Removal of Surfactants Using Rubber Granules as an Adsorbent

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Abstract- Surfactants are regarded as one of the major and most undesirable pollutants detected in the aquatic and terrestrial environment. Massive quantities of surfactants are being used in daily life and most of them end up dispersed in different environmental compartments greatly affecting the ecosystem. Surfactant toxicity has aroused worldwide attempts to reduce the after effects of these silent toxicants. In the present study, an attempt was made to find the efficiency of using rubber granules in the removal of anionic surfactant (AS) from water. Linear Alkylbenzene Sulfonate (LAS) was selected as a representative member of AS as it is the most commonly used constituent seen in detergents and soaps . The removal efficiency, maximum adsorption capacity and cost were the guiding parameters for the selection of the adsorbent in the present study. Considering all the factors, waste tire rubber granules were chosen as the best adsorbent for AS removal. A series of laboratory batch and column studies were conducted to determine the effects of various parameters such as contact time, adsorbent size and dosage, initial concentration and pH on surfactant removal. The highest efficiency obtained was 97.55 % for an adsorbent size of 75 \(\square\) at a dosage rate of 10g/l with contact time of 6 hours. With increase in initial concentration of surfactant ions, adsorption efficiency decreases. The results show that rubber granules is an efficient adsorbent for the remediation of surfactant contaminated water.

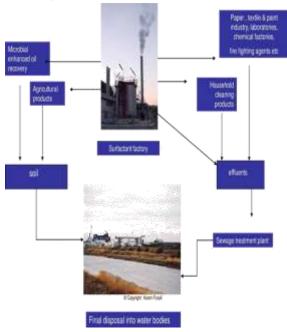
Index Terms- Anionic surfactant, Linear Alkylbenzene Sulfonate, rubber granule.

INTRODUCTION

Water is a common chemical substance that is essential for the survival of all known forms of life. It covers 75% of the earth's surface on earth and is indeed a wonderful chemical medium which has a unique property of dissolving and carrying in suspension huge varieties of chemicals as well as many microorganisms. Water is facing lot of

problems in so called development of humans, prior to about 1940, as the amount of heavy metals and synthesized organic compounds generated by industrial activities has increased, and about 10,000 new organic compounds are being added each year (Jardak et al., 2016) . Countries like Korea, Japan, US, Mexico and Turkey are especially affected by water shortages. Greater demand for water also means more competition for clean water. By 2050, one fifth of the world's inland waterways could be contaminated by algae growth. It is predicted that by 2050 at least 1.4 billion people will have to live with insufficient water supply and sanitation. Over the past few years, environmental problems associated with hazardous and toxic pollutants present in water have attracted much attention. Municipal and industrial wastewaters are one of the most important pollution sources affecting the quality of surface and ground water adversely in many developed countries. As a result, the occurrence and frequency of these pollutants present in water should be monitored and their toxic behaviour should be assessed carefully. The chemicals that are not being detected in water supply are classified as emerging contaminants. Pharmaceuticals, personal care products(PCP), endocrine disrupting compounds (EDC) are among prime examples of emerging contaminants. The fate of these contaminants and the extent of impacts caused are actually unknown as limited studies were only conducted on these contaminants. These contaminants finally find their way to water and are reconsumed thus affecting human beings as well as aquatic life. These can even cause hormonal changes in living organisms. So considering all these factors into consideration the study of emerging pollutants are gaining popularity in the present scenario. (Helwig et al., 2013). Over the past 65 years surfactants have been widely used in laundry detergents as well as in personal care and other cleaning products. Traced back from the ancestral. Babylonian ash-oil soap formula to the currently available soaps, cleansers and detergents, surfactants appear in various forms. Of these, detergents indeed have become indispensable elements of man's life all along his steps aiming cleanliness and tidiness. Apart from serving as cleansing agents, surfactants find many industrial applications as additives in paints, as textile softeners, as antistatic agents, in metal processing and in oil drilling operations. Some surfactants have antimicrobial properties which provide the basis for their utility as biocides. (Rebello et al, 2014). Surfactants (surface-active agents) are a diverse group of chemicals consisting of a polar, water-soluble head group and a non polar hydrocarbon tail group, which is not soluble in water (Antoänioc et al., 1999). They are best known for their solubility and cleaning properties which secured them a place among detergents and other cleaning products. Their excessive use as ingredients in care products (e.g., shampoos, body wash) and in household cleaning products (e.g., dishwashing detergents, laundry detergents, hard-surface cleaners) has led to the discharge of highly contaminated wastewaters in aquatic and terrestrial environment. Massive quantities of surfactants are being used in

households and industry every day, and most end up dispersed in different environmental compartments (soil, water, sediment) (TomislavIvankovic et al., 2009). Surfactants are regarded as one of the major and most undesirable pollutants detected in the aquatic and terrestrial environment (Jardak et al., 2016).



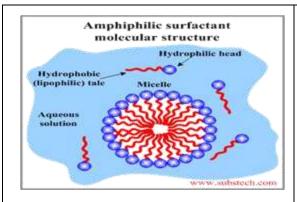


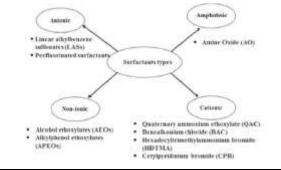
Fig. 1.2 Structure of the surfactant (http://www.substech.com)

To determine the effect of different parameters such as initial concentration, contact time, adsorbent dosage, adsorbent size and pH using a batch study as well as column

OBJECTIVES: To determine the feasibility of using rubber

tire granules in removing surfactants (anionic) from

To analyse both Langmuir and Freundlich adsorption isotherm models to determine the most appropriate model in the adsorption process.



Anionic Surfactants: Anionic surfactants (AS) are historically the oldest and the most common type of surfactants. When we think of detergents or common soaps, it is the anionic surfactants that do the washing (TomislavIvanković et al., 2009)

Cationic Surfactants: Cationic surfactants (CS) including quaternary ammonium ethoxylate and cetrimonium chloride are molecules with at least one hydrophobic long alkyl chain attached to a positively charged nitrogen atom

synthetic water.

study.

Amphoteric Surfactants: Amphoteric surfactants (AS) are surfactants that carry both a positive and a negative charge. They are capable of changing charge from net cationic to anionic from low to high pH with zwitterionic behaviour at intermediate Ph. Non Ionic Surfactants: Non-ionic surfactants (NS) are considered to be amphiphilic compounds. They do not ionize in aqueous solution because they have a non-dissociable hydrophilic group (e.g., alcohol, phenol, ester, ether, or amide) and they are less sensitive to electrolytes than are ionic surfactants.

Physical and Chemical Methods: Various physical, chemical and biological methods of surfactant detoxification are reported. Chemical treatment of surfactants by ozonation and advanced oxidation using various combinations of ozone, hydrogen peroxide, ultraviolet light irradiation and iron salts were found effective in degrading surfactants, including LAS, alkylphenolethoxylates and quaternary ammonium surfactants. Various other techniques like electro coagulation, nanofiltration, sonochemical degradation, foam fractionation and wet air oxidation are also used (Jardak et al., 2014).

Biological Methods: Biodegradability of organic pollutants is a desired property because of the relative ease of removal from waste streams. Toxicity can be reduced or eliminated by biodegradation. Often, biological organisms can completely mineralize pollutants, producing carbon dioxide and water (Hatfield et al., 2004). Biodegradation mostly depends on surfactant's chemical structure and physicochemical conditions of its environmental medium. High temperature increases the degradation rate. The presence of sediment also enhances the biodegradation rate, probably because sediments accumulate both surfactants and bacteria. Microbial biodegradation provides a safer, environmental cost-effective friendly alternative physicochemical methods for surfactant remediation (TomislavIvankovic et al., 2009).

ADSORPTION: Of the various methods available, adsorption was found to be the best in terms of cost and efficiency (Jardak et al., 2014). The advantages of adsorption over the other methods are. Convenience, Easy operation, Simple design, Low investment in terms of both initial cost and land

required, Sludge free operation, High efficiency (Basar et al., 2004), Ion exchange, Ion pairing, Hydrophobic interactions, Aromatic interactions, Adsorption by dispersion (Vander Waals) forces (Azam et al.,2013). Adsorption processes using a number of low-cost adsorbents have been studied to evaluate their efficiency for removal of cationic surfactants from aquatic environment.

Adsorption Isotherm: Adsorption process is usually studied through graphs known as adsorption isotherm. Adsorption is the amount of adsorbate on the adsorbent as a function of its pressure or concentration at constant temperature. An adsorption isotherm is the presentation of the amount of solute adsorbed per unit weight of adsorbent as a function of the equilibrium concentration in the bulk solution at constant temperature. It is a quantitative relationship describing the equilibrium between the concentration of adsorbate in solution (mass/volume) and its sorbed concentration (mass adsorbate / mass adsorbent) (Sawyer et al., 2003).

Table 2.1 Comparison study of various surfactant removal methods

SI	Method	Advantages	Disadvantages		Surfactant	Spig
20				Efficiency	removed	2
1	Ademption		The fate of advertisers a question as cortain times	-56 %	Assession, Caterior, New tenio	1
1	Rubber grandes	form contestions advocated for use an argituit	Ministers principles on the granules	87.54	Asimir, Catinair, Nes insir	*
2	Bioderral ation	safer, environmental fermility and soci-effective	Barreia get hilled due to the toxicity of nafactants. Light was found to show down bookgradation	66.5	Assess, New treat	1
3	Time	Found to be	With the	92%	Asimic.	
	mchange	tery ellimine	moreon a	1	Cabrer,	
		as assissed. Shefactuan respond is a wide range of somewhaterions.	confertant Concentration the efficiency ration decreased		Non treat.	
1 =	Activated	Later reports	Huth mesor	99.74	Asimir	5
		cationic surfactants	foun is too slow for practical quantitative analysis.			
6	Nano filtration	promitting	micelles pucked over the membrane rurface, slowly increase the	90%	Ationic	9

	cartois	because of	consequently, high core for regeneration			
4	Electric congridanc H	Clean, Bearide, and powerful technique for water and water are treatment		8514	Assess	8
1	Symmetric adaptions polyment	longer resultife time and better engrammics officiency	The sumocal officences of sufactuarie decreased with increasing communications.	8756	Anionic, Cattonics, Non-tonic	
	fractionam on.	effective method of ensurying satisfies	filane teasactive of outlant and thous water to from is too show for	90%	Antonic, Cationic	*
		ware alternate faring a ligher performance than the tradinomally used ultrafiltrance.	permeate flow resonance, the emergy communities to higher, entry method			
9	Sonochemi est degradatio	Highly officient	The rate of degradation decreases as surfactures trossures	93 14	Admin	10
1	Phone catalytic Degradatio	high seacovity	Rename Intered at large scale due to the far escontinuation of plants generated determone holes pure	90%	Alimir	11
iv .	Rice hugh	Low and advorbent	Hotes surface gets coated with the adametrate	55	Amount, Non-inuic	12

The surfactant concentration in the sorbent phase q (mg/g) was calculated from the following expression: Where: C0 = Initial concentration of the adsorbate in solution (mg/l); C = Final concentration of the adsorbate in solution (mg/l); V= Volume of solution (L); and

M = mass of the adsorbent (g) (Tripathi et al., 2015)

$$q = \frac{V (C0 - C)}{M}$$

Two commonly used isotherms are Langmuir and Freundlich. Which isotherm should be used depends on a variety of factors such as nature of adsorbates, type of adsorbent and other environmental factors. Langmuir and Freundlich adsorption isotherms are commonly used for the description of adsorption data. (Sawyer et al., 2003)

METHODOLOGY

ADSORBENT USED: The adsorbent used for the experiment was rubber granules from waste tires. An attempt was made to evaluate the efficiency of removal of surfactants (Anionic Surfactants) using the adsorbent mentioned.

Preparation of adsorbent: The rubber granules were collected from a local rubber tire recycling centre in

Chalakudy. It was confirmed that the rubber granules was not chemically treated and was free from any chemicals.

COMPOSITION OF SYNTHETIC SOLUTION:As mentioned in the objectives, the main surfactant (anionic) chosen for the study was Linear Alkyl Benzene Sulphonate (LAS).



Fig. 3.1 Rubber granules used for the experiment Preparation of Synthetic Solution: Standard LAS solution was brought from a chemical shop. The solution was assumed to be 100% concentrated. Stock solution (of concentration 1g/l) was prepared by dissolving 1 g of the standard solution in 1000 ml of distilled water. From this stock solution, standards of concentration 0.1 mg/l, 0.2 mg/l, 0.3 mg/l, 0.4 mg/l, 0.5 mg/l and so on till 2.0 mg/l was prepared for the preparation of the calibration chart. All experiments employed distilled water.

SURFACTANT ANALYSIS: LAS determination was done using methylene blue as per the standard Methylene Blue Active Substance (MBAS) method. Methylene blue is a well-known cationic dye. LAS is an MB-active substance and are designated as MBAS. It forms a complex with MB. After its formation, the complex between anionic part of LAS and the cationic part of MB was extracted into chloroform. The colour intensity of the chloroform layer gave a measure of the LAS concentration. The absorbance values were measured at max = 650 nm to quantify LAS. A calibration graph was drawn in the concentration range 0 - 2.0 mg/l of LAS concentration. A UV spectrophotometer was used for all absorbance measurements.

Chemicals and Reagents: i. Methylene Blue, Neutral Solution:Dissolve 0.350 g of methylene blue in water and dilute to 1000 ml. The solution should be prepared at least 24 hours before use. Methylene Blue, Acidic Solution:Dissolve 0.350 g of methylene blue in water and dilute to 500 ml of water and add 6.50 ml of sulphuric acid. Dilute with water to 1000

ml after mixing. The solution should be prepared at least 24 hours before use . Buffer Solution, pH 10:Dissolve 24 g of sodium hydrogen carbonate (NaHCO3) and 27 g of anhydrous sodium carbonate (Na2CO3) in water and dilute to 1000 ml. Chloroform Solution. The solution has a purity > 99% with density being 1.479 g/cm3. MBAS Anionic surfactants Procedure: are usually determined by spectrophotometric methods using methylene blue, this standard method being used to determine the surface agents in tap-water samples (ISO 13428: 2005). However, this official method is not only long and tedious but also requires great quantities of chloroform and sample. This requires three successive extractions of Anionic Surfactant-Methylene Blue content in 100 ml of sample previously alkalinized with 15, 10, and 10 ml of chloroform as shown in Figure 3.2. The ionic pair is determined by spectrophotometry, measuring the absorbance at 650 nm.

100 ml of the test sample is transferred into a separating funnel. 5 ml of neutral methylene blue solution, 10 ml of buffer solution and 15 ml of chloroform is added to it. Shake evenly and gently for 1 minute and allow the layers to separate as completely as possible. Allow to settle for 2 minutes, and then separate out the chloroform layer into a second separating funnel containing 110 ml of water and 5 ml of acidic methylene blue solution. Shake uniformly but not too vigorously for 1

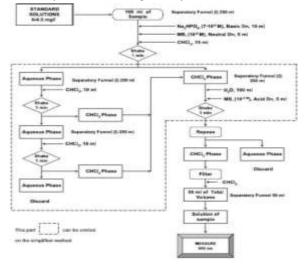


Fig. 3.2 Scheme of the simplified analytic procedure for determining anionic surfactants [8] minute as previously described and allow to settle for 2 minutes as shown in figure 3.3. Filter the

chloroform layer through a glass wool filter wetted with chloroform into a 50 ml volumetric flask.



Batch Study : Rubber tire granules were washed, dried and sieved in a mechanical siever to get various size of 75 m, 150 m, 300 m, 500 m, and 600 m. Stock Solution of LAS (1g/l) was prepared in distilled water. It was prepared fresh after every 15 days. LAS samples of required concentrations were prepared by diluting the stock solution appropriately. LAS spiked water samples (100 ml each) of varying concentration were taken in different bottles and different adsorbents were added to it at different dose and shaken in a mechanical shaker with 100 rpm speed.

Fig. 3.3 MBAS Analytical Procedure

At different contact times (1, 2,3,5,7 h) the bottles were withdrawn and the adsorbent was separated by filtration and the filtrate was analysed. Samples were collected at various time intervals and analyzed using standard MBAS procedure.

Column Study: Column adsorption studies were conducted in a chromatographic glass column having 4cm inner diameter and 60cm height. The column was packed with rubber granules up to the specific depth. LAS spiked water samples were provided at the top of the column. Effluent was collected from the bottom of the column and analyzed for LAS using standard procedures. The column studies was conducted for three different depths.

PARAMETERS CONSIDERED: The parameters considered for experimentation in the present research work include pH, time, and dosage of adsorbent, size of adsorbent and initial concentration of LAS. The ranges of these parameters considered are summarized in Table 3.1.

5 -50g1	mg I - 2.0 mg I with the size of the adsorbent ke contact as 150 m and continuous shaking for 2 hou with adsorbent dosage of 10 g / I.
5 - 50 p1	
75-600 m	Effect of Adsorbent Dosage: Adsorbent Dosage was varied between 5 - 50 gl keeping the contact tim
3 - 13	constant at 2 hours and concentration constant at 2 me I with the size of the adsorbent kept contact as 1:
1 -6Hs	m
	3 - 13

Effect of size of adsorbent: The size of the adsorbent was varied from 75 - 600 m keeping the concentration constant at $2.0 \, \text{mg/l}$ and by varying the contact time from 1- 5 hours with adsorbent dosage of $10 \, \text{g} \, / \, \text{l}$.

Effect of pH: pH was varied between 3-13 by keeping the contact time 5 hours, concentration constant at 2.0 mg/l and adsorbent dosage at 10 g/l constant with adsorbent size being 150 m.

Effect of Contact time: Contact time was varied between 1 - 6 hours keeping the adsorbent dosage constant at 10 g/l and initial concentration constant at 1.2 mg/l with the adsorbent size of 75 m.

RESULTS AND DISCUSSIONS: CALIBRATION CHART: Calibration chart with concentration 0.1 mg/l, 0.2 mg/l, 0.3 mg/l etc up to 2.0 mg/l were prepared. The calibration chart prepared is given in figure 4.1.

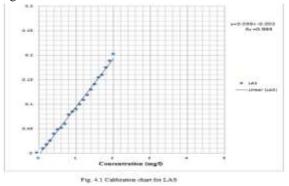


Fig. 4.1 Calibration chart for LAS

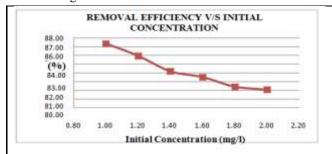


Fig. 4.2 Effect of initial concentration on the removal efficiency of LAS ions

Effect of adsorbent dosage: Different dosage of rubber granules was weighed and taken in beakers of 100 ml LAS spiked water with the initial concentration of LAS kept constant at 2.0 mg/l. The sample was then shaken in a magnetic stirrer with 120 rpm speed for 2 hours. After 2 hours, the beakers

Effect of Initial Concentration Of Surfactants: The initial concentration of LAS was varied from 1.0 - 2.0 mg/l. 100 ml of the LAS spiked water was taken in varying concentrations in different beakers and the adsorbents were added to it at a dosage of 10 g/l, with the adsorbent size being 150 m. The sample was then shaken in a magnetic stirrer with 120 rpm speed for 2 hours. After 2 hours, the beakers were withdrawn and the adsorbent was separated by filtration and the filtrate was analysed for LAS using the MBAS procedure. Using the calibration chart prepared, concentration for the corresponding absorbance was obtained. Values obtained are given in Table 4.2. The figure 4.2 shows the variation of removal efficiency with initial concentration.

SLNO.	INITIAL	FINAL	REMOVAL
	CONCENTRATION	CONCENTRATION	EFFICIENCY (%)
	(mg1)	(mgT)	
1	1.00	0.126	87.34
2	1.20	0.168	85.93
3	1.40	0.221	84.17
4	1.60	0.263	83.51
5	1.80	0.316	82.41
6	2.00	0.358	82.06

Table 4.1 Percentage removal of LAS ions for an initial concentration of 1.0 - 2.0 mg/l

This is due to the limitation of adsorption sites on the rubber granules. This can be explained as follows: with increase in the initial LAS concentration, the amount of adsorbate species in the solution increases, but the amount of adsorbent remains constant and hence the percentage removal decreases with increase in initial LAS concentration. The higher uptake of LAS at low concentration may be attributed to the availability of more active sites for lesser number of adsorbate species.

were withdrawn and the adsorbent was separated by filtration and the filtrate was analysed for LAS using the MBAS procedure. Using the calibration chart prepared, concentration for the corresponding absorbance was obtained. Values obtained are given in Table 4.3. The figure 4.3 shows the variation of

removal efficiency with adsorbent dosage. With increase in the adsorbent dosage, more adsorption takes place thereby increasing the removal efficiency of LAS ions. This is because of the enlargement in the surface area of adsorbents. With increase in surface area of adsorbent, more active adsorption sites are available thereby increasing the adsorption of ions. For 50 grams per litre adsorbent dosage, removal efficiency obtained is 93.67%. Finally at 5 hour, the removal was found to be 90.50 % for particle size 75 m whereas at that time, the percent

removal was 90.0 %, 88.4 %, 86.30 % and 84.17 % in case of the particles having average sizes 150 m, 300 m, 500 m and 600 m respectively. It is obvious that adsorption was dependent on the size of the adsorbent, and as the size of the adsorbent was smaller, more percentage removal of AS was observed. This is due to the fact that as the size of the particles decreases, surface area increases, and because adsorption is a surface phenomenon, as the size decreases, more percentage removal is observed. (Purakayastha et al., 2002)

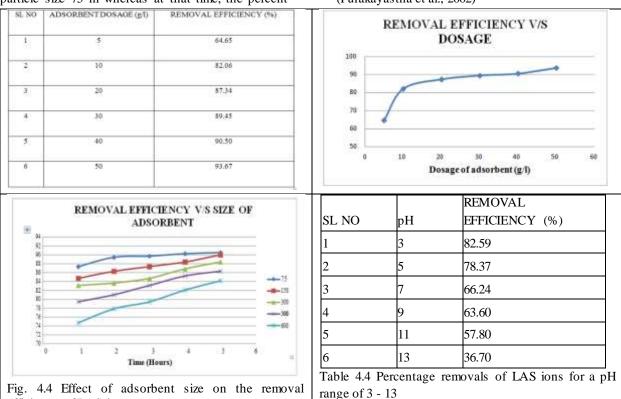


Table 4.2 Percentage removal of LAS ions for an adsorbent dosage of 5 - 50 g/l

Table	4.3	Percentage	removal	of	LAS	ions	for	an
adsorb	ent s	ize of 75 - 60	0m					

			REMOV	AL EFF	ICIENCY	(%)
SL NO	Size (m)	75	150	300	500	600
	Time					
	(Hour)					
1	1	87.34	84.70	83.12	79.42	74.68
	2	89.45	86.28	83.64	81.01	77.84
	3	89.71	87.34	84.70	83.12	79.42
	4	90.24	88.39	86.81	85.23	82.06
	5	90.50	90.00	88.40	86.30	84.17

Effect of Size of Adsorbent: 100 ml LAS spiked water with the initial concentration of LAS kept constant at 2.0 mg/l was taken. The average size of the adsorbent varied from 75–600 m. Values obtained are given in Table 4.4. The figure 4.4 shows the variation of removal efficiency with adsorbent size. With decrease in the adsorbent size, more adsorption takes place thereby increasing the removal efficiency of LAS ions. The average size of the adsorbent varied from 75–600 m. From the graph shown, it was observed that within 1h, for rubber granules with all five types of sizes, the removal of AS was within the range of 74 - 87 %.

efficiency of LAS ions

SL	CONTACT '	TIMEREMOVAL	EFFICIENCY
NO	(HOUR)	(%)	
1	0	0	
2	1	69.25	
3	2	87.69	
4	3	89.45	
5	4	94.16	
6	5	97.50	
7	6	97.55	

Table 4.5 Percentage removals of LAS ions for a contact time of 1 - 6 hours

Effect of pH: The pH of the solution was varied between 3 - 13. The current pH of the solution was 7.2. pH was adjusted using 0.1 N NaOH and 0.1 N HCl. 100 ml LAS spiked water with the initial concentration of LAS kept constant at 2.00 mg/l was taken. 150 m size adsorbent was added to the samples at a dosage of 10g/l and the samples were then shaken in a magnetic stirrer with 120 rpm speed for 5 hours. The samples were taken out after 5 hours and the adsorbent was separated by filtration and the filtrate was analyzed for LAS using the MBAS procedure for each pH. Values obtained are given in Table 4.5. The figure 4.5 shows the variation of

From the figure 4.5, it is clear that with increase in pH, the removal decreased. This probably is due to the fact that OH- ion can diffuse easily into the rubber granules, and because it is negatively charged (similar charge to that of AS), it can get adsorbed. onto it. Hence, as the pH increases, the AS molecules already adsorbed onto the adsorbent come out showing less adsorption. The adsorption sites become less available to AS molecules showing less adsorption of AS with the increase in pH may be that, with the increase in pH, the –COOH groups present in the rubber are converted into COO-, and hence, adsorption of AS is hindered due to the repulsion between similar charges. (Purakay astha et al., 2002)

removal efficiency with pH. Effect of Contact Time: 100 ml LAS spiked water with the initial concentration of LAS kept constant at 1.20 mg/l was taken.75 m size adsorbent was added to the sample at a dosage of 10g/l and the sample was then shaken in a magnetic stirrer with 120 rpm speed. Contact time was varied from 1 - 6 hours, The sample was taken out after each contact time and the adsorbent was separated by filtration and the filtrate was analysed for LAS using the MBAS procedure. Values obtained are given in Table 4.6. The figure 4.6 shows the variation of removal efficiency with contact time.

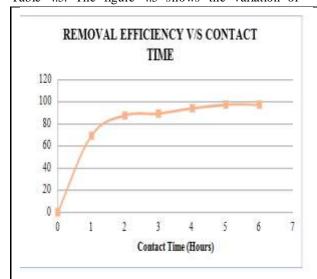


Fig. 4.6 Effect of contact time on the removal efficiency of LAS ions

With increase in contact time, more adsorption takes place thereby increasing the removal efficiency of LAS ions. This is because the adsorbate gets more contact time with the adsorbent thus increasing the

ST.300	VOLUME OF SOLUTION (1)	MASS OF Adsorbest (g M)	INITIAL CONCENTRATION (mg/l) (CV)	EQUILIBRIUM COOCENTRATION (mgD) (C)	eri(C) - C) M (mark)
1	01	1	10	0.13	0.09
1	91	1	12	0.17	0.10
3	01	1	14	0.22	0.12
4	01	1	16	0.26	0.13
Š	0.1	1	18	032	0.15
6	01	1	20	0.36	0.16

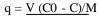
Table 4.6 Values of q (mg/g) for different initial concentrations of LAS

removal efficiency. However, after a particular time the removal efficiency remains constant. This is the optimum time required for maximum adsorption. An optimum contact time of 5 hours was obtained. The

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maximum removal efficiency obtained was 97.55 % for a contact time of 6 hours.

ADSORPTION ISOTHERM: Adsorption isotherm is expressed by relating the amount of adsorbate taken up per gram of adsorbent, q (mg/g), to the equilibrium solution concentration, C (mg/l). The type of adsorption isotherm model is very important in order to understand the adsorption behaviour for the solid - liquid adsorption system. In the present study, Langmuir and Freundlich models were tested as these two models are the most commonly used isotherm models. The adsorption surfactant concentration in the sorbent phase q (mg/g) was calculated from the following expression:



Where: C0 = Initial concentration of the adsorbate in solution (mg/L); C = Final concentration of the adsorbate in solution (mg/L); V= Volume of solution (L); and M = mass of the adsorbent (g). The values obtained for the LAS ions are given in Table 4.7. Where C is the aqueous concentration of adsorbate q Is the sorbed concentration (mass (mg/l), adsorbate/mass adsorbent; mg/g), qm is the maximum capacity of adsorbent for adsorbate (mass/volume; mg/g), Kads is the measure of affinity of adsorbate for adsorbent (L/mg). The linear form of Langmuir isotherm equation is used in the study and therefore, a plot 1/q versus 1/C is drawn and it indicates a straight line as shown in Figure 4.7.

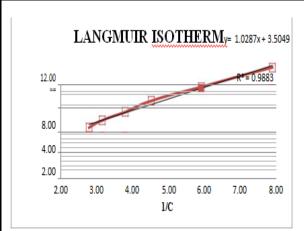


Fig. 4.7: Langmuir Isotherm Linear Plot for adsorption of LAS ions

SL NO	DEPTH (cm)	REMOVAL EFFICIENCY (%)
1	127	29.84
2	1.90	47.25
3	2.50	58.85

Table 4.7 Percentage Removal of LAS ions for different bed depths after 6 hours

Equation of the line = 1.028 x + 3.504

From Equation (1), Slope = 1/qmKads = 1.028

Intercept = 1/qm = 3.504

qm = 1/3.504

1/qmKads = 1.028

1/(0.285 x Kads) = 1.028

Kads = 0.2933

The isotherm data of LAS fits well with the Langmuir equation with a correlation coefficient, $R^2 = 0.988$ and shows excellent linearity

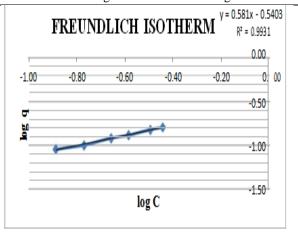


Fig. 4.8: Freundlich Isotherm Linear Plot for adsorption of LAS ions

Equation of the line = 0.581x - 0.540

From Equation (2), slope = 1/n = 0.581 $\log K = -0.540$

K = 0.288



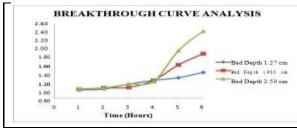
Fig. 4.9 Experimental Setup used for Column Study

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Freundlich Isotherm: The Freundlich Isotherm was proposed as the earliest emperical equation and was shown to be consistent with exponential distribution of active centre, characteristic of heterogeneous surfaces. The energy distribution for adsorptive sites follows an exponential type function which is close to the real situation. The logarithmic form of Freundlich equation is expressed as: $\log q = \log K + 1/n \log C$ ---- (2)

Where, K and n are Freundlich isotherm constants. A plot of log q versus log C for the studied samples is drawn and is shown in Figure 4.8. The value of 1/n gives an indication on the validity of the adsorption of the adsorbent - adsorbate system. The value of 1/n between 0 and 1 indicates a favourable adsorption. When 1/n > 1, the adsorption is not favourable, the adsorption connections become weak and the adsorption capacity decreases. The values of K and 1/n are determined from the intercept and slope of the linear plot of log q versus log C. The value of 1/n obtained was less than 1 thus indicating favourable adsorption conditions. The isotherm data of adsorption of LAS on rubber granules fitted well with the Freundlich equation with a correlation coefficient $R^2 = 0.993$ and shows excellent linearity. The correlation coefficient value is similar to the Langmuir value. Therefore, the experimental equilibrium adsorption data for the LAS - rubber granules system was properly explained by both Langmuir and Freundlich models.

COLUMN STUDY: Column study was performed using waste tyre rubber granules of size 75 m and LAS spiked water samples of initial concentration 2.0 mg/l. It was conducted in a chromatographic glass column having 4cm inner diameter and 60cm height as shown in figure 4.9. At the bottom of the column, there is a cistern disc, Above this, a layer of glass wool was provided which act as a support to the



adsorbent. They also help in preventing the washing out of the adsorbent. Three different depths (1.27 cm, 1.90 cm and 2.50 cm) of rubber granules were tested and separate breakthrough curves were generated. The water sample was provided at the top of the column and the study was conducted for a contact time of 6 hours. Effluent samples were collected from the bottom of the column after each hour and analysed for LAS. The removal efficiencies with respect to the bed depths after 6 hours is shown in Table 4.8.

Table 4.8 Values of C0/C for different bed depths

BL NO	DEPTH (cm)	TIME (Hour)	DOTIAL CONC. (C0)	EQUILIBRIUM CONC. [C]	C0/C
1	1.27	- 1	2.00	2.00	1.00
		. 2	2.00	1.91	1.03
		3	2.90	1.75	1.14
		- 4	2.00	1.62	1.28
		5.	2.00	1.54	1.30
		6	2.00	1.40	1.43
2	1.905	1	2.00	1.97	1,02
		2	2.00	1.90	1.05
\neg		3	2.00	1.68	1.00
		4	2.00	1.62	1.2
		5	2.00	1.24	1.61
			2.00	1.06	1.85
3	2.50	1	2.00	1.95	1.03
		2	2.00	1.90	1.03
		3	2.00	1,75	1.1
		4	2.00	1.66	1.20
		- 5	2.00	1.02	1.99
		- 6	2.00	0.62	2.44

Breakthrough Curve Analysis: To see the nature of adsorption with the variation in bed depth, breakthrough curves were developed by plotting CO/C against Time where CO is the initial concentration of the sample and C being the equilibrium concentration of the sample after each hour as shown in Table 4.9. As the solute enters the column, the upper portion of the bed becomes saturated with the solute and the adsorption zones moves down the column like a slowly moving wave. Eventually the lower edge of the adsorption zone reaches the bottom of the column and this point is called the breakthrough point.

Breakthrough curves were generated for three different bed depths, 1.27 cm, 1.90 cm and 2.50 cm. Figure 4.10 shows that the breakthrough curve gets steeper with increasing bed depth with 2.50 cm having the steeper curve. This shows that the breakthrough curve increases with increasing bed depth.

CONCLUSION

Surfactant consumption is increasing day by day with no limits and restrictions to meet the various

demands equally contributed by domestic purposes and industry. Such accumulation of these silent toxicants to the ecosystem could lead to drastic environmental problems including global warming, terrestrial and aquatic toxicity of the ecosystem and its inhabitants. Total banning of surfactants is impossible in such a modernized lifestyle needing surfactants in our food, cosmetics, cleansers, etc. Statistical analysis of surfactant concentrations worldwide reveals the fact that these pollutants are found in concentrations higher than their predicted no effect concentrations. In this study, synthetic solutions having LAS concentrations were treated using waste tire rubber granules as an adsorbent. A series of batch experiments were carried out by changing initial concentration, adsorbent dosage and size, contact time and pH. A column study was also conducted by varying the bed depth and by taking the most efficient parameters. With increase in adsorbent dosage, removal efficiency increases. With increase in initial concentration and pH, the removal efficiency of LAS decreases. As the size of the adsorbent decreases, the removal efficiency increases, the highest efficiency being 97.55 % for a size of 75 m with optimum time being 5 hours. The equilibrium data for the LAS - rubber granules system fitted well with both Langmuir as well as Freundlich isotherm equation. Hence waste tire rubber granules is an efficient adsorbent for the removal of surfactants.

SCOPE FOR FUTURE STUDIES

Comparison studies can be conducted using other low cost alternative adsorbents. Effect of other parameters such as temperature, flow rate, interference of other metal ions etc can be studied. Studies can be conducted using the wastewater samples. Further studies can be conducted on the adsorption kinetics of this work.

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