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A Comparison of Cationic Surfactant Immobilized Ion Exchange Membranes in Their Application for Use in Extraction of 4-Nitophenol

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A COMPARISON OF CATIONIC SURFACTANT IMMOBILIZED ION EXCHANGE MEMBRANES IN THEIR APPLICATION FOR USE IN EXTRACTION OF 4-NITROPHENOL

by

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Under the Direction of Dr. Eric Conte

ABSTRACT

Solid Phase Extraction has replaced distillation and liquid-liquid extraction as the most widely used method for extraction from solution. Though traditional SPE has seen great success, its downfalls are that it requires meticulous preparation procedures requiring funtionalized silanes and silica or polymerization courses. An alternative is ion exchange membranes to which long carbon chain ionic surfactants have been attached. The S1000 membrane ion exchange capacity was measured to be approximately 110 micro-equil/disc while the P81 membrane was 150 micro-equil/disc. Octadecyltri-methylammonium surfactant was immobilized on the membrane surface, qualitated through the use of ATR-FTIR, and quantified through elemental analysis. Kinetic

adsorption experiments for cationic surfactant immobilized S1000 and P81 membranes demonstrate that equilibrium times are approximately 1 hour and 3 hours respectively while adsorption isotherms results indicate that S1000 membranes are able to extract 300% of the amount of 4-nitrophenol as extracted by P81 membranes.

INDEX WORDS: Undergraduate research, Chemistry, Solid-phase extraction, Western Kentucky University, Membrane extraction, Phenol, 4-Nitrophenol, Whatman, Nysa, Estrogenic, Standard Curve, Efficiency, Surfactant, Cationic surfactant, Percent Extraction, Functionalized silanes, Student research, Kinetic adsorption, Taiwan, ATR-FTIR, HPLC, Elemental analysis, Octadecyltrimethylammonium chloride, Ion exchange capacity, Back titration, Polymerization, Priority pollutants, S1000, P81

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In the summer of 2008, I was lucky enough to be a part of a research exchange program made possible through an agreement between the governments of the United States of America and the Republic of Taiwan and funded by the National Science Foundation of the United States and the National Science Council of Taiwan. I spent my summer at National Chung Hsing University in Taichung, Taiwan working jointly with Taiwanese students on their ongoing projects. Not only did I learn a great deal about the science of solid phase extraction, a topic I had never explored during my time as a student at Western Kentucky University, but I also had a chance to explore a great culture so unlike my own. The experience gave me much insight into both the world and myself and is one I will cherish for the rest of my days. I would like to thank all those that made this opportunity possible. Dr. Eric Conte, if you hadn't written that grant three years ago none of this would have been possible. Dr. Shing-Yi Suen, thanks for accepting WKU students into your university. You made sure we had a place to stay and access to wonderful facilities. To all the Taiwanese students, you became my mentors, my peers, and most importantly my friends. You taught me so much about science, life, and the world around me. You were never too busy to lend a helping hand; even sacrificing your nights when even the smallest of problems arose. To everyone, thank you.

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ABSTRACT

In recent years, Solid Phase Extraction (SPE) has replaced distillation and liquid-liquid extraction as the most widely used method for extraction of such chemicals from solution. Though traditional SPE has seen great success, its downfalls are that it requires meticulous preparation procedures requiring the reacting of funtionalized silanes with silica or polymerization courses. An alternative is to use ion exchange membranes, such as NYSA S1000 and Whatman P81, to which long carbon chain ionic surfactants have been attached. The ion exchange capacity for the S1000 membrane was measured to be approximately 110 micro-equil/disc while the P81 membrane was slightly higher at 150 micro-equil/disc. Octadecyltrimethylammonium surfactant was immobilized on the membrane surface, qualitated through the use of ATR-FTIR, and quantified through elemental analysis. Kinetic adsorption experiments for S1000 and P81 membranes demonstrate that equilibrium times are approximately 1 hour and 3 hours respectively while adsorption isotherms results indicate that S1000 membranes are able to extract 300% of the amount of 4-nitrophenol as extracted by P81 membranes. The NYSA S1000 membrane material is more efficient at extracting 4-nitrophenol from solution than the P81 membrane material.

INTRODUCTION

One important objective in environmental chemistry today is the extraction, immobilization, and/or separation of contaminants from polluted water systems; not only to protect the wildlife in polluted areas but also to protect human health. One particular class of chemicals that is commonly found in aqueous environments and has the potential for much environmental harm are those containing phenols.

Although phenols occur naturally, they are also often associated with various industries including the production of plastics, paper and other wood pulp industries, fertilizers, textiles such as nylon, and household cleaners among others [1,2]. Because of such a wide range in their use and application, it is almost inevitable that some of these compounds will not be able to be contained. Phenols usually remain in the air for 24 hours and only 2-5 days in soil before degrading. However, once phenols are introduced to a body of water, phenols can remain there for weeks even when the initial contamination is very small and much longer for high concentration [3].

Phenols can pose a threat to organisms even at low concentrations and, thus, are considered priority pollutants. In humans, phenols can cause a wide range of symptoms and ailments. Mild skin and respiratory irritation is often reported as a result from contact with very low concentrations while severe respiratory failure, paralysis, and death can result from inhalation, dermal contact, or ingestion of higher concentrations. Phenols have many of these same effects on wildlife though severity of illness and effect varies due to slight biological differences among species [1-3]. It has also been suggested that 4-nitrophenol, the primary analyte of this study, has been shown to have estrogenic

properties, geno-toxicological qualities, and often leads to the formation of ground level ozone; all leading to severe effects on humans and wildlife [4].

In the past, distillation in which water was removed from solution was often utilized in the separation process of such chemicals since it is a general requirement that low level analytes must be preconcentrated before injection into chromatographic equipment [5, 7, 8]. This process was very energy expensive due to the need for continuous heating and cooling as well as requiring a large amount of material and laborers to maintain the equipment. In recent years, Solid Phase Extraction (SPE) has replaced distillation as the most widely used method [5-12]. Common absorbents used with SPE include C18 and C8 silica that have associated hydrophobic groups. These groups most commonly lie in the base material but could also be located on the internal surface of the absorbent itself [7, 9-11]. Though traditional SPE has seen great success, its downfalls are that it usually requires a long elution time and a vast quantity of organic solvent to extract the analyte from the stationary phase. It also requires meticulous preparation procedures requiring the reacting of funtionalized silanes with silica or polymerization courses [12-14]. An alternative is to use Ion Exchange Membranes to which long carbon chain ionic surfactants have been attached. In addition to forgoing the need for silane reactions and being capable of higher flow rates, the analyte and the surfactant can often be removed with small volumes of alcohol and/or salts [12-15]. In this study, the efficiencies of two types of ionic exchange membranes (P81 and S1000) in their potential to immobilize surfactant and to bind 4-nitrophenol were explored.

METHODS AND PROCEDURES

Materials and Reagents: Two types of cationic exchange membranes were purchased. The S1000 membrane was purchased from NYSA (Burlington, ON, Canada) who, as of now, have changed their name to Natrix Separations, Inc. This membrane is made of spherical allyl dextran and N, N'- methylenebisacrylamide. It has a thickness of 230 micrometers and contains H^+ counter ions. The P81 membrane, bought from Whatman (Maidstone, Kent, United Kingdom) also had a thickness of 230 micrometers and H^+ counter ions. Its matrix, however, is primarily composed of cellulose phosphate. The surfactant chosen for this study was octadecyltrimethylammonium chloride; purchased from TCI (Tokyo, Japan). Silver Oxide was purchased from Showa (Tokyo, Japan). 4-nitrophenol was purchased from Sigma-Aldrich. All solvents used were HPLC grade.

Ion Exchange Capacity Measurement: In order to establish the ionic exchange capacities for each type of membrane, a 47mm disc of each type of membrane was submerged in 20ml of deionized water for 1 hour. Next, each of the two discs was immersed in 50ml of 0.02 N HCl for 24 hours. The membranes were then washed repeatedly with deionized water to remove any remaining acid. After removing the acid, the membranes were incubated in 50ml of a 0.01 M NaOH solution over night to allow for complete equilibration. Back titration using 0.01 M HCl was performed on the NaOH solutions in order to assess the reduction in alkalinity. By calculating the difference between moles of NaOH in the initial solutions and moles of NaOH present after

membrane incubation procedures, the ionic exchange capacities for each type of membrane was determined.

Prewashing the Membranes: Both types of membranes, having originally come in sheets, were cut into circular discs with a diameter of 47mm. Care was taken to ensure that all discs were of the same area and that each was kept as sterile as possible. These discs were then submerged in 20ml of deionized water in a jar only slightly larger than the diameter of the disc and only as high as needed for the 20ml of water to reach halfway up the side of the jar. The jars, labeled either S or P were then placed on an agitator set so that the liquid rolled back and forth over the membrane but did not slosh and the water was periodically changed to optimize washing. After 24 hours of this, the water was removed and 20ml of .02 N HCl was added to each jar. The jars were again placed on the agitator using the same settings as before for another 24 hours with no changing of the HCl. The membranes were then removed and allowed to dry for 24 hours. The weight of each dry membrane was recorded.

Cationic Surfactant Immobilization: The cationic surfactant solution was made by reacting 3.5 grams octadecyltrimethylammonium chloride with 1.2 grams silver oxide in 100mL of methanol. Methanol was used as the solvent in this step to increase the solubility of the surfactant since the critical micellar concentration of octadecyltrimethylammonium is around 0.3mM in water. This resulted in a reaction which allowed the chloride counter ion on $C18H38N(CH3)3Cl^-$ to be replaced by a hydroxide group from the silver oxide forming $C18H38N(CH3)3OH^-$. This reaction also produced a silver chloride precipitate which was subsequently removed using a .45

micrometer filter composed of cellulous acetate. The resulting clear solution was collected and separated into 20ml aliquots. Each aliquot was added to clean jars, each containing one of the prewashed membranes.

These samples were agitated for 24 hours, rinsed with deionized water, and dried for 24 hours. A second weighing was performed and compared to the first weights to verify dryness. The immobilized surfactant was characterized using ATR-FTIR and quantified using Elemental Analysis.

Batch Adsorption of Phenolic Compounds: A stock solution of 2000ppm p-nitrophenol was made by dissolving solid reagent 4-nitrophenol in deionized water. This stock solution was diluted to form solutions of 2000, 1600, 1200, 800, and 400ppm 4-nitrophenol. These solutions were then analyzed by a HPLC system comprised of a Series II pump from Lab Alliance, State College, Pennsylvania, USA, a K-2501 UV-Vis detector (set to 254nm) from Knauer, Berlin, Germany, and a reversed phase column (C8, Supelcosil, 3micrometer, 100 x 4.6 mm) from Varian, Palo Alto, California, USA. The mobile phase consisted of 30% methanol solution with 1% formic acid. Integration software was used to calculate the areas of the phenol peaks on each HPLC sample. These areas, when coupled with their corresponding concentrations, allowed for the construction of a standard curve.

Each of the S1000 and P81 membranes were cut in equal quarters to maximize utility. Each quarter was placed in a jar to which was added 5ml of 100ppm 4-nitrophenol solution. The jars were then placed on agitator. Random jars were taken off agitator every 15-30 minutes for 3 hours. The membranes were removed from the jars and the amount

of time each membrane had stayed in the solution was recorded. Each solution was then transferred to its own vial. To prevent evaporation, each vial was sealed with paraffin and stored in a refrigerator until each could be analyzed by the same HPLC instrumentation as mentioned previously. The HPLC results were quantified using a standard curve.

RESULTS AND DISCUSSION

Ion Exchange Capacity Measurement: The ion exchange capacity for the S1000 membrane was measured to be approximately 110 micro-equil/disc while the P81 membrane was slightly higher at 150 micro-equil/disc. This difference in ion exchange capacities is most likely due to the different matrix materials used in each type of membrane however no attempt was made at verifying this as it was not an objective of this study.

Cationic Surfactant Immobilization: According to the literature, if CC18H38N(CH3)30H^{-} surfactant had been immobilized on either type of membrane a signal should appear in an ATR-FTIR spectrum in the range of 2850 and 2920 cm^{-1} [22]. The vibrations of the CH2 bonds of the surfactant are responsible for the peaks in this range. As shown in Figure 1A and 1B, a peak falling within this range is evident for both S1000 and P81 membranes when treated with cationic surfactant solutions. Furthermore, the spectra for membranes that were not treated with the surfactant solution did not show any signals in this range. The comparison of spectra from treated and untreated membranes verified that surfactant had been successfully immobilized on both the S1000 and P81 membranes.

Figure 1A: ATR-FTIR for S1000 membranes

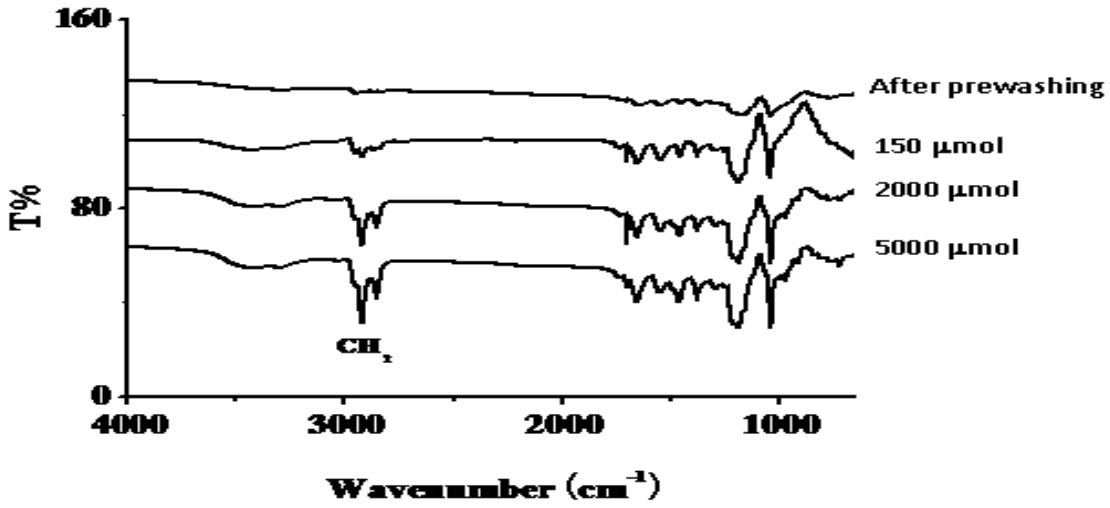
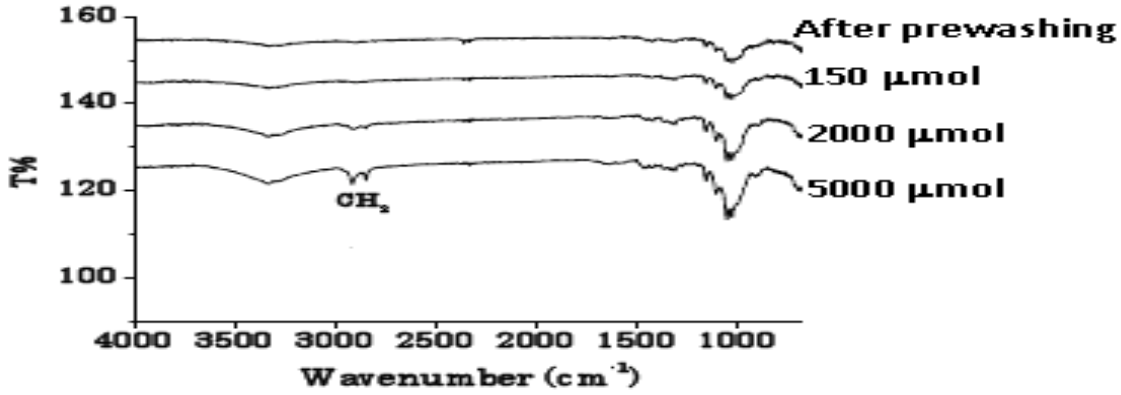


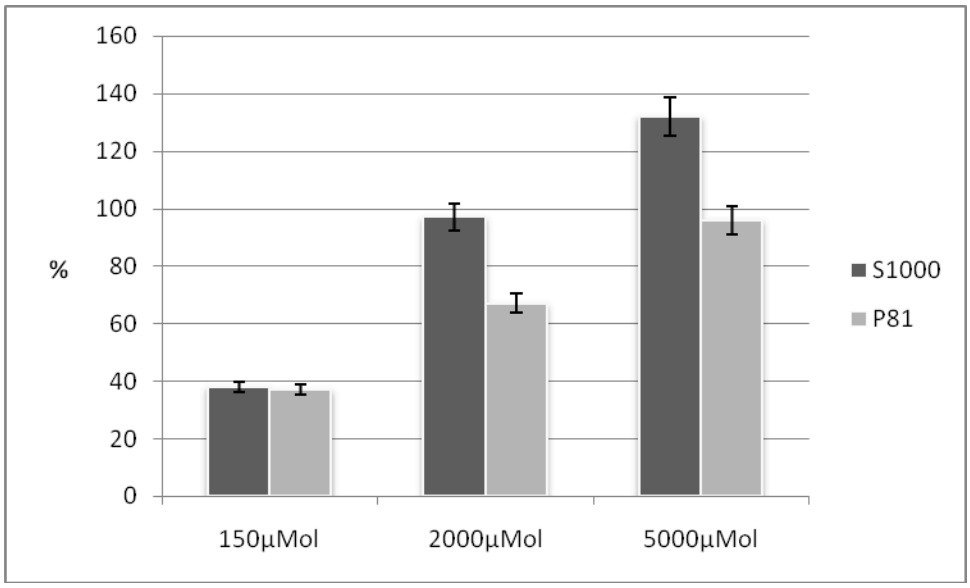
Figure 1B: ATR-FTIR for P81 Membranes



The amount of surfactant immobilized on each membrane was quantified by Elemental Analysis by measuring the difference in mass of carbon from untreated membranes and those which surfactants had been immobilized. The percentage of immobilization was calculated by comparing the observed amount of immobilized surfactant from elemental analyses results and the ionic exchange capacity. The

percentage of immobilization for S1000 and P81 membranes are depicted in Figure 2. S1000 membranes have a higher percentage of surfactant immobilization than P81 membranes at all concentrations. Also according to Figure 2, the S1000 membrane is capable of immobilizing more than 100 percent of its ionic exchange capacity. A possible explanation for this phenomenon is that once 100 percent immobilization is reached and a complete single layer of surfactant forms on the surface of the membrane, the surface surfactant is still capable of binding with other surfactant molecules through hydrophobic interactions with the hydrocarbon chains; resulting in the formation of a partial bilayer.

Figure 2: Percentage Immobilization of Surfactant



Batch Adsorption of Phenolic Compounds: The standard curve obtained from HPLC analysis of samples of various concentrations of 4-nitrophenol, shown in Figure 3, has an R value of 0.9987 when fixed to a linear model. This high R value validates and qualifies the curve to be used to quantify the amount of 4-nitrophenol adsorped by the surfactant immobilized membranes in the kinetic adsorption experiments.

Figure 3: Standard Curve for Concentrations of 4-Nitrophenol

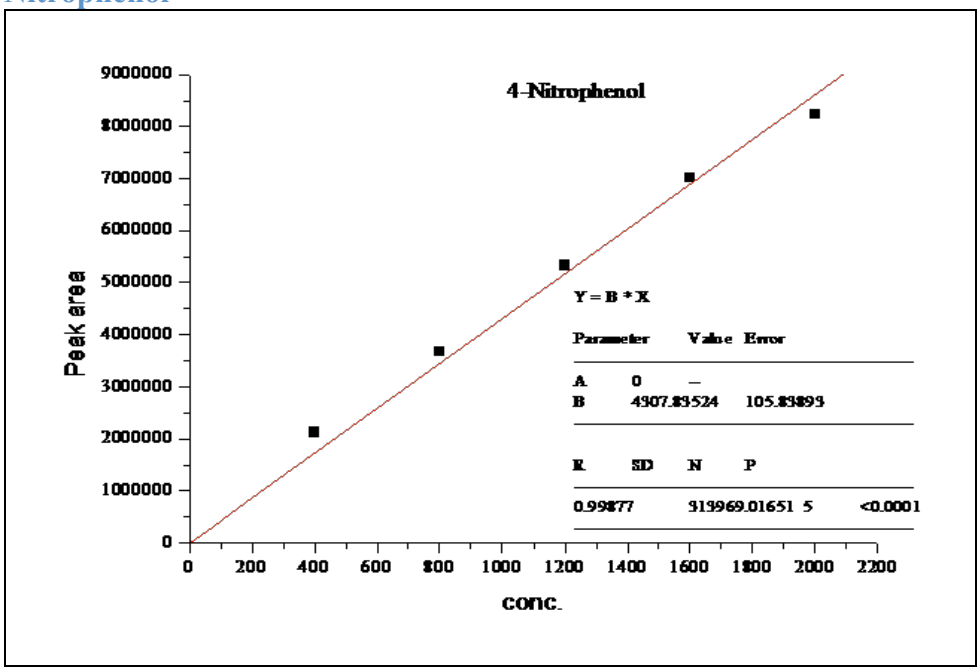


Figure 4 depicts kinetic adsorption of 4-nitrophenol for S1000 and P81 membranes. The S1000 membranes reach equilibrium faster, around one hour, than the P81 membranes which did not show equilibration until after three hours. The S1000 membrane also extracted a higher amount of 4-nitrophenol from solution. Adsorption isotherms for the membranes with 100 % surfactant immobilization are plotted in Figure 5. While the S1000 membrane was able to extract up to 1mg of 4-nitrophenol per square centimeter, the P81 membrane was not able to reach its maximum extraction level. During the adsorption course for the P81 membrane, the solution became more and more cloudy as the concentration of 4-nitrophenol was increased. The likely cause of this cloudiness is 4-nitrophenol bonded to immobilized surfactant molecules detaching them from the P81 membrane surface. This phenomenon was not observed for the S1000

membrane. The matrix material for the S1000 membrane may bind more strongly than the cellulous phosphate of the P81 membrane. It is also a possibility that surfactant molecules were becoming detached from the surface of the S1000 membrane but became aggregated and produced partial bilayers with surfactant molecules still bound to the surface of the membrane.

Figure 4: Kinetic Adsorption of 4-Nitrophenol

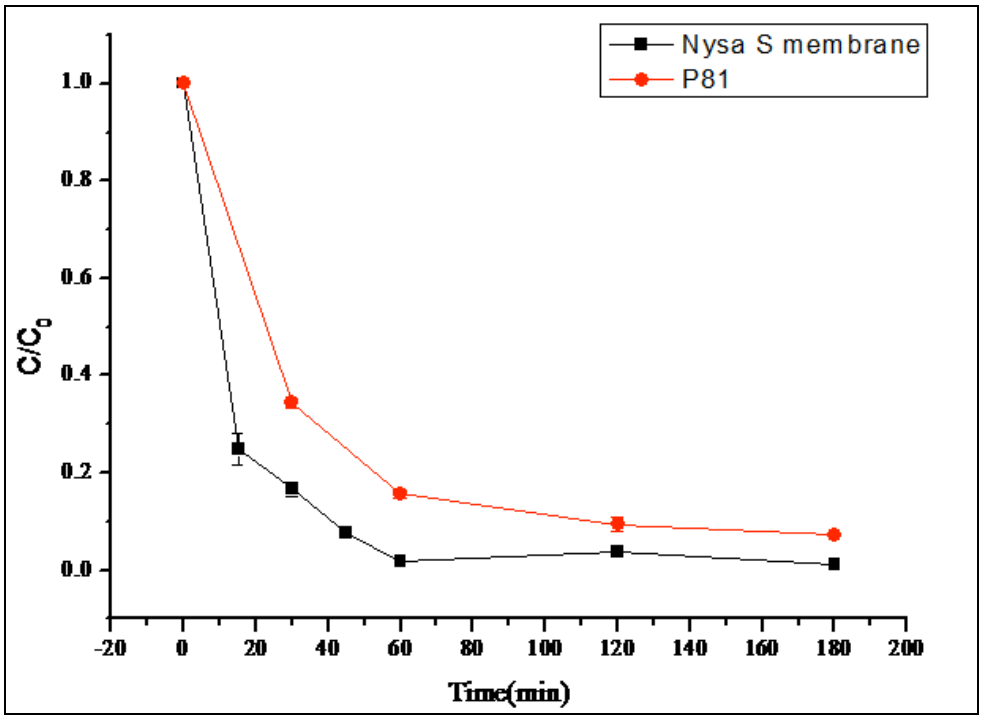
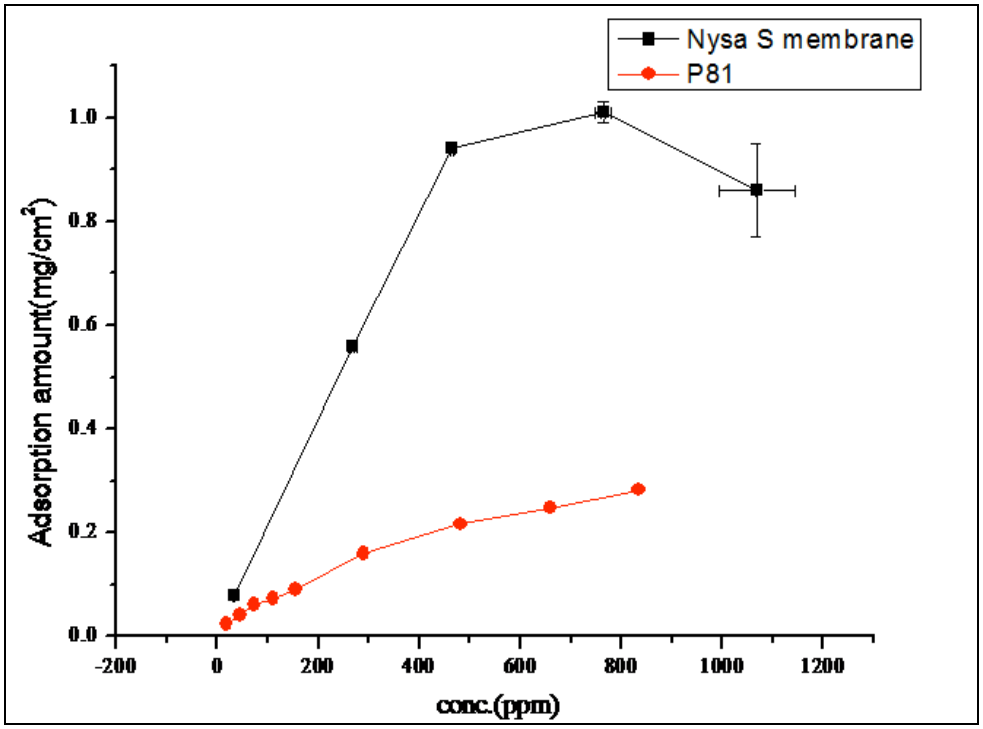


Figure 5: Adsorption Isotherms for 4-Nitrophenol



CONCLUSIONS

This study has shown that octadecyltrimethylammonium surfactant can be immobilized on both NYSA S1000 and Whatman P81 cation exchange membranes. The percent of immobilization of surfactant has the potential to reach levels over 100 percent due to the formation of partial bilayers. Once surfactant has been immobilized on the membrane surface, S1000 and P81 membranes each have the potential to serve as absorbents for the extraction of 4-nitrophenol. The use of these membranes in SPE did not require meticulous silane reactions or other preparations as is found in traditional methods of Solid Phase Extraction. When the NYSA S1000 membrane is compared to the Whatman P81 membrane, the S1000 membrane is more efficient. S1000 membranes can extract more 4-nitrophenol out of solution at all observed concentration and equilibrates faster under isothermic conditions than P81 membranes.

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