time or volume of solution usually yields as S-shaped curve, at which the solute concentration reaches its maximum allowable value referred to as a breakthrough curve. The point where the effluent solute concentration reaches 95% of its influent value is usually called the point of column exhaustion. For performing this experiment, 1.0 g of adsorbent was packed in a glass column (bed depth=5 cm), and then SDS solution with inlet concentration of 10 mg L^{-1} passed through the column with constant flow rate (2 mL min^{-1}) at pH=6. The outlet solution was analyzed for unadsorbed SDS solution. The breakthrough curves obtained for the SGTL and SBTL used for sorption of SDS a column system are shown in Figure 9. As the results show, SGTL was found to be a better adsorbent for SDS removal when used in column system.

To study the influence of flow rate, the SDS solutions were allowed to flow through the adsorbent bed at different flow rates such as 1, 2 and 5 mL min^{-1}. The eluents from the column were collected and analyzed for the respective residual SDS concentration. The breakthrough plot of SDS obtained for SGTL at different flow rates is shown in Figure 10. As the results show, with increasing flow rate, the service time and the volume treated were shortened.

The breakthrough analysis was also conducted in the presence of various salts in order to find out the effect of salt on performance of adsorbents toward SDS removal. In this investigation, the breakthrough curves were obtained in the presence of $AgNO_3$, $CuSO_4$ and $CaCl_2$ salts with concentration of 0.01 M. The other conditions were the same as described for Figure 9. As the results indicate, among the salts used, SDS removal has been affected by the presence of silver ion considerably (Figure 11). The other salts had not any important effect on the performance of the spent tea leaves for SDS removal.

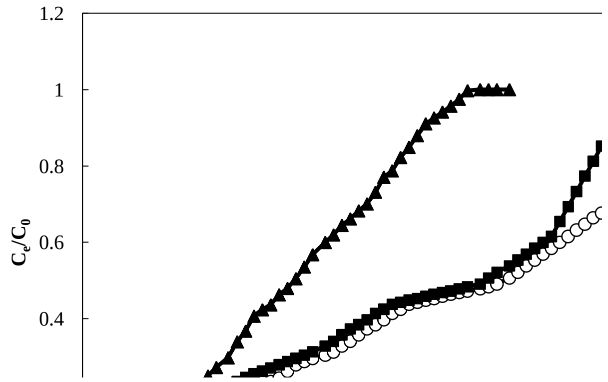

Figure 10. Breakthrough curves for the adsorption of SDS onto SGTL at different flow rates

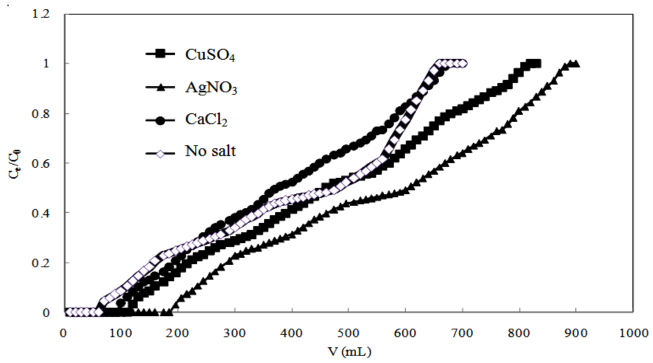

Figure 11. Breakthrough curves for the adsorption of SDS onto SGTL at different salt solution

Conclusion

Three adsorbents sawdust, spent green tea leaves and spent black tea leaves were used for SDS removal. Among the examined adsorbents in this study, SGTL showed maximum removal efficiency. Both Langmuir and Freundlich isotherms for all adsorbents depicted and q_m values were compared. In batch study the optimum adsorbent dose and equilibrium time were found to be 0.50 g and 2 h, respectively. Under optimized conditions 93.6%, 75.4% and 53% SDS could be removed from wastewater with SGTL, SBTL and SD, respectively. According to results spent green tea leaves (SBTL) showed the highest performance for SDS removal from aqueous solutions. However, in column system, SGTL was found to be more efficient. Spent tea leaves seem to be efficient and very cost effective adsorbents for removal of SDS from aqueous solutions.

Acknowledgment

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References

[1] Levine, L. H., Garland J. L., Johnson J. V., *J. Chromatogr. A*, **2005**, *1062*, 217.

[2] Dhouib, A., Hdiji, N., Hassaïri, I., Sayadi, S., *Process. Biochem*, **2005**, *40*, 2715.

[3] Cullum, D. C., *Introduction to Surfactant Analysis*, Blackie Academic & Professional, **1994.**

[4] Porter, M. R., *Handbook of Surfactants*, Blackie Academic & Professional ,**1991**.

[5] Amat, A. M., Arques, A., Miranda, M. A., Sequi, S., *Solar Energy*, **2004**, *77*, 559.

[6] Lewis, M. A., *Water Res*., **1992**, *26*, 1013.

[7] Mathur, A. K., Gupta, B. M., , *Ind. J. Environ. Prot.*, **1998**, *18*, 90.

[8] Whiting V. K., Cripe G. M., Lepo J. E., *Arch. Environ. Contam, Toxical*, **1996**, *31*, 293.

[9] Gonza, ılez .S, Petrovic, M., Barcelo, D., *Chemosphere*, **2007**, *67*, 335.

[10] Yüksel, E., Ayhan, Ş. İ., Özacar, M., *J. Chem. Eng*., **2009**, *152*, 347.

[11] Mezzanotte, V., Castiglioni, F., Todeschini, R., Pavan, M., *Bioresour. Technol*, **2003**, *87*, 87.

[12] Garcia, M. T., Ribosa, I, Guindulain, T., Sanchez, L. J., *J. Environ. Pollut.* **2001**, *111*, 169.

[13] Scott, M. J., Jones, M. N., *Biochem. Biophys. Acta*, **2000**, *1508*, 235.

[14] Dhouib, A., Hamad, N., Hassaıri, I., Sayadi, S., *Process Biochem*., **2003**, *38*, 1245.

[15] Somasundaran, P., Huang, L., *J. Adv. Colloid Interface Sci*, **2000**, *88*, 179.

[16] Musselman, S. W., Chander, S., *J. Colloid Interface Sci*., **2002**, *256*, 91.

[17] Li, F., Rosen, M. J., *J. Colloid Interface Sci*, **2000**, *224*, 265.

[18] Adak, A., Bandyopadhyay, M., pal, A., *J. Colloids surfaces A: Physicochem. Eng. Aspects*, **2005**, *254*, 165.

[19] Adak A., Bandyopadhyay M., Pal A., *J. Environ. Sci. Health. A. Tox. Hazard. Subst. Environ. Eng*, **2005**, *40*, 167.

[20] Gonzalez-Garcia, C. M., Gonzalez-Martin, M. L., Denoyel, R., Gallardo-Moreno, A. M., *J. Colloid Interface Sci*, **2004**, *278*, 257.

[21] Chiming, M., Chenglong, L., *J. Colloid Interface Sci*, **1989**, *131*, 485.

[22] Wenzhi, H., Haddad, P. R., *Anal. Commun*, **1998**, *35*, 191.

[23] Basar, C. A., Karagunduz, A., Cakici, A., Keskinler, B., *Water Research*, **2004**, *38*, 2117.

[24] Kuei, C., Yeh, J., *J. Environ. Sci. Health (Part A)* **2003**, *38*, 1145.

[25] Atia, A. A., Radwan, A. A., Adsorption Sci. Technol, **1997**, *15*, 619.

[26] Lunkenheimer, K., Fruhner, H., Theil F., *Colloids Surf.*, **1993** *A*, *76*, 289.

[27] Rouquerol, J., Partylra, S., *J. Chem. Tech. Bio-Tech*, **1981**, *31*, 584.

[28] Khan, M. N., Zareen, U., *J. of Hazard. Mater.*, **2006**, *133*, 269.

[29] Purakayastha, P. D., Pal A., *J. Environ. Sci. Health*, **2001** A, *37*, 925.

[30] Beltran, F. J, Garcia-Araya, J. F, Alvarez, P. M, *Ind. Eng. Chem. Res*, **2000**, *39*, 2214.

[31] Tianyong, Z., Toshiyuki, O., Satoshi, H., Jincai Z., Nick S., Hisao H., *Appl Catal. B: Environ*, **2003**, *42*, 13.

[32] Sheng, H. L., Lin, C. M., Leu, H. G., *Water Res*., **1999**, *33 (7)* 1735.

[33] Suˇ ıarez-Ojeda, M. E., Kimb, J., Carrera, J., Metcalf, I. S., Font, J., *J. Hazard. Mater*, **2007**, *144*, 655.

[34] Kong, W., Wang, B., Ma, H., Gu, L., *J. Hazard. Mater*. B, **2006**, *137*, 1532.

[35]Lissens, G., Pieters, J., Verhaege, M., Pinoy, L., Verstraete, W., *Electrochim. Acta*, **2003**, *48*, 1655.

[36]APHA-AWWA-WPCF, *American Public Health Association*, New York, **1989**.

[37]Ansari, R., Mosayebzadeh, Z., Mohammad-khah, A., *J. Ads Sci Res***, 2011**, *2(3),* 25.

[38]Lagergren, S., *Kungliga Svenska Ventenskapsakad Handlingar*, **1898**, *24*, 1.

[39]Ho, Y. S., McKay, G., *Process Biochem*. **1999**, *34(5)* 451.

[40]Bulut, E., Özacar, M., Şengil, İ. A., J. Hazard. Mater., **2008**, *154*, 613.

[41]Benefield, L. D., Randall, C. W., Prentice-Hall Inc. **1980**.

[42]Ansari, R., and Dezhampanah, H., Eur. Chem. Bull. **2013**, *2(4)* 220.

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