ENTRY TO THE

STOCKHOLM JUNIOR WATER PRIZE 2012

INVESTIGATION OF THE USE OF SODIUM-ACTIVATED BENTONITE CLAY IN THE REMOVAL AND RECOVERY OF NON-IONIC SURFACTANTS FROM WASTEWATER

Names of Finalists

NG, Tian Ting Carrie-Anne

LIM, Jun Yong Nicholas

CHAM, Luigi Marshall

Anderson Junior College

SINGAPORE

Acknowledgements

The team would like to thank our mentors for their continuous guidance in one way or another in helping us complete the project. Also, special thanks to Dr Sarasa of the North Zone Centre of Excellence for Science for allowing us to have use of the Elementz Lab in Anderson Junior College and for her tremendous guidance in the use of laboratory equipment for the purpose of this project such as the HPLC.

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Investigation of the Use of Sodium-Activated Bentonite Clay in the Removal and Recovery of Non-ionic Surfactants from Wastewater

I. Abstract

In this study, the feasibility of the use of Sodium Activated Bentonite Clay in the removal and recovery of non-ionic surfactants, in which Triton X-100 is used; from waste water through a novel flocculation-flushing method is validated. A ratio of sodium carbonate is introduced into the Bentonite Clay to activate it. There are investigations on how the concentration of non-ionic surfactants in waste water, and amount of Activated Bentonite Clay used affects the absorption rate, determined through the use of the modified Freundlich and Langmuir isotherm adsorption models in order to investigate its feasibility for the flocculation mechanism. This study also validates the feasibility of recovery of non-ionic surfactants from the Bentonite Clay mixture by alcohol group compounds, in which Ethanol and Propan-1-ol, are used in this study whilst being unable to desorb in ionised solutions. Thus, the relationship between recovery rate percentage and the changing volume of a 50% Alcohol solution is determined through the use of Langmuir equation in order to validate its feasibility for the flushing mechanism.

Keywords: Non-ionic surfactants; Triton X-100; Freundlich/Langmuir model; Alcohols; Flocculation-flushing method

II) Introduction

The limited water supply has led the world into re-using more of these resources. Yearly, the percentage of water re-used has been increasing. This fact has been the driver for the improvement of water purification, and indeed, it has advanced greatly.

The process of purifying water involves tremendous amounts of resources and processes. One of such processes is flocculation; a process together with coagulation is used in order to remove organic and inorganic particles from water. While such method is effective enough to remove these suspended particles, however, the resulting formation of sludge, as shown in Figure 1.1 due to recovered waste and used flocs is hazardous and may contribute into worsening of pollution of the environment.

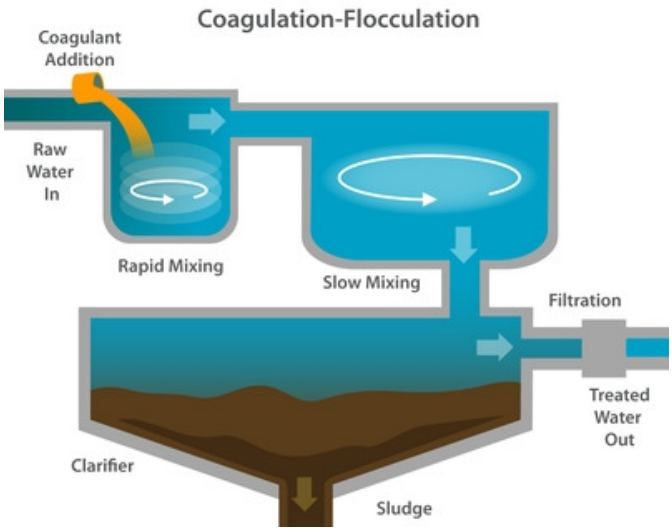


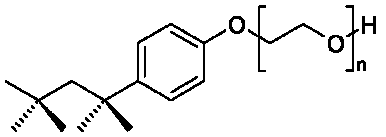
Figure 1.1 Coagulation-Flocculation mechanism ©US-EPA

Activated porous materials are widely used for removing pollutants through flocculation. The adsorption of organic compounds by activated carbon is partly controlled by physical interactions, which are affected by surface area available for reaction. Having a porous nature and a high surface area, activated porous materials have feasible properties for adsorption.

One of such porous materials is bentonite clay. Bentonite is an absorbent aluminium phyllosilicate, essentially impure clay consisting mostly of montmorillonite. Bentonite has been known to be a good sorbent of inorganic particles such as metal cation through the process of ionic exchange with the bentonite's ionic layer. Natural bentonite, however, is shown to be an ineffective sorbent for inorganic particles in water, even though they have a high surface area. Yet, with a simple ion-exchange, the surface properties of natural bentonite

can be changed. An ion-exchange reaction with Sodium Carbonate, for example, calcium cations are replaced by sodium cations and activated sodium bentonite is obtained[7].

Non-ionic surfactants (Triton X-100 non-ionic surfactant structural formula pictured) are of widespread use in industrial, detergency, agricultural, and cosmetic products. Their common presence has made them, together with other types of surfactants, major pollutants to water and the environment alike.



They are generally mild–toxic to aquatic life and could also cause further environmental damage. Large amounts of non-ionic surfactants, especially in urban areas, are released into the sewer network every day and chemicals are only removed at the same time at the filtration plant with the use of chemicals or chemically activated absorbents. Removal of non-ionic surfactants is expensive and lessens chances of actual recovery and recycling of non-ionic surfactants. Oils, grease and other particles in wastewater react with non-ionic surfactants, like other surfactants, while they are traveling through sewer lines from the source to the wastewater treatment centres and form sludge that congests the pipelines and filtration systems, which may cause massive damage to them, and could result to flooding.

Recent studies[6] have shown that activated bentonite has a relatively rigid, non-polar surface amenable to Non-ionic organic compounds uptake by adsorption by activated carbons, resulting to its possibility in adsorbing non-ionic surfactants through chemical bonding with its silica layer as shown in Figure 1.[10]

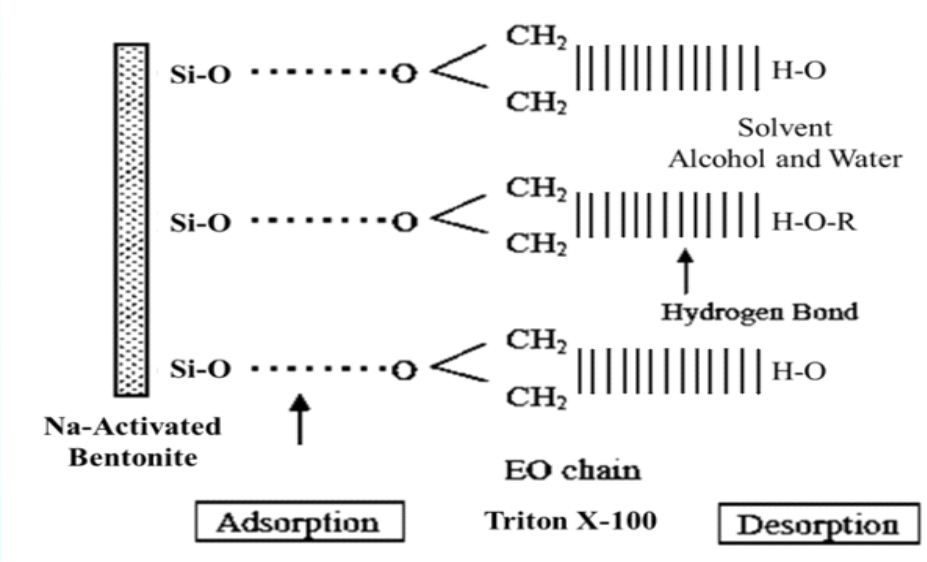


Figure 1.2: Removal and Recovery System of Triton X-100 from Waste Water (Illustration only)

Furthermore, there is a relative ease for non-ionic surfactants to dissolve in alcohol and water solutions due to the ability of ethylene oxide (EO) chains[1] that are present in surfactants to form hydrogen bonding with alcohol/water molecules as shown in Figure 1. The recovery of non-ionic surfactants from bentonite into diluted alcohol could allow the recovery of non-ionic surfactants such that they can be re-used for surfactant synthesis and not released to the environment.

Why recover non-ionic surfactants? Nowadays, non-ionic surfactants are being disposed of after the water filtration process (through activated carbon adsorption or through addition of bacteria) through combustion and/or left in sludge. Such is expensive on its own accord. However, by recovering non-ionic surfactants through alcohols and the use of Na-Activated Bentonite, not only it prevents this potentially dangerous chemical to enter main-stream, it is also cheaper and such recovery allows the recycling of non-ionic surfactants for re-use on household products and allows the by-passing of the first phase of surfactant syntheses for such products, making manufacturing of these products cheaper.

2.1 Objectives of Study

This study will examine the feasibility of using bentonite activated with Sodium Carbonate, in order to remove non-ionic surfactants from waste-water with the use of a flocculation-flushing method. Activated bentonite will be flocculated into waste-water to absorb the non-ionic surfactants. The bentonite will then be removed through sedimentation. After which, the activated bentonite will be flushed with alcohol to facilitate the recovery of non-ionic surfactants. The study will also examine how the organic non-ionic surfactant would desorb into ionised water as compared to that of diluted alcohol.

Figure 2 presents the proposed process flow diagram:

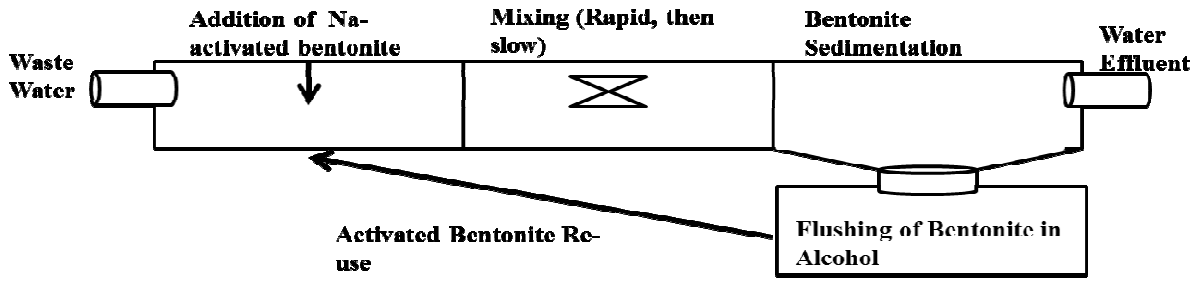


Figure 2: Proposed Process Flow Diagram for Flocculation-Flushing method

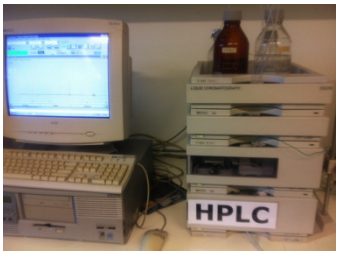
Such feasibility will be examined in this study by first proving that sodium carbonate activated bentonite has a very good affinity, therefore having efficient adsorption with Triton X-100 and suitable for the method shown above at non-ionic surfactant concentrations of up to 300ppm reflecting the average concentration in water sewage through the plotting of the modified-Freundlich and Langmuir adsorption models. Moreover, through an adsorption graph, it is to be also proved that the flushing of diluted alcohol solution would desorb and recover Triton X-100 surfactant from the Na-Activated Bentonite at near 100% rate while unable to desorb in ionised water. Results will be assessed whether the proposed Flocculation-Flushing method to recover and non-ionic surfactants by the use of Na-Activated Bentonite and separating it from inorganic particles would be suitable for preliminary real-world water filtration before reaching the main sewage channels.

Flocculation, being an integral part of water filtration, could allow this mechanism to complement the present mechanism instead of starting from scratch.

III) Materials and Methodology

3.1 Materials

Laboratory-grade Triton X-100 having density 1.07g/cm^3 was used as the non-ionic surfactant in this study. Natural Bentonite was also used with an activating solution of 1% Sodium Carbonate to activate the bentonite clay. Alcohols in their concentrate form, such as ethanol and propan-1-ol, were also used.



In order to detect non-ionic surfactant concentration, an HP 1100 high-performance liquid chromatographic system (HPLC) was used. Such is equipped with a reverse-phased C-18 column. For the elution, mobiles phases used were 60% water (mobile phase A) and 40% methanol (mobile phase B). Injection volume was 20 µL, and flow rate was 1.0ml/min at room temperature. Detection was carried out by measuring absorbance at 280nm.

Micro-pipettes and a centrifuge machine of maximum 3000rpm were also used for this study.

3.2 Preparation of Materials and Samples

A 30g amount of bentonite was submerged into 200mL solution of 1% Sodium Carbonate, and was left until the Na-activated bentonite (shown on right) settled. After which it was extracted through sedimentation.

A number of solutions of the contaminated water, which contains 100ppm, 150ppm, 200ppm and 300ppm of Triton X-100 non-ionic surfactants, were also prepared in a 200mL beaker through the use of a micro-pipette.

The alcohol solution was also prepared, in which the alcohols, ethanol and propan-1-ol, were diluted into 50% volume at 30, 50 and 80 mL solutions.

3.3 Flocculation of Non-ionic surfactants from waste-water

Controlled samples of 20 µL from 200mL water contaminated with 100ppm, 150ppm, 200ppm and 300ppm of Triton X-100 were first injected into the HPLC in order to find the controlled peak and time appearance.

The 300ppm Triton X-100 solution was separated into four 50mL solutions, in which 2g, 4g, 6g and 8g respectively of activated bentonite were added into each beaker. 8g of bentonite were also added to solutions with 100, 150, 200, and 300ppm of Triton X-100. Solutions were stirred for a few minutes to assure homogeneity. After which, a portion of these solutions were placed in a centrifuge machine at 400rpm for 5 minutes. The bentonite's sediment at the bottom was extracted, and the remaining solution was tested through HPLC.

3.4 Flushing of Na-Activated Bentonite with Alcohol Solution.

The bentonite from the 300ppm Triton X-100/8g bentonite batch, after extraction, was separated then placed on top of separate filter papers and flushed with 30, 50 and 80mL of 50 volume% alcohol solutions of ethanol and propan-1-ol respectively by mixing and is left overnight. After which, these alcohol solutions were then tested through HPLC for concentration of Triton X-100.

The same process as above was done for a 1% Sodium ion solution and was tested through HPLC for presence of concentration of Triton X-100

IV) Results and Discussions

4.1 Adsorption of Non-ionic Surfactants to Sodium-Activated Bentonite

These sorption experiments were conducted at constant temperature and relatively constant pH (6-8). In order to verify that activated sodium bentonite is feasible for flocculation method, it must be shown that a) Adsorptive affinity of Na-Bentonite to Triton X-100 must be malleable to the fluctuating concentration and pressure through the modified Freundlich adsorption isotherm model curve and b) the bentonite must have a good saturated capacity of Triton X-100 adsorption shown through the Langmuir isotherm model.

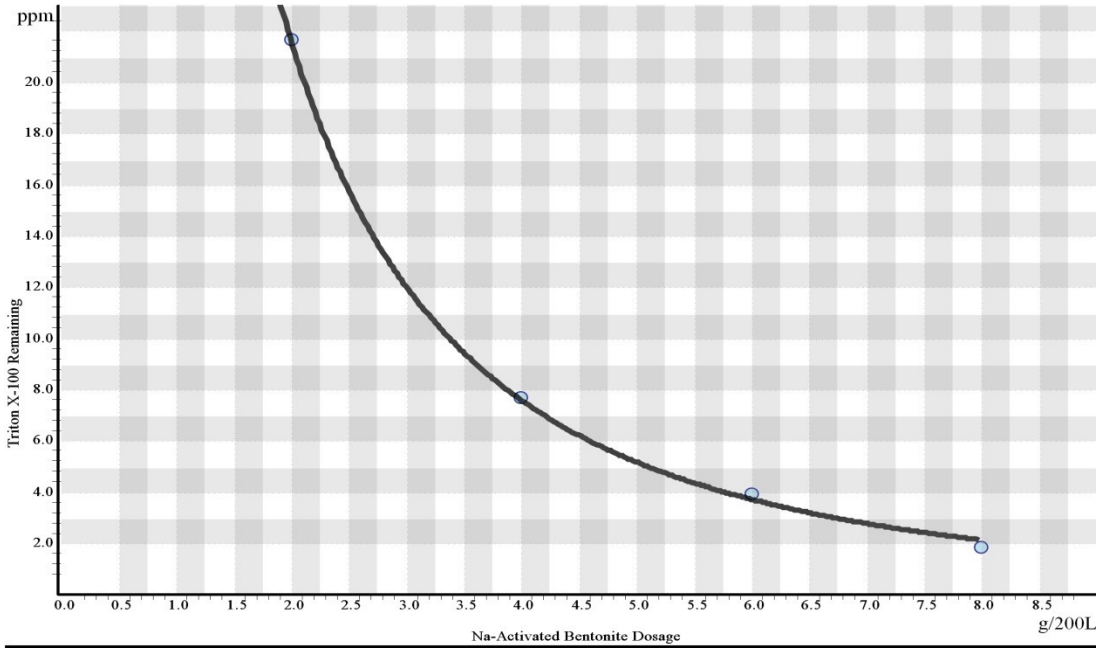


Figure 3: Adsorption curve of a 300ppm non-ionic surfactant (Triton X-100) in which remaining Triton X-100 is plotted against Na-Activated Bentonite Dosage

From Figure 3, it can be seen that Sodium activated bentonite absorbs more Triton X-100 when its mass increases. For example, there would be about 6.5% of Triton X-100 left when only 2g of Bentonite is used, as compared to about 0.4% of Triton X-100 when 8g is used. It can be said that the Na-Activated bentonite has a good adsorption towards TritonX-100 non-ionic surfactant.

Since there would always be fluctuations of non-ionic surfactant concentrations in waste water, therefore, the modified Langmuir (Freundlich) adsorption model has also been used in this study to observe how Na-activated bentonite would fare in its adsorption rate

when there is a change on the amount of concentration of non-ionic surfactants present in waste-water.

In the purpose of this study, we would like to ensure that the modified Langmuir (Freundlich) adsorption isotherm model equation is effective within the range of the concentration used in this study. The equation is given as:

$$\lg(X/M) = \lg K + \lg C^{(1/n)}$$

where:X=Amount of Triton X-100 absorbed; M=Mass of Na-Bentonite used

C=Concentration of Triton X-100 used

K&n= Constants specific to adsorbent and adsorbate conditions and substance

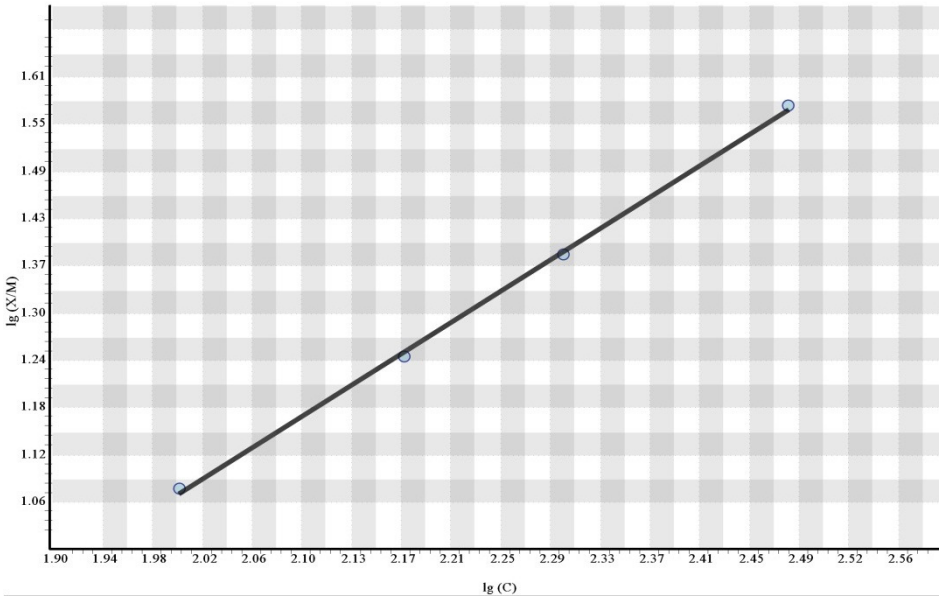


Figure 4: Verification of Langmuir (Freundlich) Equation (lg(X/m) vs. lg(C))

As can be seen from Figure 4, when log(X/M) is plotted against log(C), a straight line has been obtained in which gradient=1/n=1.04 (3sf) and log k being the y-intercept. It can be said that the modified Freundlich equation is applicable for the range of concentration of Triton X-100 used in this study. Furthermore, given that the power of concentration is near 1, according to the equation, amount of concentration can be considered as intermediate and thus, also shows that the adsorption isotherm of Triton X-100 to Na-activated Bentonite can be approximated and be applicable to the more accurate Langmuir equation, which was used in this study.

The Langmuir equation model has then been used for this study and is fitted with experimental data as shown in Figure 5.

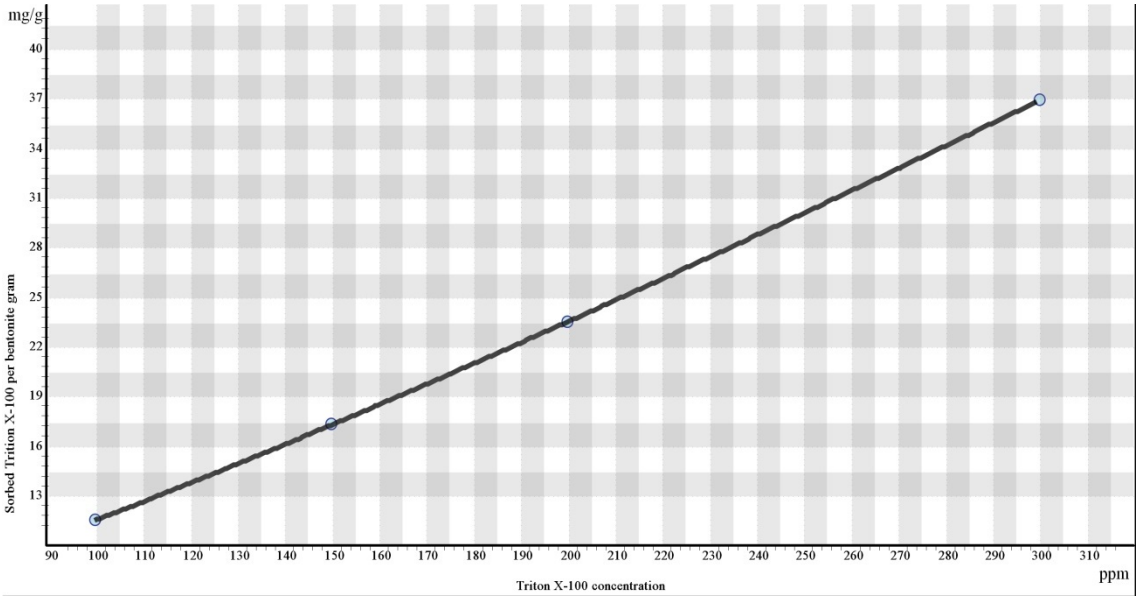


Figure 5: Langmuir equation curve of sorbed non-ionic surfactant (Triton X-100) ppm/bentonite gram vs. differing concentrations of 8g Bentonite sorption

As can be seen from Figure 5, the concentrations of Triton X-100 tested, have still not reached their saturation point. As can be deduced from the Langmuir graph, as the maximum absorption amount as determined by the graph has not been reached yet by 300ppm, it means that adsorbed amount of Triton X-100 still increases when concentration of Triton X-100 is increased, provided that the Langmuir isotherm still applies when concentration is increased. Given that the average maximum concentration of non-ionic surfactants in waste-water does not extend beyond 300ppm, it would be feasible to use Na-bentonite for the adsorption of Non-ionic surfactants.

The reason which could attribute sodium-activated bentonite to having good adsorption of non-ionic surfactants (Triton X-100) is that by activating the bentonite, the non-ionic surfactant would have more affinity to attach to the bentonite's silica layer. Furthermore, the presence of hydrogen bonding also makes Triton X-100's affinity more stable. This would make such adsorption rather spontaneous. As a result, activated sodium bentonite is feasible for the flocculation method.

4.2 Recovery of Non-ionic Surfactants from Sodium-Activated Bentonite by Alcohols

Due to non-ionic surfactants' ability to react with alcohols to form ethylene glycols, the Langmuir equation model has also been used to show alcohols adsorption rate of Triton X-100.

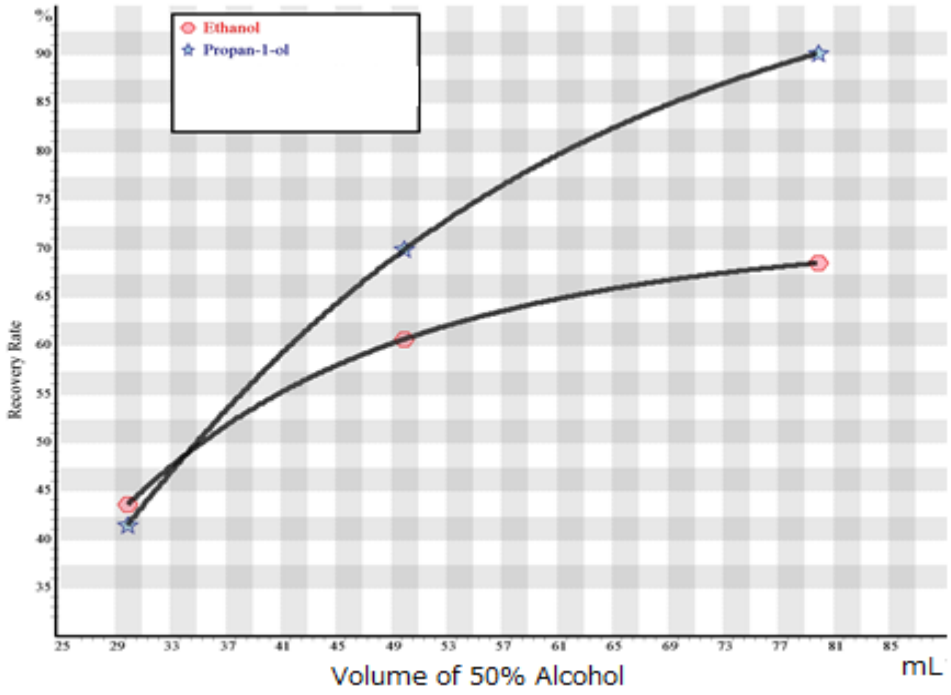


Figure 6: Langmuir-fitted equation curve of a non-ionic surfactant (Triton X-100) sorped percentage in differing volumes of 50% of Alcohol Concentration

The acquired recovery rate may have been caused by the presence of hydroxide ions in the alcohol solution, which have resulted in a spontaneous reaction of the non-ionic surfactants ethylene oxides with water and alcohol to form ethylene glycol since hydroxide ions act as catalyst for this reaction.

From Figure 6, it can be seen that the maximum adsorption rate reached by the alcohols is only about 90% with propan-1-ol having the higher adsorption rate. A possible reason why propan-1-ol has a higher recovery rate is because with a longer alcohol group, the O atom in the OH functional group would become more electronegative, inclining it to react with non-ionic surfactants to form ethylene glycol.

With ionised water, which contains 1% Sodium ions, however, no presence of non-ionic surfactants were detected and such remains chemisorbed at the bentonite layer.

The lower adsorption rate of the non-ionic surfactants by alcohol could be attributed to the non-ionic surfactant's ethylene oxide settling in between the bentonite's silica layer and such layer may already have collapsed and the non-ionic surfactants chemisorbed, and due to the non-ionic surfactant's hydrogen bonding with the bentonite, more energy is required to break such bonds than the energy is released with the reaction with the alcohol solution.

The reason of a 50% volume of alcohol in the solution is such that in order to increase the recovery rate. Too low a volume would not cause a recovery of non-ionic surfactants, while a high volume percentage require the use of external heat since alcohol saturation could prevent surfactant desorption. Such instance leads to little to no reaction with alcohol or water by non-ionic surfactants to form ethylene glycol.

With still a rather high adsorption rate, the usage of alcohol can still be considered for the flushing method, although it must be done in excess volume until saturation point as determined by the Langmuir curve is reached.

V) Conclusion

The experimental results in this study do demonstrate that the proposed flocculation-flushing method may be feasible, albeit with some limitations. The high affinity of non-ionic surfactants (Triton X-100) with sodium-activated bentonite, able to reach an almost 100% adsorption rate, makes the bentonite feasible for the flocculation mechanism. Moreover, the recovery rate of alcohols, while just having a maximum 90% recovery rate from the experimental results, could still be an acceptable recovery range as studies[8] have also shown that presence of non-ionic surfactants in activated clays could also help in the adsorption of cationic surfactants, a much more toxic pollutant, which could also be applicable to Na-Activated Bentonite . Still, further investigation could be done by varying the % volume of alcohol in the solution and the alcohol used to find the optimal volume %. Moreover, how the non-ionic surfactant is unable to desorb by ionised water while inorganic particles can dissolve into. Thus, this shows that it can be separated from inorganic particles, preventing its mixture into sludge.

With such, an implementation of such kinds of mechanism within sewer systems, especially in urban ones, could prevent a high concentration of non-ionic surfactants from entering the main sewage channels and filtration plants, which can clog and damage them. As

said, flocculation, being an integral part of water filtration, could allow this mechanism to complement the present mechanism instead of starting from scratch.

With the dangers of phenol being released to waste-water, such mechanism may help in alleviating this problem. A more efficient recovery method, and how this can be used for adsorption of cationic and anionic surfactants and how it can be expanded for use with inorganic metal ions, can be further studied.

VI) Recommendations

We would like to recommend more verifications of the hypothesis through the use of more sophisticated equipment such as a more powerful HPLC or other equipment in order to verify suitability of the Na-Sodium Activated Bentonite for flocculation-flushing method above 300ppm Triton X-100 non-ionic surfactants and introducing other models to verify the hypotheses such as the Beer-Lambert model. Furthermore, time and pH changes were not factors in the experiment, as there is no proper equipment to be able to measure such.

This project can be further expanded such that to determine the effects of pH in desorption of non-ionic surfactant into the alcohol solution. Furthermore, the flocculation-flushing method can be further expanded to include metal ion recovery which constitutes a large percentage of sludge waste. The adsorption of metal ions from waste-water into Na-activated bentonite can be studied. Moreover, desorption and subsequent recovery of these metal ions can also be studied. Research[11] has shown that the ionic radius, consequently the charge density, of metal ions plays a part in desorption of these metal ions from clay, in which bentonite is one of them. Heavy metals such as Mercury and Uranium can desorb at low pH and at different acid concentrations and reagents, sulfuric acid solution for mercury and nitric acid solution for uranium for example, while higher pH solutions and ion-exchange are required to desorb lighter metals such as copper, using basic sodium ion solutions for example. Organic compounds may be easily separated as they should not desorb into polar solutions. As such, it can be hypothesised and further studied that those different metal ions and organic compounds can be recovered and separated through the use of the flocculation-flushing method by using Na-activated bentonite and using differing solutions for recovery, making them available for re-use and thus prevent the build-up of hazardous and unusable sludge waste. An impression of an extended flocculation-flushing method is shown.

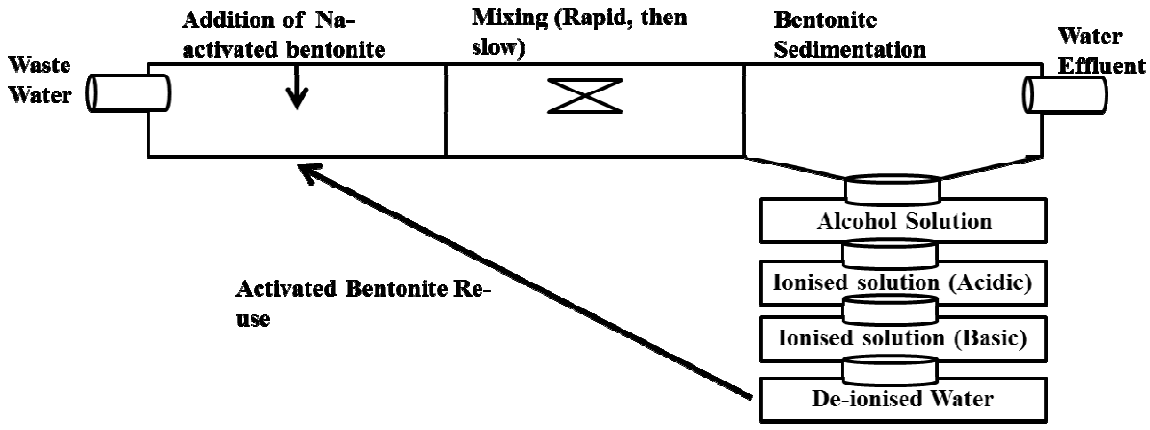


Figure 7: Proposed Process Flow Diagram for the extended Flocculation-Flushing method

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References

1) Chiaki K. et al. (2003) Detergency of Clay/Soil Particles in Water. Effect of Ethanol Mixture
2) Chien H.C. (1994) Adsorption dynamics of surfactants at the air/water interface: a critical review of mathematical models, data, and mechanisms
3) Espantaleón A. G. et al. (n.d.) use of Clays in the Removal of Dyes and Surfactants from Tannery Waste Waters
4) FIU (2003) Sorption characteristics of a nonionic surfactant during remediation of contaminated soil with different organic content, from http://digitalcommons.fiu.edu/dissertations/ AAI3110376/
5) Karlsson Go¨ran (2001) Determination of Triton X-100 in plasma-derived coagulation factor VIII and factor IX products by reversed-phase high-performance liquid chromatography
6) Narkis et al. (1983) Adsorption Of Non-Ionic Surfactants On Activated Carbon And Mineral Clay
7) Saidi A. (2004) Hyperactivation of Bentonite in Pelletizing Process
8) Su et al. (2003) Adsorption of surfactants from water onto raw and HCl-activated clays in fixed beds
9) Trathnigg B. (2001) Liquid exclusion–adsorption chromatography, a new technique for isocratic separation of nonionic surfactants II. Quantitation in the analysis of fatty alcohol ethoxylates
10) Zhang et al. (2011) Effects of Surfactants on montmorillonite Structure
11) Zwaanders FB, JG van der Watt (2011) Clay and Rare-Earth Metals

VII) ANNEXES

a. Summary of Experimental Data

Carbon Dosage /g	HPLC Area /mA*s	Ratio of remaining Triton X-100	Triton X-100 Remaining /ppm
*(300ppm)	289.16031	1	
2.00	20.84358	0.07208	21.62494
4.00	7.35109	0.02542	7.62666
6.00	3.76079	0.01301	3.90177
8.00	1.74764	0.00604	1.81315

Freundlich Adsorption Isotherm model (8.00g Carbon)			
Triton x-100 Concentration/ppm	Triton X-100 Absorped /ppm	lg (C)	lg (X/M)
100	95.34765	2.00000	1.07622
150	141.55398	2.17609	1.24783
200	191.11809	2.30103	1.37821
300	298.18685	2.47712	1.57140

Triton X-100 Concentration /ppm	HPLC Pure Reading /mA*s	HPLC Remainder Reading /mA*s	Ratio	Amount Adsorped /ppm	Per Bentonite Gram Sorped ppm/g
100	97.67802	4.54432	0.04652	95.34765	12.75275
150	145.55884	8.19595	0.05631	141.55398	18.93285
200	190.00122	8.43787	0.04441	191.11809	25.56204
300	289.16031	1.74764	0.00604	298.18685	39.88249

Volume of Ethanol /mL	Adsorped Bentonite HPLC Area /mA*s	HPLC Reading /mA*s	Recovery Percentage /%
30	47.90211	20.84358	43.51286
50	47.90211	29.00769	60.55618
80	47.90211	32.78559	68.44289

Volume of Propan-1-ol /mL	Adsorped Bentonite HPLC Area /mA*s	HPLC Reading /mA*s	Recovery Percentage /%
30	47.90211	19.84358	41.42527
50	47.90211	33.41229	69.75118
80	47.90211	43.14031	90.05931

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