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Article

Effect of Time on the Adsorption of Metallic Soaps onto Hematite in Aqueous Media

Asuquo, J. E.[1], Ugwuja, D. I.[2], and Etim, E. E*[2]

[1]*Department of Chemistry, University of Uyo, Uyo, Nigeria*

[2]*Department of Chemical Sciences, Federal University Wukari, Nigeria*

* Author to whom correspondence should be addressed; E-Mail: emmaetim@gmail.com

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Abstract: The effect of time on the adsorption of potassium, calcium and aluminum soaps of rubber seed oil, Shea butter and castor oil onto hematite in aqueous phase was investigated as a prelude to determine the possible use of these soaps as collector reagents in metal ore beneficiation. The result shows that the most adsorbed of all the soaps with respect to time is potassium soap of castor oil. The soaps containing potassium in all soaps type adsorb faster followed by the soaps containing calcium. Aluminum soap has the least adsorption but the result however shows that between 48 and 50 minutes, all type of soaps attains equilibrium adsorption. The level of adsorption of all the adsorbates on the surface of the adsorbent suggests that all the potassium soaps of castor oil in this study show reasonable degree of surface coverage with time that may warrant their use as collector reagents in flotation separation of hematite from its ore.

Keywords: adsorption; rubber seed oil; castor seed oil; Shea butter; soap; ore; hematite

1. Introduction

Adsorption is a process in which some surfaces attract and retain molecules of other species when they are brought into contact. Adsorption science has exhibited great potential in many technological and industrial systems such as the filtration of impurities from liquids or gases, the bonding of reactant molecules to the solid surface of a heterogeneous catalyst, the segregation of surfactant molecules onto the surface of a liquid, and the migration of ions to the surface of a charged electrode. The adsorption of soaps onto the surface of an adsorbent as a function of time is one of the important parameters in determining adsorption efficiency. Adsorption and its phenomena have received a lot of attention by several investigators who reported the dependence of the process on factors such as temperature, pressure, effective surface area, pH, concentration, ionic charge, and ionic strength, nature of adsorbate and time [1-10].

Metallic soaps are understood to refer to the sparingly soluble or insoluble salts of saturated and unsaturated, straight-chain and branched, aliphatic carboxylic acids with 8 - 22 carbon atoms. They are reaction products of saturated or unsaturated fatty acids (carboxylic acids) with alkaline, alkaline earth or transition metals [11]. Metal soaps are also known as fatty acid salts [12]

A crude castor oil is a pale straw colour but turns colorless or slightly yellowish after refining and bleaching. The crude oil has distinct odour, but it can easily be deodorized in the refining process. Like any other vegetable oils and animal fats, it is a triglyceride, which chemically is a glycerol molecule with each of its three hydroxyl group esterified with a long clown fatty acid. Its major fatty acid is the unsaturated, hydroxylated 12-hydroxy, 9-octadecenoic acid, known as ricinoleic acid. The fatty acid composition of a typical castor oil contains about 87% of ricinoleic acid [13]. The seeds of rubber tree (Hevea brasiliensis) have been found to be rich in oil. Its content in the dried kernel varies from 35 to 45%. It is semi-drying and consists of 17 - 22% saturated fatty acids and 17 - 82% unsaturated fatty acids and is comparable to drying oils commonly used in surface coating. It is composed mainly of linolenic acid (50%) [14]. Shea butter oil botanically called Butyrospermum parkii is a soft paste of melted fat with a milky colour in solid form and brownish when melted. It has a characteristic odour. It contains fatty acid triglyceride and a high amount of unsaponifiable matter, which ranges from 2.5 to 15% [15]. Equally, unrefined shea butter oil is superior in that it retains all its natural vitamins, especially vitamins A and E. Crude shea butter has natural antioxidant properties due to its tocopherol content [16]. Shea butter oil has the following fatty acid composition: palmitic acid (C16) 8.5%, stearic acid (C18) 35.9%, oleic acid (C18) 49.9% and linoleic acid (C18) 5.3% [16].

2. Materials and Methods

Ore containing samples of hematite obtained from Itakpe, Nigeria (76.9% iron) were crushed in the laboratory using jaw and roll crushers. Gravimetric method of jigging and tabling was employed in removing siliceous materials, while magnetic separation method was used in separating magnetic materials from the ore sample. Sieve analyses were performed using the British standard sieve plates to obtain sample of hematite – 70 micron. Mineralogical analysis of the ore sample was performed with volumetric and atomic absorption spectrometric (Buck scientific atomic absorption spectrophotometer - model 205A) methods of analyses. Solutions of reagents were prepared with distilled de-ionised water. Sodium hydroxide and hydrochloric acid solutions were used for pH adjustments. BDH chemical reagents analytical grade (of not less than 98% purity) were used in this study. Determination of specific surface area (SSA) was done by the ethylene-glycol-monethyl ether (EGME) method [17].

2.1. Soap Preparation

The 50 g different types of oil (rubber seed oil, castor seed oil and shea butter) was added to each 50 mL of 30% potassium hydroxide, calcium hydroxide and aluminum hydroxide, and 30 mL of ethanol was added into each of the 600 mL beakers, then heated at 90 ^{o}C for 1 h in a water bath with vigorous stirring until creamy-pasty soaps are formed. A 50 mL of hot saturated sodium chloride solution was then added to each of the pasty soaps with vigorous stirring for short period and allowed to cool overnight. The soaps cake formed on the surface of the 'lye' were removed and air dried and stored in plastic containers [18].

2.2. Calibration Studies

The electrical conductance of 25 cm^3 soap (potassium, calcium and aluminum soaps of rubber seed oil, castor seed oil and shea butter) solutions of different concentrations were measured at 29 0C and pH 7.31, using an electronic conductivity meter (model-90 check-mate deluxe field system-corning). From the result, a calibration graph of the soap conductance was plotted against the square root of soap concentrations based on the Kohlrausch law equation [19]:

$$^{\wedge}m = {}^{\wedge\circ}m - KC^{1/2} \quad \ldots\ldots\ldots\ldots\ldots\ldots \text{(1)}$$

where $^{\wedge}$m is the molar conductivity, $^{\wedge\circ}$m is the limiting molar conductivity, C is the concentration of the solution and K is a constant.

3. Results and Discussion

The % adsorption of soaps onto the surface of an adsorbent as a function of time is one of the important parameters in determining adsorption efficiency. The % adsorption of these soaps as a function of time are presented in tables below.

Table 1: Percentage Absorption of K^+ Shea Butter Soap onto Hematite at Different Contact Times

Time (min)	Initial K^+ shea Butter conc. (g/L)	Equilibrium conductance (u S/m)	Equilibrium K^+ shea butter soap conc. (g/L)	Conc. of shea butter soap adsorbed (g/L)	% of K^+ shea butter soap adsorbed
0	1.0	0.0	00	0.0	0.0
5	1.0	67	0.0899	0.0227	22.7
10	1.0	59	0.0740	0.0361	36.1
20	1.0	53	0.0571	0.0470	47.9
30	1.0	50	0.0518	0.0521	52.1
40	1.0	49	0.0495	0.0535	53.5
50	1.0	47	0.0495	0.0542	54.2
60	1.0	47	0.0945	0.0542	54.2

Table 2: Percentage Adsorption of Ca^{++} Shea Butter Soap onto Hematite at Different Contact Times

Time (min)	Initial Ca^{++} shea butter conc (g/L)	Equilibrium conductance (u S/cm)	Equilibrium Ca^{++} shea butter soap conc. (g/L)	Conc. of Ca^{++} shea butter soap adsorbed (g/L)	% of Ca^{++} shea butter soap adsorbed
0	1.0	0.0	0.0	0.0	0.0
5	1.0	90.1	0.0821	0.0179	17.9
10	1.0	87.0	0.0829	0.0309	30.9
20	1.0	85.0	0.0745	0.0429	42.9
30	1.0	83.0	0.0695	0.0482	48.2
40	1.0	72.0	0.0486	0.0505	50.5
50	1.0	70.0	0.0430	0.0505	50.5
60	1.0	70.0	0.0430	0.0505	50.5

Table 3: Percentage Adsorption of Al^{3+} Shea Butter Soap onto Hematite at Different Contact Times

Time (min)	Initial Al^{3+} shea butter conc (g/L)	Equilibrium conductance (u S/cm)	Equilibrium Al^{3+} shea butter soap conc. (g/L)	Conc. of Al^{3+} shea butter soap adsorbed (g/L)	% of Al^{3+} shea butter soap adsorbed
0	1.0	0.0	0.0	0.0	0.0
5	1.0	104.0	0.0899	0.0101	10.1
10	1.0	84.0	0.0829	0.0171	17.1
20	1.0	78.0	0.0745	0.0255	25.5
30	1.0	76.0	0.0695	0.0287	28.7
40	1.0	73.0	0.0713	0.0305	30.5
50	1.0	73.0	0.0683	0.0317	31.7
60	1.0	73.0	0.0683	0.0317	31.7

Table 4: Percentage Adsorption of K^+ Castor Oil Soap onto Hematite at Different Contact Times

Time (min)	Initial K^+ shea butter conc (g/L)	Equilibrium conductance (u S/cm)	Equilibrium K^+ shea butter soap conc. (g/L)	Conc. of K^+ shea butter soap adsorbed (g/L)	Conc. of K^+ shea butter soap adsorbed (g/L)
0	1.0	0.0	0.0	0.0	0.0
5	1.0	58	0.0730	0.0270	27.0
10	1.0	48	0.0530	0.0470	47.0
20	1.0	40	0.0365	0.0635	63.5
30	1.0	44	0.0300	0.0700	70.0
40	1.0	39	0.0274	0.0726	72.6
50	1.0	36	0.0252	0.0748	74.8
60	1.0	36	0.0252	0.0748	74.8

Table 5: Percentage Adsorption of Ca^{++} Castor Oil Soap onto Hematite at Different Contact Times

Time (min)	Initial K^+ castor oil conc (g/L)	Equilibrium conductance (u S/cm)	Equilibrium K^+ castor oil soap conc. (g/L)	Conc. of K^+ castor oil soap adsorbed (g/L)	Conc. of K^+ shea castor oil soap adsorbed (g/L)
0	1.0	0.0	0.0	0.0	0.0
5	1.0	54.0	0.0770	0.0230	23.0
10	1.0	49.0	0.0570	0.0430	43.0
20	1.0	43.0	0.0405	0.0595	59.5
30	1.0	38.0	0.0340	0.0660	66.0
40	1.0	36.0	0.0316	0.0684	68.4
50	1.0	34.0	0.0294	0.0706	70.6
60	1.0	34.0	0.0294	0.0706	70.6

Table 6: Percentage Adsorption of K^+ Rubber Seed Oil Soap onto Hematite at Different Contact Times

Time (min)	Initial K^+ rubber oil conc (g/L)	Equilibrium conductance (u S/cm)	Equilibrium K^+ rubber oil soap conc. (g/L)	Conc. of K^+ rubber oil soap adsorbed (g/L)	Conc. of K^+ rubber oil soap adsorbed (g/L)
0	1.0	0.0	0.0	0.0	0.0
5	1.0	103	0.0794	0.0206	20.6
10	1.0	94	0.0658	0.0341	34.1
20	1.0	86	0.0597	0.0403	40.3
30	1.0	79	0.0545	0.0455	45.5
40	1.0	76	0.0526	0.0474	47.4
50	1.0	73	0.0503	0.0497	49.7
60	1.0	73	0.0503	0.0497	49.7

Table 7: Percentage Adsorption of Ca^{++} Rubber Seed Oil Soap onto Hematite at Different Contact Times

Time (min)	Initial Ca^{++} rubber oil conc (g/L)	Equilibrium conductance (u S/cm)	Equilibrium Ca^{++} rubber oil soap conc. (g/L)	Conc. of Ca^{++} rubber oil soap adsorbed (g/L)	Conc. of Ca^{++} rubber oil soap adsorbed (g/L)
0	1.0	0.0	0.0	0.0	0.0
5	1.0	68	0.0802	0.0198	19.8
10	1.0	64	0.0676	0.0324	32.4
20	1.0	62	0.0614	0.0386	38.6
30	1.0	60	0.0561	0.0439	46.0
40	1.0	57	0.0523	0.0460	46.0
50	1.0	57	0.0523	0.0460	46.0
60	1.0	57	0.0523	0.0460	46.0

Table 8: Percentage Adsorption of Al^{3+} Rubber Seed Oil Soap onto Hematite at Different Contact Times

Time (min)	Initial Al^{3+} rubber oil conc (g/L)	Equilibrium conductance (u S/cm)	Equilibrium Al^{3+} rubber oil soap conc. (g/L)	Conc. of Al^{3+} rubber oil soap adsorbed (g/L)	Conc. of Al^{3+} rubber oil soap adsorbed (g/L)
0	1.0	0.0	0.0	0.0	0.0
5	1.0	68	0.0918	0.0082	8.20
10	1.0	65	0.0849	0.0151	15.2
20	1.0	61	0.0766	0.0234	23.4
30	1.0	57	0.0747	0.0253	25.3
40	1.0	55	0.0714	0.0286	28.6
50	1.0	52	0.0695	0.0305	30.5
60	1.0	52	0.0695	0.0305	30.5

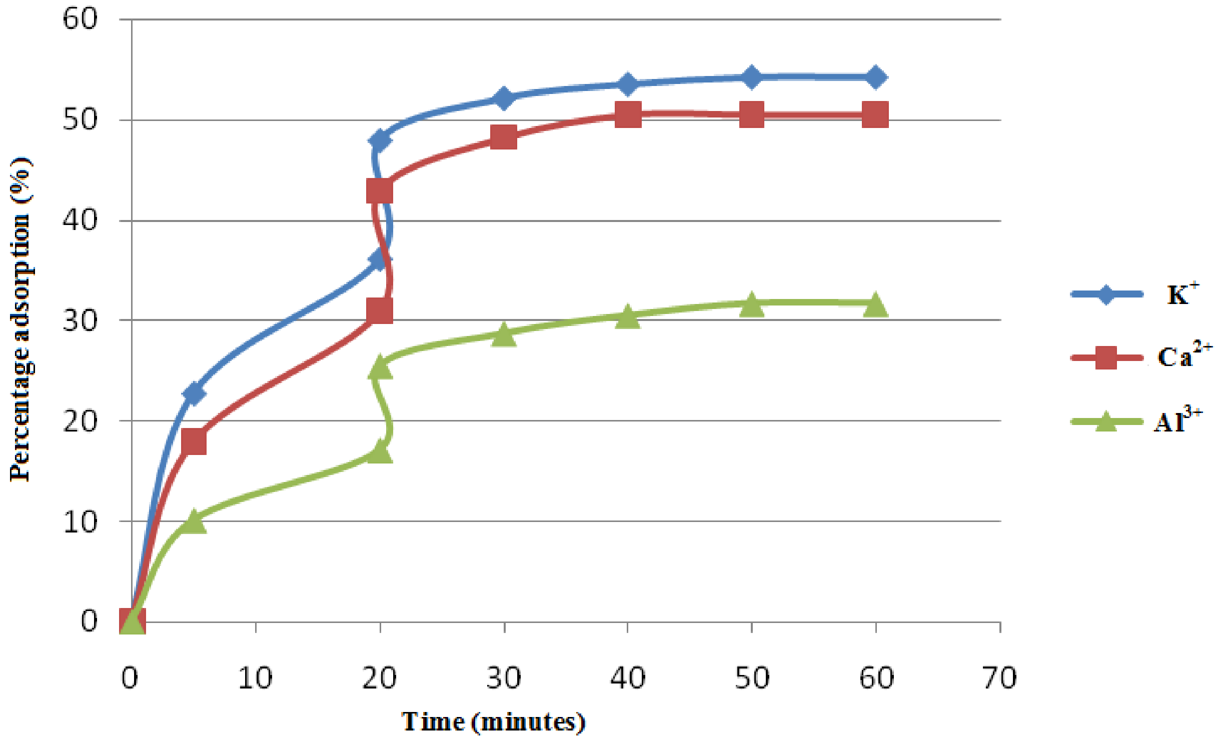

Figure 1. Plot of percentage of K^{+}, Ca^{2+}, Al^{3+} soaps % adsorption against time

From the figures, the rate of adsorption of the soaps are initially rapid for the first ten minutes and thereafter decrease until equilibrium is attained, the time taken to attain equilibrium adsorption and percentage adsorption at equilibrium was also obtain from the figures above and were tabulated below.

Table 9: Percentage Adsorption of Soaps with time at equilibrium

Types of soap	Time (mins) taken to attain equilibrium	Percentage (%) adsorption
K^+ shea butter	49	54.2
Ca^{++} Shea butter	50	50
Al^{3+} shea butter	50	32
K^+ castor oil	48	74
Ca^{++} castor oil	49	71
K^+ rubber oil	50	50
Ca^{++} rubber oil	50	46
Al^{3+} rubber oil	50	30

Table 9 above shows the various times taken to attain equilibrium and the percentage of adsorption at equilibrium**.** These results show that between 48 and 50 minutes all soaps attained equilibrium adsorption. The results also reveal that the most adsorbed soap was potassium soap of castor oil at 75%. The possible explanation is that the more homogeneous the oil, the greater the degree of adsorption. Castor oil has Ricinoleic acid (90.4%), while Shea butter oil and rubber seed oil have oleic acid (49.9%) and Linoleic acid 50% respectively. As can be seen the adsorptions of the soaps of Shea butter and Rubber oil soaps are similar. The order of percentage adsorption is potassium castor oil> calcium soap of castor oil > Shea butter soap of potassium > calcium soap of Shea butter > potassium soap of rubber oil > calcium soap of rubber oil > aluminum Shea butter soap > rubber oil soap of aluminum. This may not be the only reason for the observed differences in the values of the adsorption density. It is likely that the differences in adsorption densities may also rise from the differences in the predominant fatty acid composition of the oils. Castor oil is predominantly composed of ricinoleic acid (90.4%), an 18 carbon unsaturated acid with a hydroxyl group, while Shea butter Shea butter oil is predominantly made up of oleic acid (50%) and rubber seed oil composed of linoleic acid (50%). Oleic acid is an 18 carbon unsaturated acid, while linoleic acid also has 18 carbon atoms but more unsaturated fatty acid with three double bonds. The presence of the hydroxyl group in the linoleic acid is the only significant different between these acids and may therefore enhance a higher degree of adsorption as evidenced in the case of the castor oil soap. It is also observed that the % adsorption with time has a correlation with the size to charge ratio which are 0.75 Λ^0, 2.02 Λ^0, and 5.77 Λ^0, for K^+, Ca^{2+} and Al^{3+} respectively. Hence, we may conclude that the smaller the size to charge ratio, the higher the adsorption percentage. This is affirmed by the relative values of the % of adsorption of rubber seed oil where percentage are 50, 46, and 30 for K^{+}, Ca^{2+} and Al^{3+} respectively. We can therefore conclude that the % of adsorption and by extension the adsorption density is influenced by the predominant fatty acids in the oils, unsaturation and the degree of unsaturation as well as the size to charge ratio of the ions.

4. Conclusion

The % adsorption of soap onto the surface of an adsorbent as a function of time has been investigated for three types of soaps; three factors determines the adsorbent potential of each soap with respect to time, these are 1.The homogeneity of the oil. The fatty acid composition of the oil. 3. The size to charge ratio of the metal in the soap. In conclusion, oils that are more homogeneous, has saturated fatty acids in its composition has better adsorbent property on hematite with time, also the smaller the charge on the metal, the better the adsorbent properties with respect to time. So in making of soap for the purpose of adsorption on hematite, metals with least size to charge ratio, saturated and more homogeneous oil should be considered.

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