

Summer 2015

A pH Switchable Responsive Surface for the Trapping And Release of a Hydrophobic Substance

Ali Esmail Karim

Follow this and additional works at: <http://digitalcommons.wku.edu/theses>



Part of the [Physical Chemistry Commons](#)

Recommended Citation

Karim, Ali Esmail, "A pH Switchable Responsive Surface for the Trapping And Release of a Hydrophobic Substance" (2015). *Masters Theses & Specialist Projects*. Paper 1522.
<http://digitalcommons.wku.edu/theses/1522>

This Thesis is brought to you for free and open access by TopSCHOLAR®. It has been accepted for inclusion in Masters Theses & Specialist Projects by an authorized administrator of TopSCHOLAR®. For more information, please contact connie.foster@wku.edu.

A pH SWITCHABLE RESPONSIVE SURFACE FOR THE TRAPPING AND
RELEASE OF A HYDROPHOBIC SUBSTANCE

A Thesis
Presented to
The Faculty of the Department of Chemistry
Western Kentucky University
Bowling Green Kentucky

In Partial Fulfillment
of the Requirement for the Degree
Master of Science

By
Ali Esmail Karim

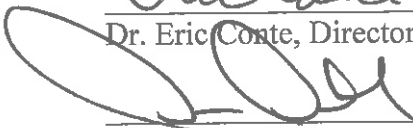
August, 2015

A pH SWITCHABLE RESPONSIVE SURFACE FOR THE TRAPPING AND
RELEASE OF A HYDROPHOBIC SUBSTANCE


Date Recommended 7/13/15




Dr. Eric Conte, Director of Thesis



Dr. Darwin Dahl



Dr. Stuart Burris

 8-2-15

Dean, Graduate Studies and Research Date

To my family

ACKNOWLEDGEMENTS

There are a great number of people I would like to thank. Without their uncountable support, this thesis would never have been finished.

First and foremost, I would like to express my sincerest gratitude and appreciation to my research adviser Dr. Eric Conte, for his guidance, encouragement, and trust. He has given his valuable time, advice, and correction throughout each stage of this thesis. Moreover, he inspires and motivates me to go forward continuously in the field of analytical chemistry. I appreciate him for all the cultivation he has done for me.

I also would like to thank Dr. Kane Jennings for the endless support for the project.

Next, I want to express my feeling of gratitude to Dr. Cathleen Webb, Department Head, for her help and inculcate. She is a responsible leader and also an amiable listener. I am thankful to all her encouragement and support.

In addition, I would like to express my hearty gratitude to my thesis committee members Dr. Stuart Burris and Dr. Darwin Dahl for their willingness to serve as my committee members to consummate the final vision of my thesis. I appreciate all their patience and guidance for the thesis and defense.

Moreover, I would like to thank Dr. Quentin Lineberry for his help with Fourier transform infrared spectroscopy at Thermal Analysis Laboratory, Ms. Pauline Norris for her help with elemental analysis at Advanced Material Institution, Mrs. Alicia McDaniel for her backup for chemicals. I want to thank everyone who has ever helped me: all the faculty and staff in the chemistry department; the Office of Graduate Studies, and everyone in our research group.

In addition I would like to thank the Higher Committee for Education Development in Iraq for the financial support.

Last but not least, I give the biggest thanks to my family, and friends, for their endless love, encouragement, and support throughout my journey. None of my achievements would have been possible without them.

TABLE OF CONTENTS

Introduction.....	1
1.1 Overview	1
1.2 General Goal of the Research	2
BACKGROUND	4
2.1 Contact angle measurements.....	4
2.2 Smooth and Rough surfaces.....	5
2.3 Hydrophobic and hydrophilic surfaces.....	7
2.4 Switchable surfaces	9
EXPERIMENTAL.....	13
3.1 Materials and Reagents	13
3.2 Major instrumentations were used.....	13
3.3 Microscope slide procedures	14
3.3.1 Microscope slide vinyl surface group reaction step.....	14
3.3.2 Carboxylic acid surface group reaction step (microscope slide)	14
3.3.3 Anthranilic acid surface group reaction step (microscope slide)	15
3.3.4 Aniline surface group reaction step (microscope slide)	15
3.4 Thin Layer Chromatography (TLC) Plate procedures.....	15
3.4.1 Thin Layer Chromatography (TLC) Plate vinyl surface group reaction step	15

3.4.2 Carboxylic acid surface group reaction step [Thin Layer Chromatography (TLC) Plate]	16
3.4.3 Anthranilic Acid surface group reaction step [Thin Layer Chromatography (TLC) Plate].....	16
3.4.4 Aniline surface group reaction step [Thin Layer Chromatography (TLC) Plate]	17
3.5 Silica particles procedures.....	18
3.5.1 Vinyl surface group reaction step [silica particles]	18
3.5.2 Carboxylic acid surface group reaction step [silica particles].....	18
3.5.3 Anthranilic Acid surface group reaction step [silica particles]	19
3.5.4 Aniline surface group reaction step [silica particles]	19
3.6 Trapping of 2-naphthol on the anthranilic acid functionalized silica	20
3.7 Trapping of 2-naphthol on the aniline functionalized silica.....	20
3.8 The release of 2-naphthol from functionalized anthranilic acid silica surface.	20
3.9 The release of 2-naphthol from the silica aniline surface	21
Result and Discussion	22
4.1 Synthesis of the silica particles surface	22
4.2 Synthesis of the TLC plate surface	33
4.3 Synthesis of the Microscope slide surface	42
4.4 Anthranilic acid functionalized silica	45

4.5 Calibration curve.....	47
4.6 Trapping of 2-naphthol.....	47
4.6.1 Trapping of 2-naphthol on the frits	47
4.6.2 Trapping of 2-naphthol on the blank silica	49
4.6.3 Trapping of 2-naphthol on the aniline functionalized silica	49
4.6.4 Trapping of 2-naphthol on the anthranilic acid functionalized silica	50
4.7. The recovery of 2-naphthol from the frits	50
4.8 Stability of the functionalized anthranilic acid silica surface	52
Conclusion	55
APPENDIX.....	56

LIST OF FIGURES

Figure 1. Contact angles on hydrophobic and hydrophilic surfaces ⁵	1
Figure 2. Contact angle - the angle between the tangent line contact point and the horizontal line of the solid surface ¹¹	4
Figure 3. Wetting states (a) Wenzel, (b) Cassie-Baxter and (c) combined models ¹²	6
Figure 4. A schematic representation of hydrophilic, hydrophobic and ultra (super) hydrophobic surfaces ¹⁹	8
Figure 5. Contact angle measurement for switchable surface at different pHs ⁶	10
Figure 6. Surface chemistry of MUABA based hydrophobic and hydrophilic switchable surface ³⁰	11
Figure 7. Vinyl surface group reaction	22
Figure 8. FTIR spectra of blank silica	23
Figure 9. FTIR spectra of the Vinyl surface group silica	23
Figure 10. CHN analysis data silica particles.	24
Figure 11. Carboxylic acid surface group reaction	25
Figure 12. FTIR spectra of the Carboxylic acid modified silica particles	26
Figure 13. Anthranilic Acid surface group reaction	27
Figure 14. FTIR spectra of the anthranilic acid modified silica particles.....	28
Figure 15. Aniline surface group reaction	29
Figure 16. FTIR spectra of the aniline modified silica particles.....	30
Figure 17. Silica anthranilic acid modified surface in a mixture of pH4, 10, and toluene	31
Figure 18. Silica aniline modified surface group in a mixture of buffers and toluene	32
Figure 19. FTIR spectra of the Blank TLC plate	34

Figure 20. FTIR spectra of the Vinyl surface group TLC plate.....	34
Figure 21. CHN Analysis data TLC plate.....	35
Figure 22. FTIR spectra of the Carboxylic acid modified TLC plate.....	37
Figure 23. FTIR spectra of the anthranilic acid surface group TLC plate.....	39
Figure 24. Contact angle measurement for TLC switchable surface at different pHs.....	39
Figure 25. FTIR spectra of the an amide aniline surface group TLC plate	41
Figure 26. TLC modified plates contact angles	41
Figure 27. Microscope modified slides contact angles.....	43
Figure 28. Anthranilic acid surface at low and high pH.....	46
Figure 29. 2-naphthol Calibration curve.....	47
Figure 30. Trapping of 2-naphthol.....	48
Figure 31. Total recovery of 2-naphthol.....	51
Figure 32. FTIR spectra of the anthranilic acid surface group silica particles.....	53
Figure 33. FTIR spectra of the anthranilic acid surface group silica particles after one time of extraction.....	53
Figure 34. FTIR spectra of the anthranilic acid surface group silica particles after two times of extraction.....	54
Figure 35. FTIR spectra of the anthranilic acid surface group silica particles after several times of extraction.....	54

A pH SWITCHABLE RESPONSIVE SURFACE FOR THE TRAPPING AND RELEASE OF A HYDROPHOBIC SUBSTANCE

Ali Karim

August 2015

60 Pages

Directed By: Dr. Eric Conte, Dr. Darwin Dahl, and Dr. Stuart Burris

Department of Chemistry

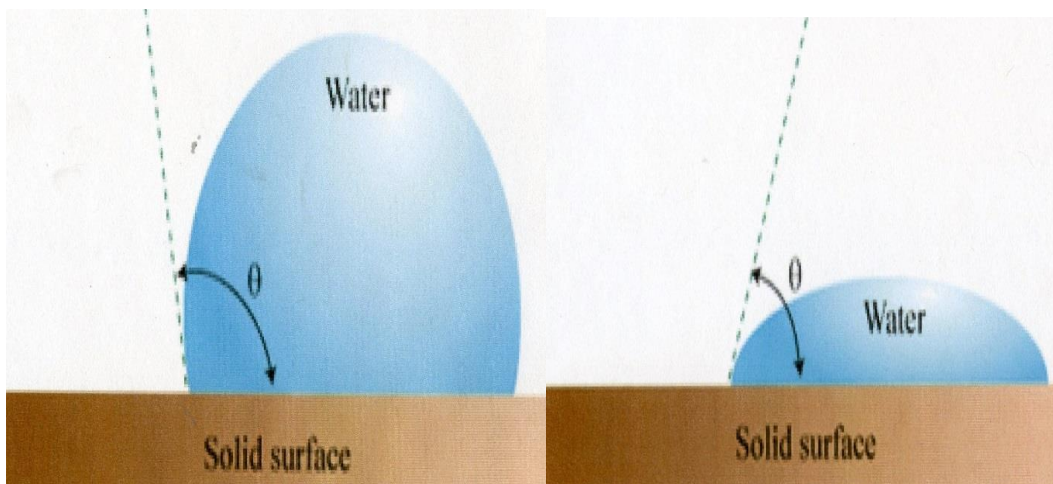
Western Kentucky University

Solid phase extraction is one of the most widely used techniques to trap and release compounds in a solution. A hydrophobic substance will stick efficiently to a hydrophobic surface (the “like dissolves like” principle). With an introduced response (i.e. pH change), a responsive surface can change from hydrophobic to hydrophilic, weakening the hydrophobic substance’s attraction and thus facilitate in an easy removal. A surface has been prepared having a terminal anthranilic acid (AA) moiety on silica gel particles, microscope slides, and TLC plates in three steps. First, a vinyl group was attached to the surface. Then, this vinyl group was reacted to form a surface carboxylic acid group. Finally, the carboxylic acid group was converted to an amide group that linked to the silica surface. FT-IR, and elemental analysis were used to confirm each step of the synthesis. At low pHs the –COOH group on the AA moiety is neutral and intra-hydrogen bonding keeps this moiety’s phenyl (hydrophobic) portion exposed to the surface. The effect has been investigated by measuring contact angles at various pH values. At higher pHs the AA’s carboxylic acid group becomes the charged carboxylate, rendering the surface hydrophilic. Substances can be trapped and released using this unique switching approach. 2-naphthol, for example, is hydrophobic and thus was trapped at lower pHs (pH 4) (hydrophobic surface) and released at higher pHs (pH 10) (hydrophilic surface) on this responsive surface

Introduction

1.1 Overview

The attention to the development of controlled switchable surfaces has been increasing for many decades. These surfaces are also called smart surfaces that can respond to changes in pH^{1,2,6}. With a change in pH, the surface can switch wettability between hydrophobic and hydrophilic. Wettability is a very important property that is governed by both chemical composition and surface structure^{3,4}. Very dramatic changes in the wetting behavior of specific chemically modified surface, observed through water contact angle measurement, can be seen when the pH is changed (Figure 1)⁵.



A. Hydrophobic surface

B. Hydrophilic surface

Figure 1. Contact angles on hydrophobic and hydrophilic surfaces⁵

A unique surface has been prepared having a terminal anthranilic acid (AA) group. At low pHs the carboxylic acid groups are protonated and hydrogen bonding keeps this group with the phenyl (hydrophobic) portion exposed to the surface. At higher pHs the AA group's carboxylic acid becomes the charged carboxylate (hydrophilic)⁶.

After the switchable surface has been prepared, it is used to trap a hydrophobic molecule at low pH. Then the switchable surface changes from hydrophobic to hydrophilic, with an introduced solution of high pH. The resulting surface switch weakens the hydrophobic substance's attractions to this surface which results in an easier release of the hydrophobic molecule compared without this "switch".

1.2 General Goal of the Research

The focus of this work is to develop and synthesizes a switchable surface and use it to trap a hydrophobic substance at low pH and release it at high pH. A switchable surface having a terminal anthranilic acid group on silica particles, TLC plates, and microscope slides was prepared. This surface changes from hydrophobic to hydrophilic with an introduced response (pH change). A surface having a terminal aniline group, which is unaffected by pH changes, was used as a control surface. The aniline surface will not have a hydrophobic/hydrophilic switch with a pH change.

The synthesis of these surfaces was prepared in three steps. First, the vinyl group was attached to the surface. Then, the vinyl group was converted to a carboxylic acid group. Finally, the carboxylic acid group reacted with the amine of the anthranilic acid to produce the switchable surface.

After the switchable surface has been prepared, it was packed in a solid phase extraction column. This SPE column was used to trap the hydrophobic molecule at low pH and then release it at high pH. HPLC was used to measure the amount of the hydrophobic molecule that was trapped and released.

Solid phases have been used as media to collect or trap different types of chemical and biological molecules ⁷. The benefits of trapping molecules begins with removing pollutants (such as pesticides and herbicides) from drinking water, ⁸ to isolating important biological macromolecules such as proteins ⁹. Hydrophobic and hydrophilic switchable surfaces have the ability to be anti-reflecting, anti-bacterial, and anti-fogging ^{2,10}. These surfaces can also be used as easy cleaning surfaces on windows. With a simple rinse of dilute ammonia, it is possible to remove the dirt and the grime from these self-cleaning surfaces. No manual cleaning using a cloth or squeegee would be required because rinsing with ammonia would change the window surface from hydrophobic to hydrophilic and result in an easy removal of the dirt and grime.

BACKGROUND

2.1 Contact angle measurements

The contact angle is the angle between the surface and the meniscus near the line of droplet contact as depicted in Figure 2¹¹. To determine the hydrophobicity of any surface, the contact angle of a water droplet is usually measured which provides an indication of surface wettability. The drop size can affect the contact angle. The contact angle would be different when a different volume of drop is used. An advancing angle would be produced when the volume of the drop is increased and the receding angle would be produced when the volume of the drop is decreased. This difference, termed the *contact-angle hysteresis*, gives a measure of the surface ‘stickiness’. The greater this difference (larger hysteresis) the more the water drops will stick to the surface. Usually low hysteresis is desired when dealing with superhydrophobic surfaces where water droplets will roll off the surface extremely easily. Theoretical equilibrium angles lie between the advancing and receding angles, sometimes being determined by vibrating the drop¹².

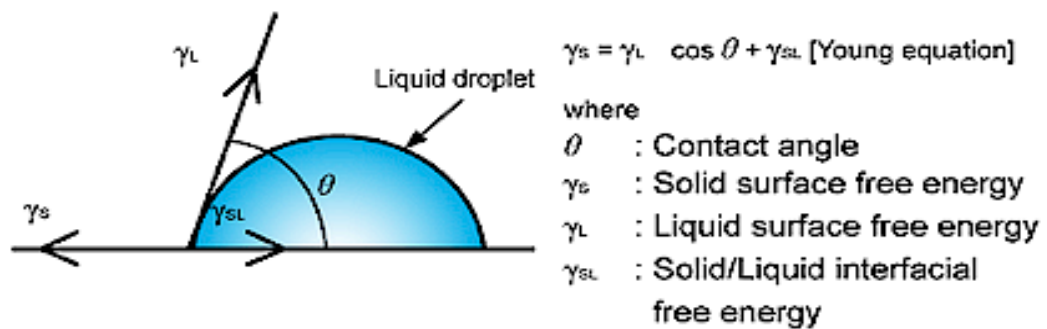


Figure 2. Contact angle - the angle between the tangent line contact point and the horizontal line of the solid surface¹¹.

2.2 Smooth and Rough surfaces

In 1936 Wenzel was the first to outline hydrophobicity principles on surfaces ¹³ and then, in 1944 Cassie and Baxter outlined their version of hydrophobicity principles ¹⁴. Wenzel suggested that when liquid contact followed the contours of a rough surface, the effect of roughness should emphasize the intrinsic wetting tendency towards either enhanced contact angle or film formation. On this type of surface the contact angle observed is given by Wenzel's equation,

$$\cos \theta_e^w = r \cos \theta_e \dots\dots\dots (Equation 1) \supseteq 12$$

Where $r (>1)$, the roughness factor, is the ratio between the solid's true surface area and its horizontal projection; θ_e is the angle of equilibrium contact on a smooth flat surface of the similar type of material. Figure. 3(a), shows roughness and θ_e a measures of surface chemistry. However, a liquid can move across the tops of surfaces, by which the droplet stays on a surface of flat solid tops and the gaps of air between the solid tops. This phenomenon is described by the Cassie–Baxter relationship, Figure 3(b). Using a weighted average of the cosines of the contact angles on the solid and air between solids, a contact angle can be determined ¹².

$$\cos \theta_e^c = \varphi_s (\cos \theta_e) + (1 - \varphi_s) \cos \theta_x \dots\dots\dots (Equation 2) \supseteq 12$$

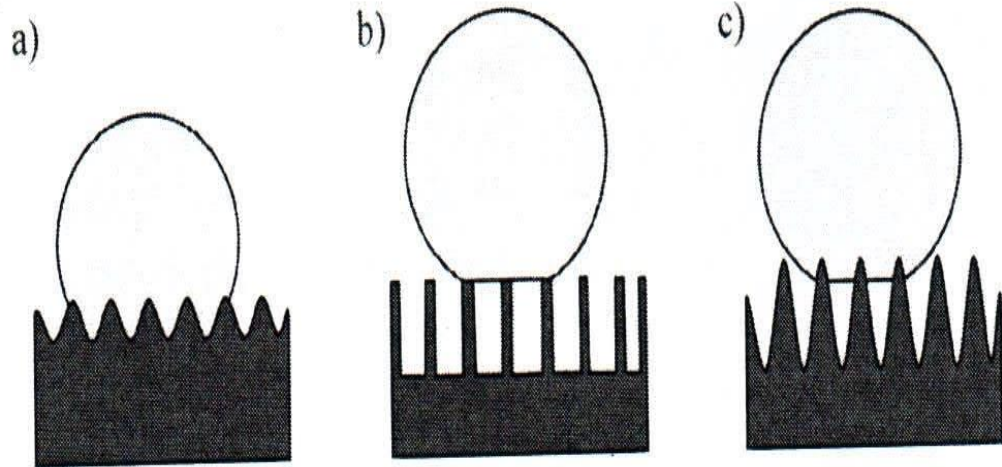


Figure 3. Wetting states (a) Wenzel, (b) Cassie-Baxter and (c) combined models¹²

If $Q < 1$, protrusions of the tops of the surface are present, and $(1 - \phi_s)$ represents the air gaps. This will increase the contact angle when the droplet is bridged by the gaps as shown in Figure 3b. If the gaps become filled with water, then θ_x reaches 0° , and the contact angle will fall below that of a flat surface. This case is usually seen on surfaces having contiguous pores as in soils or sol-gels, where rapid internal spreading or filling from below can be possible. Two equations described by Roach and Shirtcliffe¹² can be combined to obtain a third equation, which explains the circumstance when the contacting areas are rough (Figure. 3(c))¹².

$$\cos\theta_e^{CW} = \phi_s r (\cos\theta_e) + \phi_s - 1 \dots\dots\dots (\text{Equation 3})^{12}$$

Hence, the contact angle of a liquid can be impacted by surface roughness.

As a result angles that are greater than 90° on a flat surface always increase and those that are having an angle less than 90° can move in both directions¹². In general, the surfaces that follow the total wetting Wenzel regime are “adhering” in nature, where the drops of water stick stronger than a flat surface of similar type; the surfaces that follow the regime of Cassie and Baxter are “sliding”, where the drops of water roll off higher than on a flat surface¹⁵.

2.3 Hydrophobic and hydrophilic surfaces

In chemistry, hydrophobicity (originating from the Greek word hydro, meaning *water*, and phobos, meaning *fear of*), is a physical property of a molecule (known as a hydrophobe) that is repelled from a mass of water¹⁶.

Hydrophobic molecules tend to be non-polar, preferring other neutral molecules and non-polar solvents. Hydrophobic molecules in water often cluster together, forming micelles. Water on hydrophobic surfaces will exhibit a high contact angle. Examples of hydrophobic molecules include alkanes, oils, fats, and greasy substances in general. Hydrophobic materials are used for oil removal from water, the management of oil spills, and chemical separation processes to remove non-polar substances from polar compounds¹⁷.

A hydrophile (originating from the Greek word hydro, meaning *water*, and philia meaning *love*), is a molecule that is attracted to, and can be dissolved by, water.

A hydrophilic molecule or portion of a molecule is one that has a tendency to interact with or be dissolved by water and other polar substances¹⁸. Hydrophilic substances can seem to attract water out of the air, the way salts (which are hydrophilic) do. Sugar is hydrophilic too, and like salt is sometimes used to draw water out of foods.

A hydrophilic surface is the surface in which the contact angle of water is less than 90° , and a hydrophobic surface is the surface in which the contact angle is greater than 90° as shown in Figure 4¹⁹. The hydrophilic, or hydrophobic quality of a surface, arises from its chemical make-up. These qualities are enhanced by the roughness of the surface, because of the trapping of air in the cavities between a drop and a rough hydrophobic surface and by capillary wicking on a hydrophilic surface²⁰.

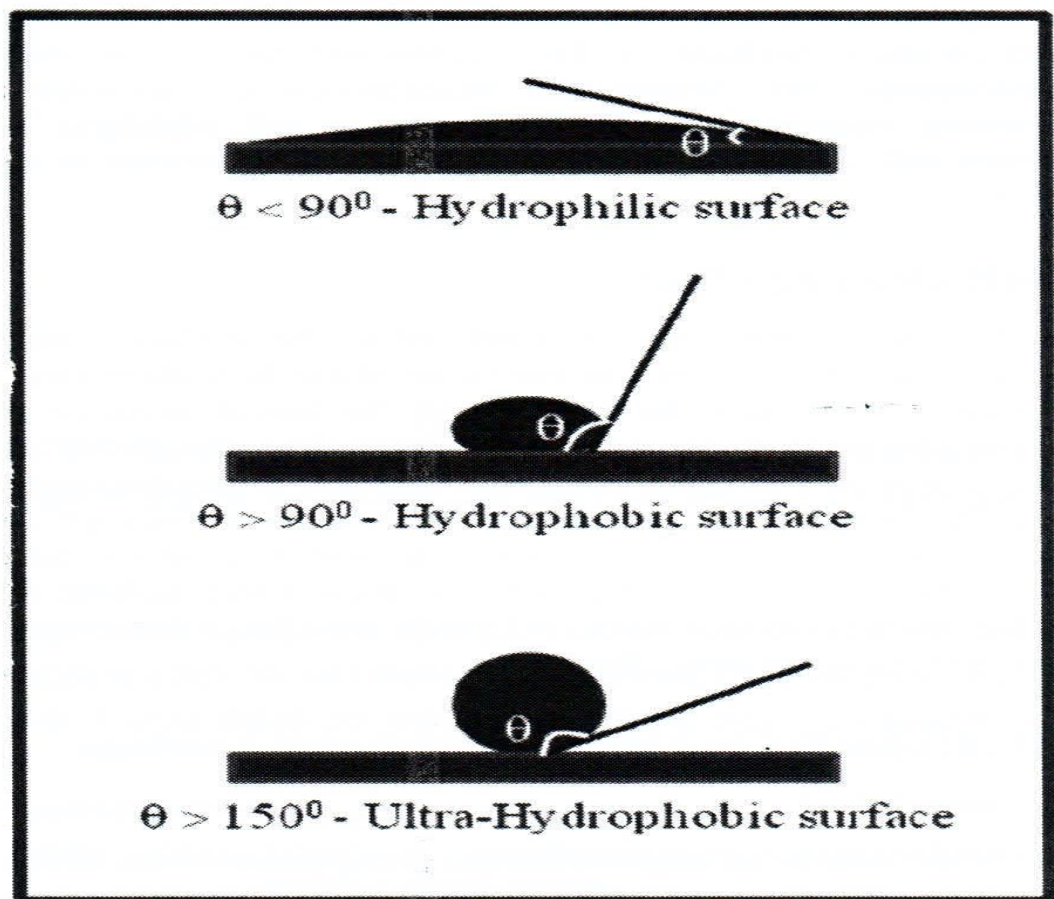


Figure 4. A schematic representation of hydrophilic, hydrophobic and ultra (super) hydrophobic surfaces¹⁹.

2.4 Switchable surfaces

Some superhydrophobic surfaces can cause water and even oils to roll off leaving little or no residue and carry away any resting surface contamination. Recently more and more researchers are becoming interested in the switchable surface field. As a result there is a greater number of methods reported to produce switchable surfaces by using simpler and cheaper means to achieve high water-contact angles and low hysteresis (causing roll-off).

There are many types of catalysts that can be used to change the surface from hydrophobic to hydrophilic. Changing the surface can be done in several ways such as changes in electrical potential ^{21,22}, temperature ^{4,23}, pH ^{6,24–27}, and solvent ^{28,29}. For this purpose my research will focus on pH changing.

In 1988, Mark D. Wilson and George M. Whitesides from Harvard University's, Department of Chemistry have found that the anthranilate amide of polyethylene carboxylic acid shows an exceptionally large change with pH in its wettability by water⁶. At low pHs the contact angle was 110° (more hydrophobic) (Figure 5); because the carboxylic acid groups are protonated and hydrogen bonding keeps this group with the phenyl (hydrophobic) (Figure 5) portion exposed to the surface. At higher pHs the contact angle drops to 20° (more hydrophilic) because the group's carboxylic acid group becomes the charged hydrophilic carboxylate⁶.

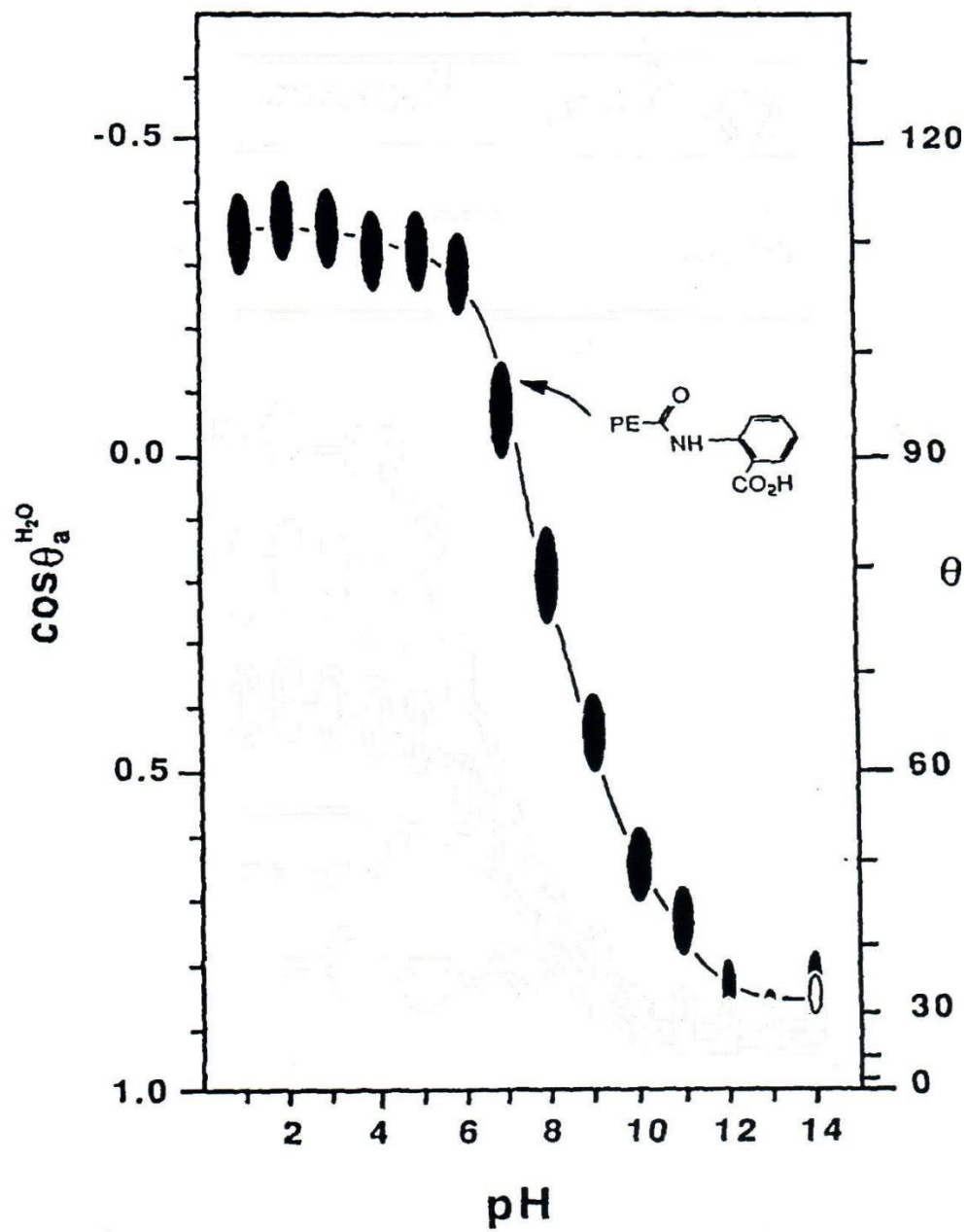


Figure 5. Contact angle measurement for switchable surface at different pHs⁶.

In this thesis, the preparation, characterization, and application using a similar switchable surface, based upon 2-(11-Mercaptoundecanamido) Benzoic Acid (MUABA) on a gold surface, is presented and depicted in Figure 6,³⁰. In this paper³⁰ surface studies of MUABA attachment have been conducted by examining water droplets. Very large changes in hydrophobicity and hydrophilicity were measured with a change in pH.

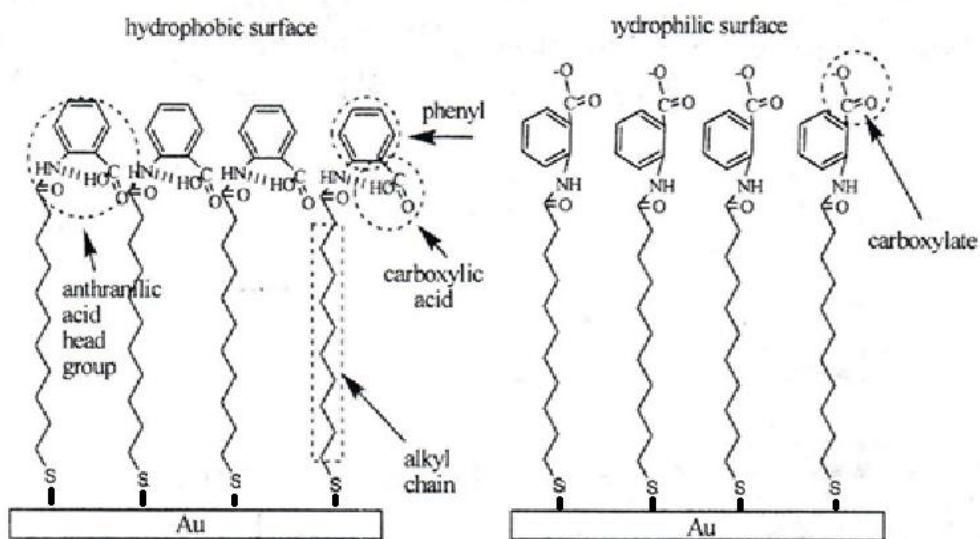


Figure 6. Surface chemistry of MUABA based hydrophobic and hydrophilic switchable surface³⁰.

While the attachment of this chemical onto gold surface works well for studying the switchable nature of this surface, it is not suited to trap and release sufficient quantities of analytes in real world applications. A column of packable material with a large surface area is required. In this thesis, the same switchable material modified to

attach to silica gel particles is prepared. Silica gel has a porous network and thus a high surface area will allow it to capture more analytes than on a gold based planar template.

EXPERIMENTAL

3.1 Materials and Reagents

Trichlorovinylsilane, 2, 2- Azobis (2-methyl-propionitrile) AIBN, (1-(3-dimethylaminopropyl)-3ethylcarbodiimide) EDCI, N-hydroxysuccinimide, Anthranilic acid, and 11-Mercaptoundecanoic acid were purchased from Sigma Aldrich. Aniline was purchased from Mallinckrodt. Silica gel (40-70 Micron), and TLC plates were purchased from International Sorbent Technology Ltd. Plain microscope slides were purchased from Fisher Scientific.

3.2 Major instrumentations were used

Perkin Elmer Spectrum 100 FT-IR Spectrometer with an attenuated total reflectance (ATR) attachment was used to confirm functional groups on the modified silica surfaces. A True spec CHN Analyzer was used to measure the percentage of carbon, hydrogen and nitrogen in the sample. A Leco SC-432 Sulfur Analyzer was used to measure the percentage of sulfur in the sample. The high performance liquid chromatography HPLC was composed of a 9012 pump, a C₈ column, and a Prostar 330 PDA detector, all from Varian. The mobile phase was a mixture of HPLC grade methanol and water, in a 70:30 ratio and was pumped at a rate of 0.5 mL/min for 10 min. For detection, the wavelength range of the photodiode array detector was set at 200 nm to 400 nm with a monitored wavelength of 250 nm.

3.3 Microscope slide procedures

3.3.1 Microscope slide vinyl surface group reaction step

A microscope slide was cut into small sections (4 cm x 1cm x 2 cm). The slides were sonicated in 20 milliliters of 1M NaOH and 20 milliliters of 1M HCl sequentially. Then the slides were sonicated in deionized water three times. Next, they were rinsed in deionized water and ethanol sequentially. The slides were dried under a nitrogen stream and then the cleaned slides were submerged into a solution containing 50 microliters of trichlorovinylsilane in 20 milliliters toluene for 12 hours. After 12 hours the slides were removed and rinsed in 20 milliliters of toluene for 1 minute. The slides were rinsed sequentially with ethanol, deionized water, and again with ethanol. Then the slides were dried under a nitrogen stream. The contact angle was measured using an Aven Inc 2.0 megapixel USB Digital microscope with ProScope software³¹. The microscope was connected to a Dell E207WFP desk top computer with Microsoft windows 7 as the operating system. Both buffer solutions of pH 4 and pH 10 were used for the contact angle measurement.

3.3.2 Carboxylic acid surface group reaction step (microscope slide)

Vinyl functionalized microscope slides were exposed to a solution contain 30 milliliters ethanol, 0.15 g of 2, 2- Azobis(2-methyl-propionitrile)AIBN and 0.5220 g of 11-Mercaptoundecanoic acid. The mixture was bubbled with nitrogen gas and heated at 45 °C for 30 minutes. Then the mixture was heated at 80 °C using a reflux set up for 24 hours. The slides were then rinsed with ethanol and deionized water multiple times. Then the slides were rinsed with ethanol and dried using a nitrogen stream. Contact angles were measured at pHs 4 and 10.

3.3.3 Anthranilic acid surface group reaction step (microscope slide)

The carboxylic acid functionalized slides were exposed to an aqueous solution containing 10 milliliters of 0.05M (1-(3-dimethylaminopropyl)-3ethylcarbodiimide) EDCI and 10 milliliters of 0.005M N-hydroxysuccinimide for 1 hour. Then these slides were exposed to 10 milliliters of 0.015 M anthranilic acid. This mixture was heated at 90 °C for 24 hours. The slides were then rinsed with deionized water and methanol multiple times. Next, the slides were rinsed with methanol again and dried under a nitrogen stream. Contact angles were measured at pHs 4 and 10.

3.3.4 Aniline surface group reaction step (microscope slide)

The carboxylic acid functionalized slides were exposed to 10 milliliters of 0.05M (1-(3-dimethylaminopropyl)-3ethylcarbodiimide) EDCI and 10 milliliters of 0.005M N-hydroxysuccinimide in ethanol for 1 hour. Then 20 microliters of aniline was added to the mixture. This mixture was heated at 90 °C for 24 hours. Then the slides were rinsed with deionized water and methanol multiple times. Next, the slides were rinsed with ethanol and dried under nitrogen stream. Contact angles were measured at pHs 4 and 10.

3.4 Thin Layer Chromatography (TLC) Plate procedures

3.4.1 Thin Layer Chromatography (TLC) Plate vinyl surface group reaction step

A silica TLC plate was cut to small sections (4 cm x 1 cm x 2 cm). The TLC plate sections were submerged into a solution contain 300 microliters of trichlorovinylsilane in 20 milliliters of toluene for 12 hours. Then the TLC sections were removed and rinsed in 20 milliliters of toluene for 1 minute. Sequentially the TLC plates were rinsed with ethanol, deionized water, and again with ethanol. The TLC plate sections were dried under high pressure, using a Gast solid phase extraction manifold. The TLC plate surface

was scraped off and the collected silica waste analyzed by FTIR. A PerkinElmer Spectrum 100, FT-IR Spectrometer was used to confirm the attaching of the vinyl group on the TLC plate. Also, a True spec CHN Analyzer was used to measure the percentage of carbon and hydrogen in the sample. In addition, contact angles were measured at pHs 4 and 10.

3.4.2 Carboxylic acid surface group reaction step [Thin Layer Chromatography (TLC) Plate]

Previously prepared vinyl functionalized TLC plates were exposed to solution containing 60 milliliters ethanol, 0.30 g of 2, 2- Azobis (2-methyl-propionitrile) AIBN and 1.4400 g of 11-Mercaptoundecanoic acid. The mixture was bubbled with nitrogen gas and heated at 45 °C for 30 minutes. The mixture was then heated at 80 °C using a reflux set up for 24 hours. Next, the TLC plates were rinsed with ethanol and deionized water multiple times. The TLC plates were then rinsed with ethanol again and dried under high pressure, using a Gast solid phase extraction manifold. PerkinElmer Spectrum 100, FT-IR Spectrometer was used to confirm the existence of carboxylic acid group. Also, a True spec CHN Analyzer was used to measure the percentage of carbon and hydrogen in the sample. In addition, contact angles were measured at pHs 4 and 10.

3.4.3 Anthranilic Acid surface group reaction step [Thin Layer Chromatography (TLC) Plate]

Previously prepared carboxylic functionalized TLC plates were exposed to an aqueous solution containing 15 milliliters of 0.05M (1-(3-dimethylaminopropyl)-3ethylcarbodiimide) EDCI and 15 milliliters of 0.005M N-hydroxysuccinimide for 1 hour. Then 20 milliliters of 0.015M anthranilic acid was added to the mixture. The

mixture was heated at 90 °C for 24 hours. After cooling, the TLC plates were rinsed with deionized water and methanol multiple times. Then the TLC plates were rinsed with methanol again and dried under high pressure, using a Gast solid phase extraction manifold. A FT-IR Spectrometer was used to confirm the conversion of the carboxylic acid group to the amide group. Also, a True spec CHN Analyzer was used to measure the percentage of carbon, hydrogen, and nitrogen in the sample. In addition, contact angles were measured at pHs 4 and 10.

3.4.4 Aniline surface group reaction step [Thin Layer Chromatography (TLC) Plate]

The carboxylic functionalized TLC plates, that were previously prepared, were exposed to ethanol solution containing 15 milliliters of 0.05M (1-(3-dimethylaminopropyl)-3ethylcarbodiimide) EDCI and 15 milliliters of 0.005M N-hydroxysuccinimide for 1 hour. Then 30 microliters of aniline was added to the mixture. This mixture was heated at 90 °C for 24 hours. The TLC plates were rinsed with deionized water and methanol multiple times. The TLC plates were rinsed with methanol and dried under high pressure using a Gast solid phase extraction manifold. A FT-IR Spectrometer was used to confirm the conversion of carboxylic acid group to the amide group. Also, a True spec CHN Analyzer was used to measure the percentage of carbon, hydrogen, and nitrogen in the sample. In addition, contact angles were measured at pHs 4 and 10.

3.5 Silica particles procedures

3.5.1 Vinyl surface group reaction step [silica particles]

The silanization of the silica particles was performed by immersing 1.00 gram of silica gel into a solution contain 1 milliliters of trichlorovinylsilane in 40 milliliters of toluene for 12 hours. A magnetic stirrer was used to rotate the silica particles in the solution. Next, the silica particles were removed and rinsed in 40 milliliters of toluene for 1 minute. Then the silica particles were rinsed multiple times with methanol, and deionized water sequentially. Next, the silica particles were rinsed with methanol and air dried, using a Gast solid phase extraction manifold. The attachment of the vinyl group on the silica particles was confirmed using the FTIR Spectrometer. Also, a True spec CHN Analyzer was used to measure the percentage of carbon and hydrogen in the sample.

3.5.2 Carboxylic acid surface group reaction step [silica particles]

1.00 gram of previously prepared vinyl functionalized silica was exposed to a solution containing 100 milliliters ethanol, 1.00 g of 2, 2- Azobis (2-methyl-propionitrile) AIBN and 3.480 g of 11-Mercaptoundecanoic acid. The mixture was bubbled with nitrogen gas while being heated and stirred, using a magnetic stirrer, at 45 °C for 30 minutes. The mixture was then stirred and heated at 80 °C, using reflux set up, for 24 hours. Next, the silica was cooled and rinsed with ethanol and deionized water multiple times. The silica was then rinsed with ethanol again and air dried, using a Gast solid phase extraction manifold. PerkinElmer Spectrum 100, FT-IR Spectrometer was used to confirm the existence of the carboxylic acid group. Also, a True spec CHN Analyzer was used to measure the percentage of carbon and hydrogen in the sample.

3.5.3 Anthranilic Acid surface group reaction step [silica particles]

1.00 g of previously prepared carboxylic functionalized silica was exposed to an aqueous solution containing 25 milliliters of 0.05M (1-(3-dimethylaminopropyl)-3ethylcarbodiimide) EDCI and 25 milliliters of 0.005M N-hydroxysuccinimide for 1 hour. Then 40 milliliters of 0.015M anthranilic acid was added to the mixture. The mixture was then stirred and heated at 90 °C for 24 hours. After cooling, the silica was rinsed with deionized water and methanol multiple times. Then the product was rinsed with methanol again and air dried, using a Gast solid phase extraction manifold. A PerkinElmer Spectrum 100, FT-IR Spectrometer was used to confirm the conversion of the carboxylic acid group to the amide group. Also, a True spec CHN Analyzer was used to measure the percentage of carbon, hydrogen, and nitrogen in the sample.

3.5.4 Aniline surface group reaction step [silica particles]

1.00 g of carboxylic functionalized silica, that was previously prepared, was exposed to ethanol solution containing 25 milliliters of 0.05M EDCI (1-(3-dimethylaminopropyl)-3ethylcarbodiimide) and 25 milliliters of 0.005M N-hydroxysuccinimide for 1 hour. Then 60 microliters of aniline was added to the mixture. Using a reflux set up for 24 hours, this mixture was stirred and heated at 90 °C. The silica was then rinsed with deionized water and ethanol multiple times. Then the silica was rinsed with methanol and air dried, using a Gast solid phase extraction manifold. A PerkinElmer Spectrum 100, FT-IR Spectrometer was used to confirm the conversion of the carboxylic acid group to the amide group. Also, a True spec CHN Analyzer was used to measure the percentage of carbon, hydrogen, and nitrogen in the sample.

3.6 Trapping of 2-naphthol on the anthranilic acid functionalized silica

1.00 gram of anthranilic acid functionalized silica was packed between two frits in a solid phase extraction (SPE) column. A solution of 80 ppm 2-naphthol was prepared in deionized water. Three milliliters of this 80 ppm 2-naphthol solution was passed through this SPE column, using a SPE manifold, drop wise (approximately 2 milliliters per minute). The volume of 2-naphthol was measured after passing through the SPE column and this solution was injected into High Performance Liquid Chromatography HPLC. Peak areas were used to calculate the amount of 2-naphthol not trapped on the anthranilic acid silica surface.

3.7 Trapping of 2-naphthol on the aniline functionalized silica

1.00 gram of aniline functionalized silica was packed between two frits in a solid phase extraction (SPE) column. A solution of 80 ppm 2-naphthol was prepared in deionized water. Three milliliters of this 80 ppm 2-naphthol solution was passed through this SPE column, using a SPE manifold, drop wise (approximately 2 milliliters per minute). The volume of 2-naphthol was measured after passing through the SPE column and this solution was injected into the HPLC. Peak areas were used to calculate the amount of 2-naphthol not trapped on the aniline silica surface.

3.8 The release of 2-naphthol from functionalized anthranilic acid silica surface

A solution of pH 10 in 10 % methanol in water was prepared using sodium hydroxide (NaOH). After the 2-naphthol had been trapped on the anthranilic acid silica surface, 20 milliliters of the pH 10 solution (10 % methanol in water) was passed through the SPE column drop wise (approximately 2 milliliters per minute). The volume of the collected solution was measured after passing through the SPE column. The solution that

passed through the SPE column was analyzed by HPLC and the 2-naphthol peak area was used to measure the amount of 2-naphthol that was released.

3.9 The release of 2-naphthol from the silica aniline surface

A solution of pH 10 in 10 % methanol in water was prepared using sodium hydroxide (NaOH). After the 2-naphthol had been trapped on the silica aniline surface, 20 milliliters of the pH 10 solution (10 % methanol in water) was passed through the SPE column drop wise (approximately 2 milliliters per minute). The volume of the solution was measured after passing through the SPE column. The solution that passed through the SPE column was analyzed by HPLC and the 2-naphthol peak area was used to measure the amount of 2-naphthol that was released.

Result and Discussion

4.1 Synthesis of the silica particles surface

Step 1:

Vinyl surface group reaction step [silica particles]

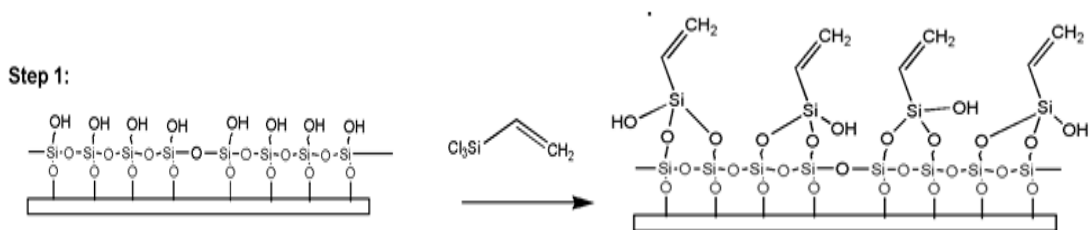


Figure 7. Vinyl surface group reaction

Vinyl groups were attached to silica particles overnight via immersion in trichlorovinylsilane in toluene as shown in Figure 7. After this step, a FTIR analysis was performed to determine the existence of the vinyl group on the silica particles.

As shown in Figure 8, blank silica, and 9, after the reaction, the absorption peaks appear at 878 cm^{-1} and 1603 cm^{-1} which are characteristic peaks for the vinyl group ($-\text{CH}=\text{CH}_2$). The absorption peaks at 1042 cm^{-1} and 1412 cm^{-1} are characteristic peaks for Si - C vibration. This confirmed the presence of the Si - CH = CH₂ group attachment.

A True spec CHN Analyzer was used to measure the percentage of carbon and hydrogen in the sample. As shown in Figure 10, the amount of carbon was increased to an average of 6.95% which is equal to 5.67 micromoles per gram of silica. This also confirmed the existence of the attached vinyl group on the silica particles.

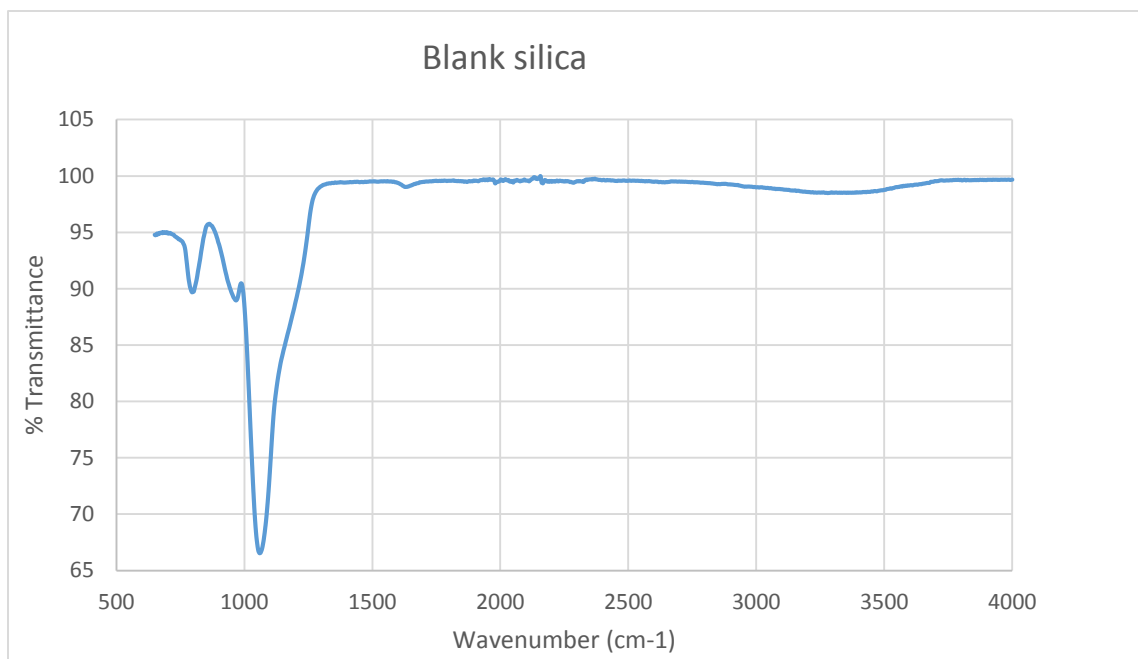


Figure 8. FTIR spectra of blank silica

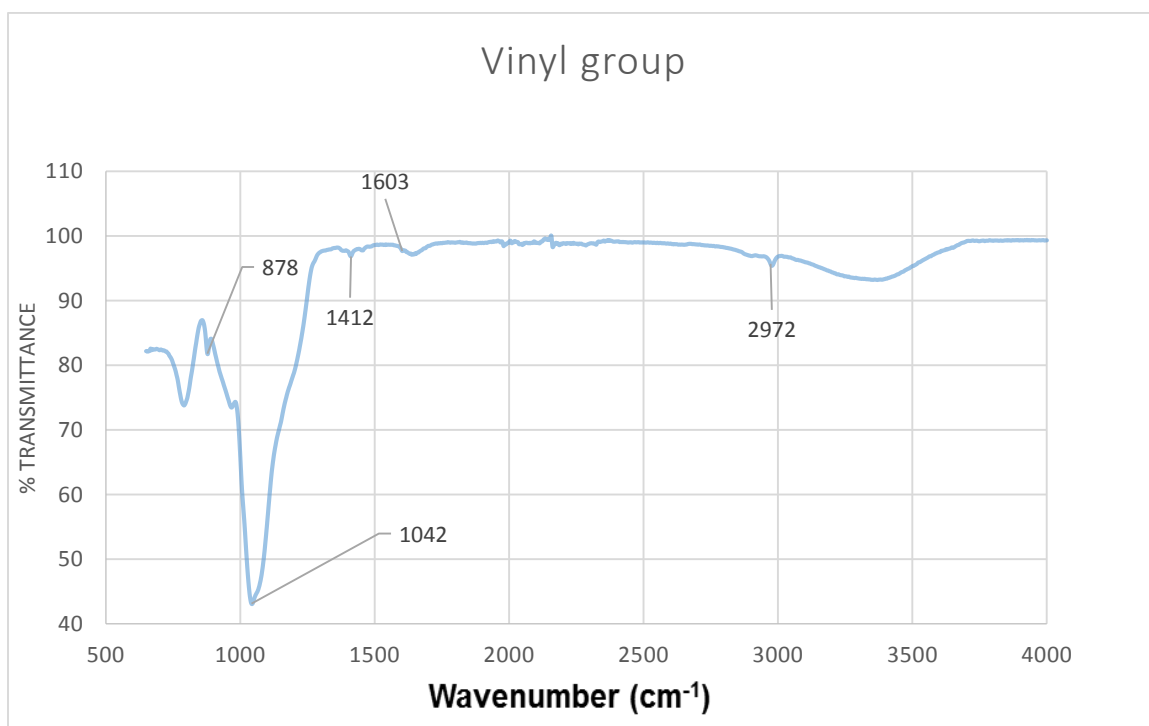


Figure 9. FTIR spectra of the Vinyl surface group silica

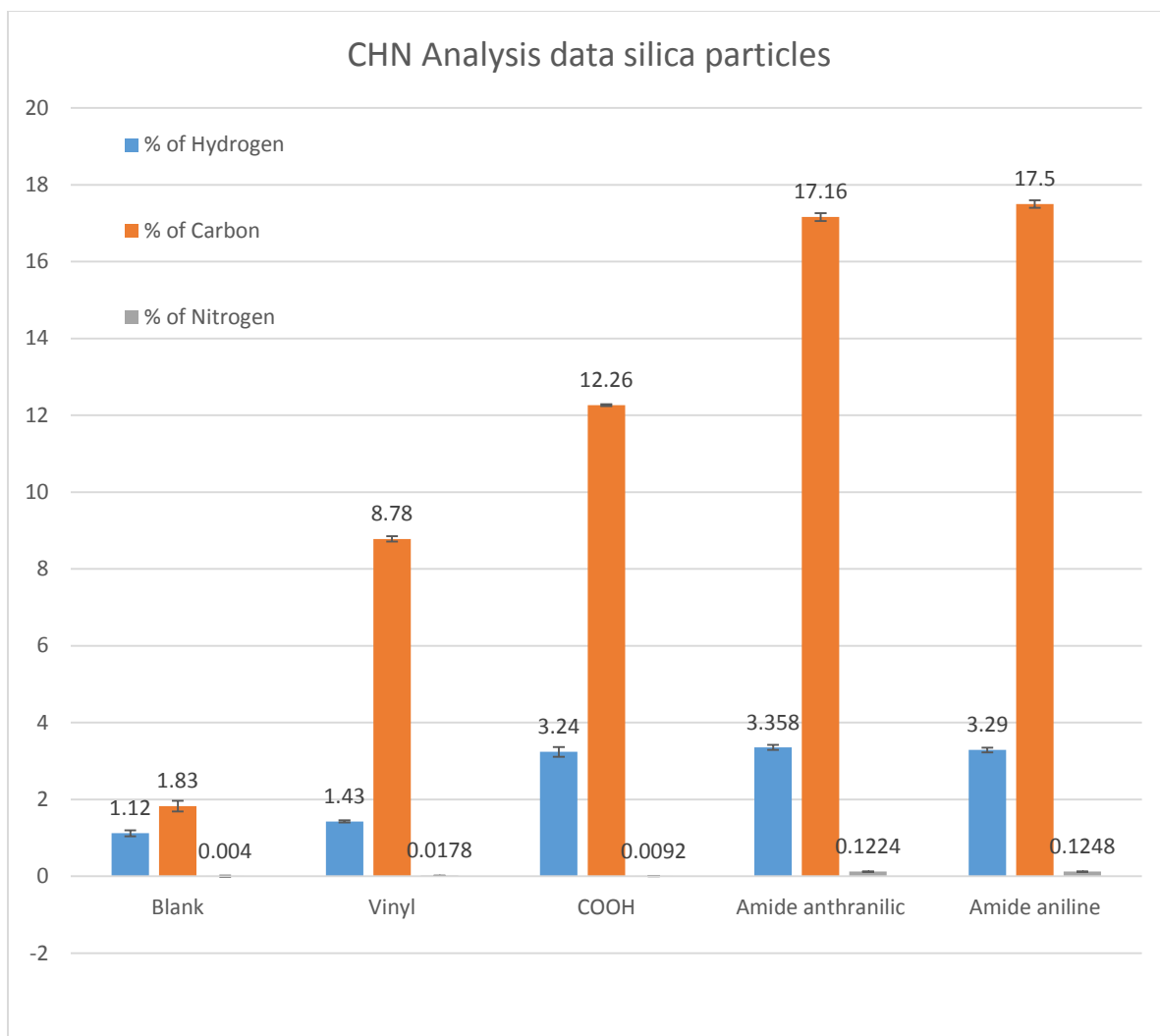


Figure 10. CHN analysis data silica particles.

Step 2

Carboxylic acid surface group reaction step [silica particles]

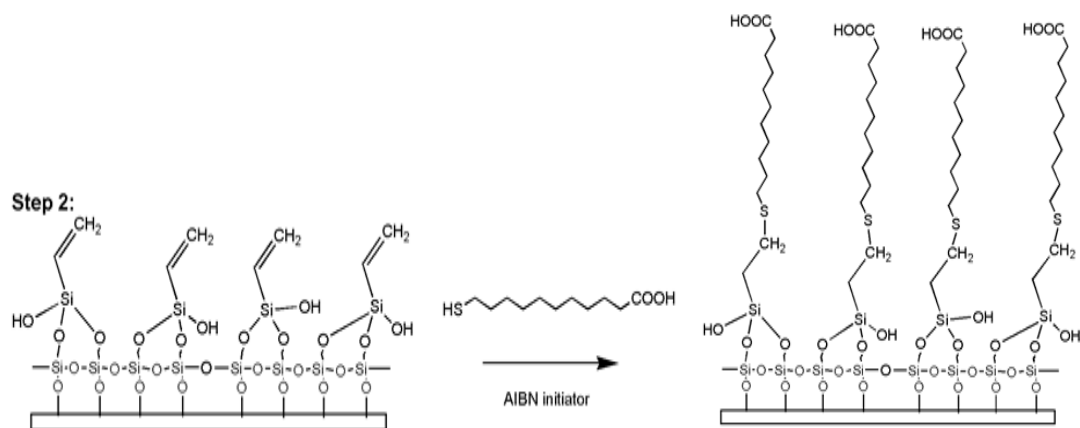


Figure 11. Carboxylic acid surface group reaction

The previously prepared vinyl functionalized silica was modified with 11-mercaptopundecanoic acid, with a molar ratio of 2:1 (thiol: alkene), through a click reaction between the thiol group and the surface vinyl group initiated by AIBN [2, 2-Azobis (2-methyl-propionitrile)], as depicted in Figure 11.

In its most characteristic reaction, AIBN decomposes, eliminating a molecule of nitrogen gas to form two 2-cyanoprop-2-yl radicals. These radicals can initiate free radical polymerizations and other radical-induced reactions³². AIBN was used here to initiate the anti-Markovnikov hydro halogenation of alkenes.

As shown in Figure 12, the appearance of the FTIR peak at 1715 cm^{-1} (-C=O) supports the successful attachment of carboxyl groups on the silica particle surface as well as the disappearance of the vinyl peaks which were at (878 cm^{-1} and 1603 cm^{-1}).

In addition, a Leco SC-432 Sulfur Analyzer was used to measure the percentage of sulfur in the sample. The amount of sulfur increased to an average of 1.40 micromoles

per gram of silica which confirmed the conversion of the vinyl group to carboxylic acid in a 1.40/5.67 mole ratio. In a separate reaction the amount of thiol was doubled but no improvement in the mole ratio was observed.

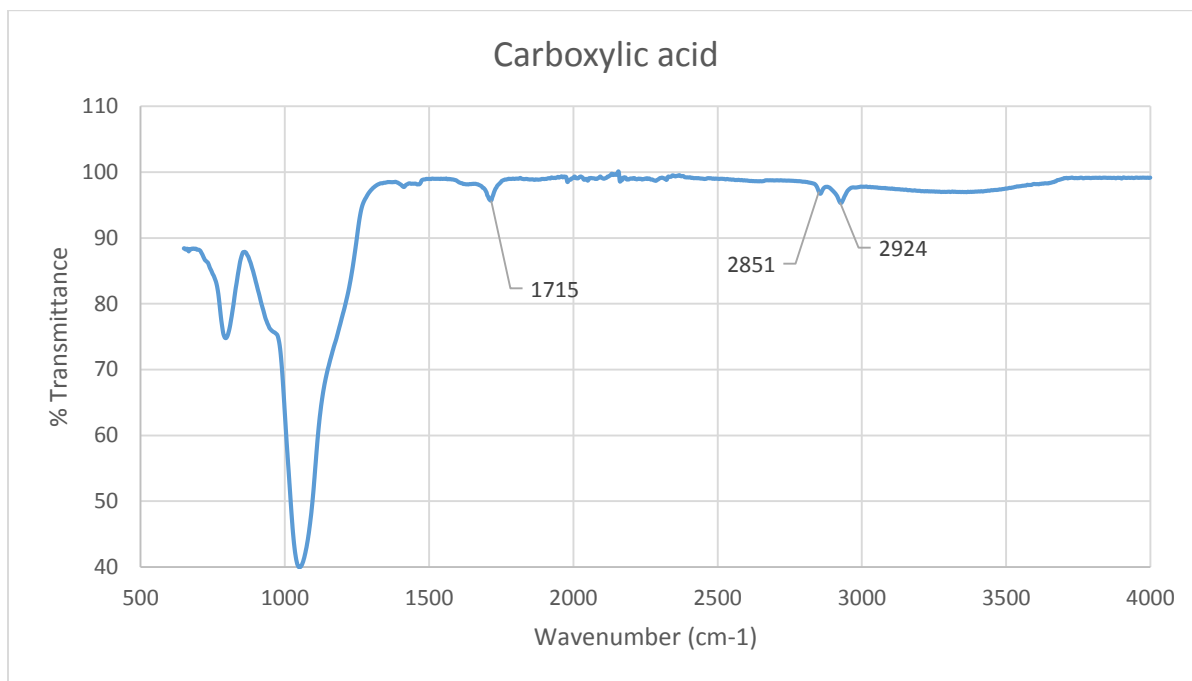


Figure 12. FTIR spectra of the Carboxylic acid modified silica particles

Step 3

Anthranilic Acid surface group reaction step [silica particles]

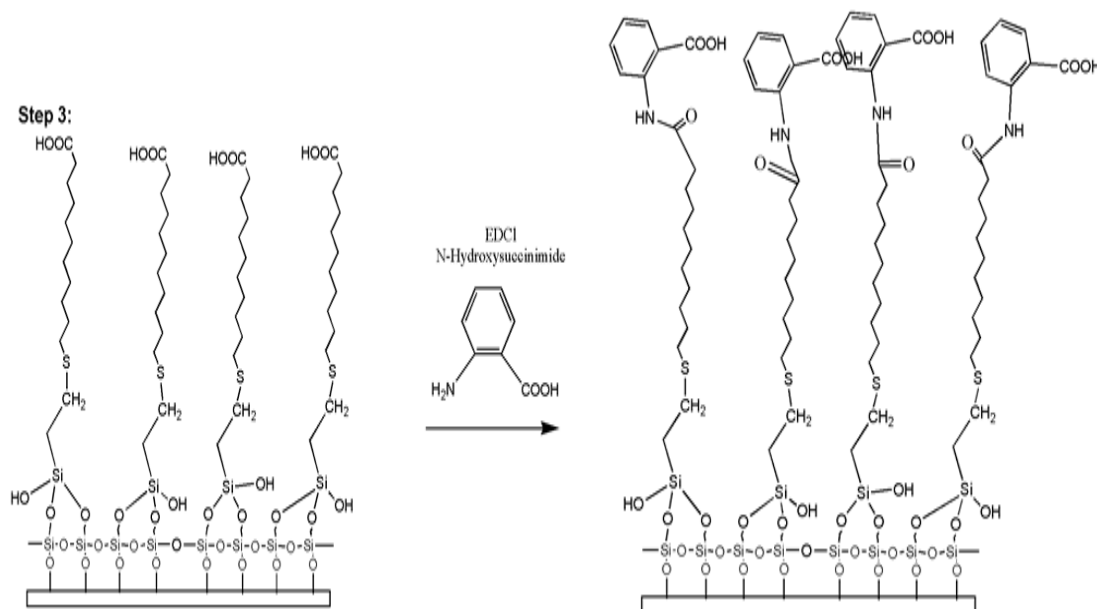


Figure 13. Anthranilic Acid surface group reaction

The previously prepared carboxylic functionalized silica was modified with an anthranilic acid moiety, through a reaction between the surface carboxyl group and the anthranilic acid moiety, through a reaction between the surface carboxyl group and the anthranilic acid amine group (NH₂), with a molar ratio of 2:1 (anthranilic acid: carboxylic acid). This reaction was initiated by EDCI (1-Ethyl-3-(3-dimethylaminopropyl) carbodiimide chloride) and N-Hydroxysuccinimide at 80 °C as shown in Figure 13.

As shown in Figure 14, the appearance of the FTIR peaks at 1525 cm⁻¹ and 1703 cm⁻¹ (peaks for amide I and amide II) support the successful conversion from carboxylic acid to amide. Also, the appearance of the FTIR peaks at 1453 cm⁻¹ and 1588 cm⁻¹ support the existence of the phenyl ring and the appearance of the C-N peak at 1378 cm⁻¹.

A CHN Analyzer was also used to measure the percentage of carbon, hydrogen and nitrogen in the sample. As shown in Figure 10, the amount of nitrogen increased to

an average of 0.1155% which is equal to 0.165 micromole per gram of silica. This confirmed the conversion of the carboxylic acid to an amide group at a 0.165/1.40 mole ratio. In a separate reaction the amount of anthranilic acid was doubled but no improvement in the mole ratio was observed.

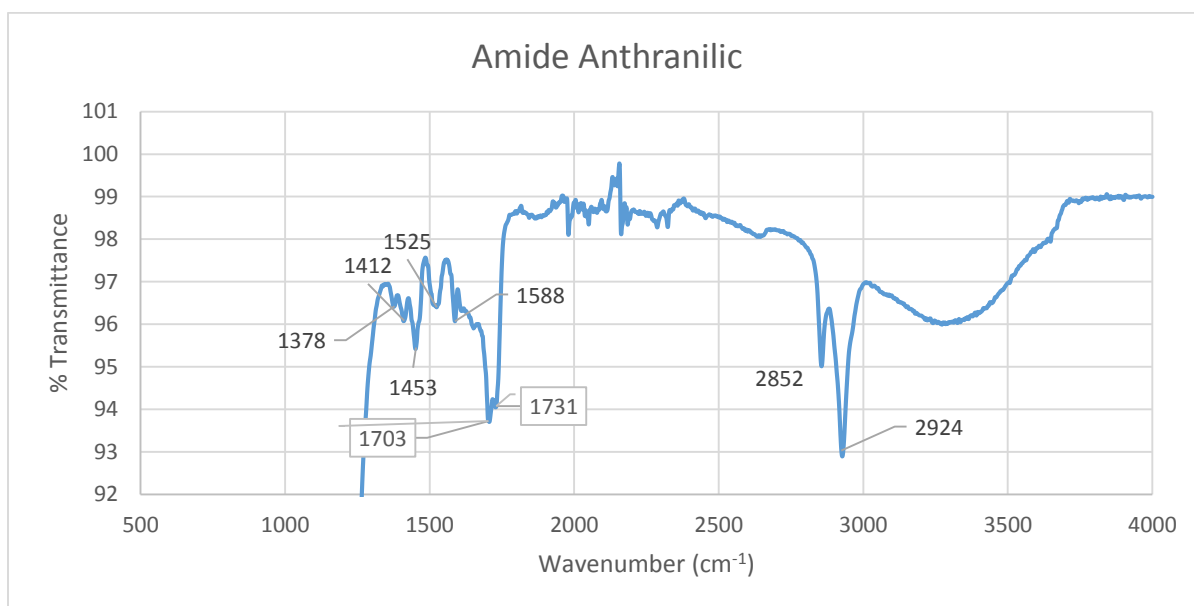


Figure 14. FTIR spectra of the anthranilic acid modified silica particles

Aniline surface group reaction step [silica particles]

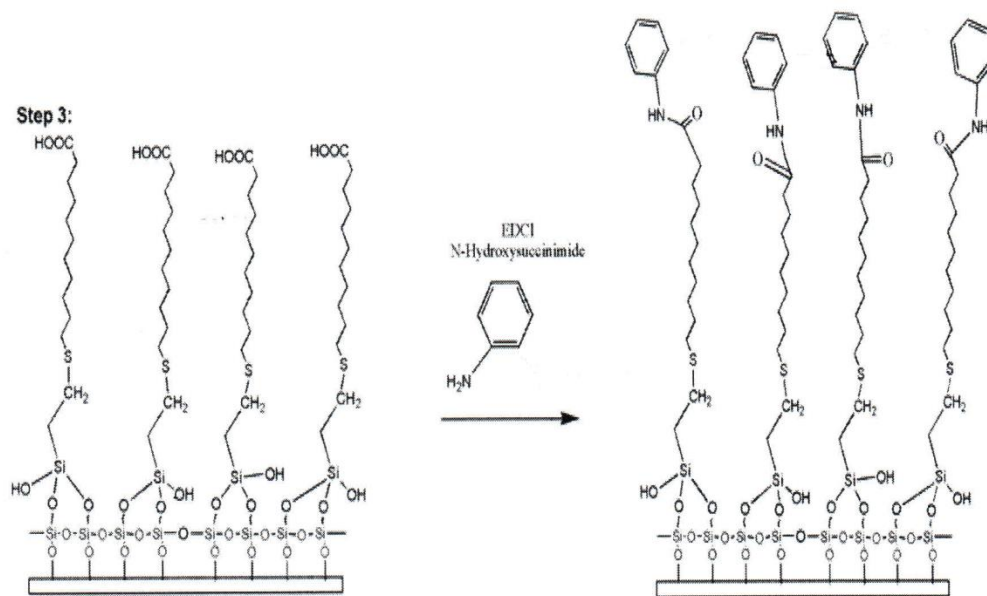


Figure 15. Aniline surface group reaction

Previously prepared carboxylic functionalized silica was modified with an aniline moiety through a reaction between the surface carboxyl group and the aniline amine group (NH₂), with a molar ratio of 2:1 (aniline: carboxylic acid). This reaction was initiated by EDCI (1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide chloride) and N-Hydroxysuccinimide at 80 °C as shown in Figure 15.

As shown in Figure 16, the appearance of the FTIR peaks at 1544 cm⁻¹ and 1664 cm⁻¹ (peaks for amide I and amide II) support the successful conversion from carboxylic acid to amide. Also, the appearance of the FTIR peaks at 1444 cm⁻¹ and 1601 cm⁻¹ support the existence of the phenyl ring and the appearance of the C-N peak at 1374 cm⁻¹.

Also, a CHN Analyzer was used to measure the percentage of carbon, hydrogen, and nitrogen in the sample. As shown in Figure 10, the amount of nitrogen was increased to an average of 0.1195% which is equal to 0.170 micromoles per gram silica. This confirmed the conversion of the carboxylic acid to an amide group in a 0.170/1.40 mole ratio. In a separate experiment, the amount of aniline was doubled but no improvement in mole ratio was observed.

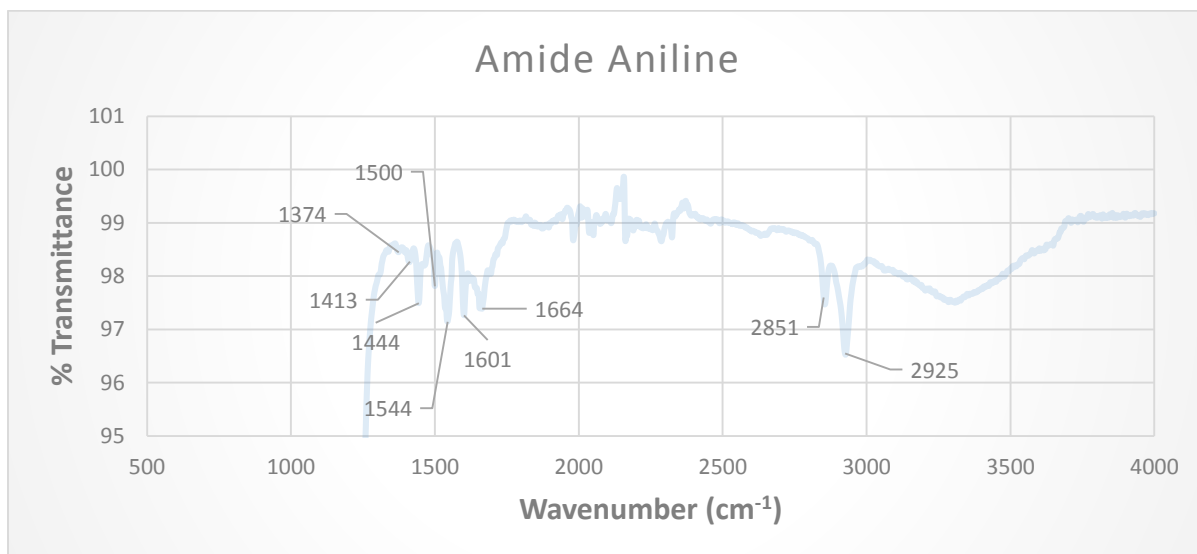


Figure 16. FTIR spectra of the aniline modified silica particles

We were unable to measure the contact angle on the silica particles. However, a small amount of the Anthranilic Acid surface group silica particles was added to a mixture of toluene and pH 4 buffer solution. The Anthranilic Acid group functionalized silica particles were found in the hydrophobic organic phase at pH 4 as shown in Figure 17. This confirmed that this material was in a hydrophobic state at pH 4. Another portion of Anthranilic Acid functionalized silica particles was added to a mixture of toluene and pH 10 buffer solution. These Anthranilic Acid surface group silica particles were drawn into the hydrophilic pH 10 buffer as depicted in Figure 17. This confirmed that this material was in a hydrophilic state because the carboxylic acid group becomes the more hydrophilic carboxylate at this higher pH, it is drawn into the hydrophilic aqueous buffer pH 10.

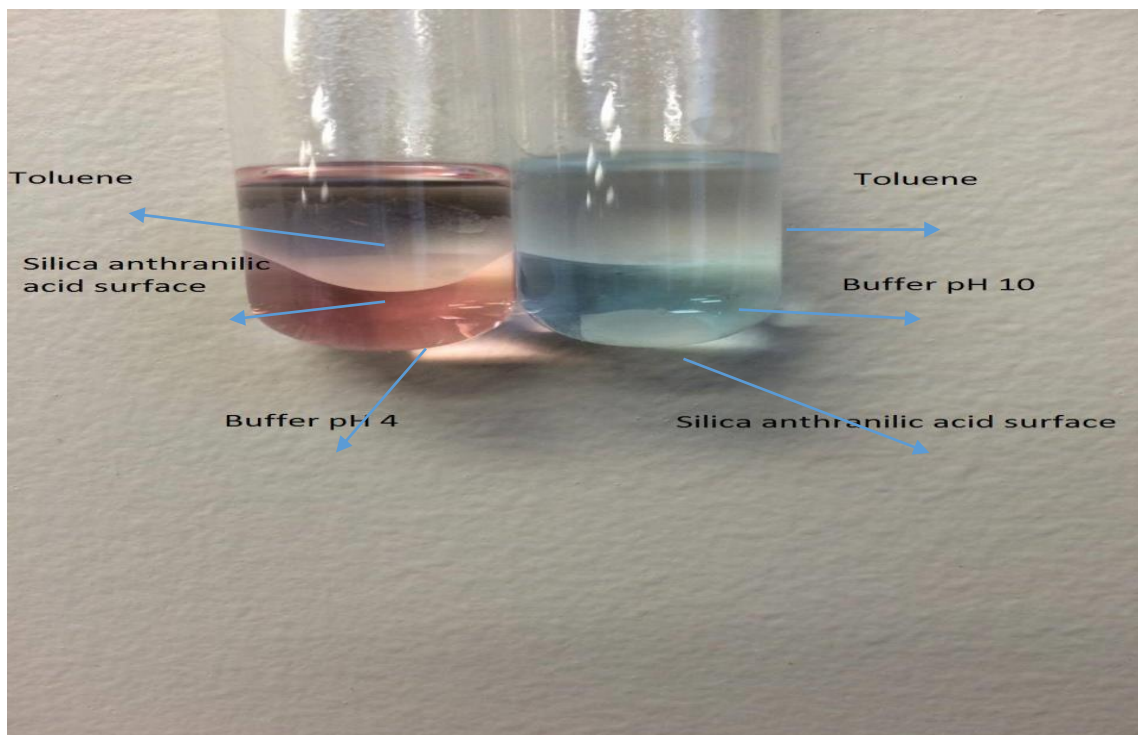


Figure 17. Silica anthranilic acid modified surface in a mixture of pH4, 10, and toluene

A small amount of the Aniline modified surface group silica particles were added to a mixture of toluene and pH 4 buffer solution. The Aniline functionalized silica particles were found in the hydrophobic organic phase at pH 4 as it is shown in Figure 18 which confirmed that this material was in a hydrophobic state. Another portion of aniline functionalized silica particles was added to a mixture of toluene and pH 10 buffer solution. The aniline surface group silica particles were found in the hydrophobic organic phase at pH 10 as depicted in Figure 18. This confirmed this material was also hydrophobic at pH 10. This aniline functionalized silica has no acid / base properties at the pHs investigated. Therefore no hydrophobic / hydrophilic switching is expected.

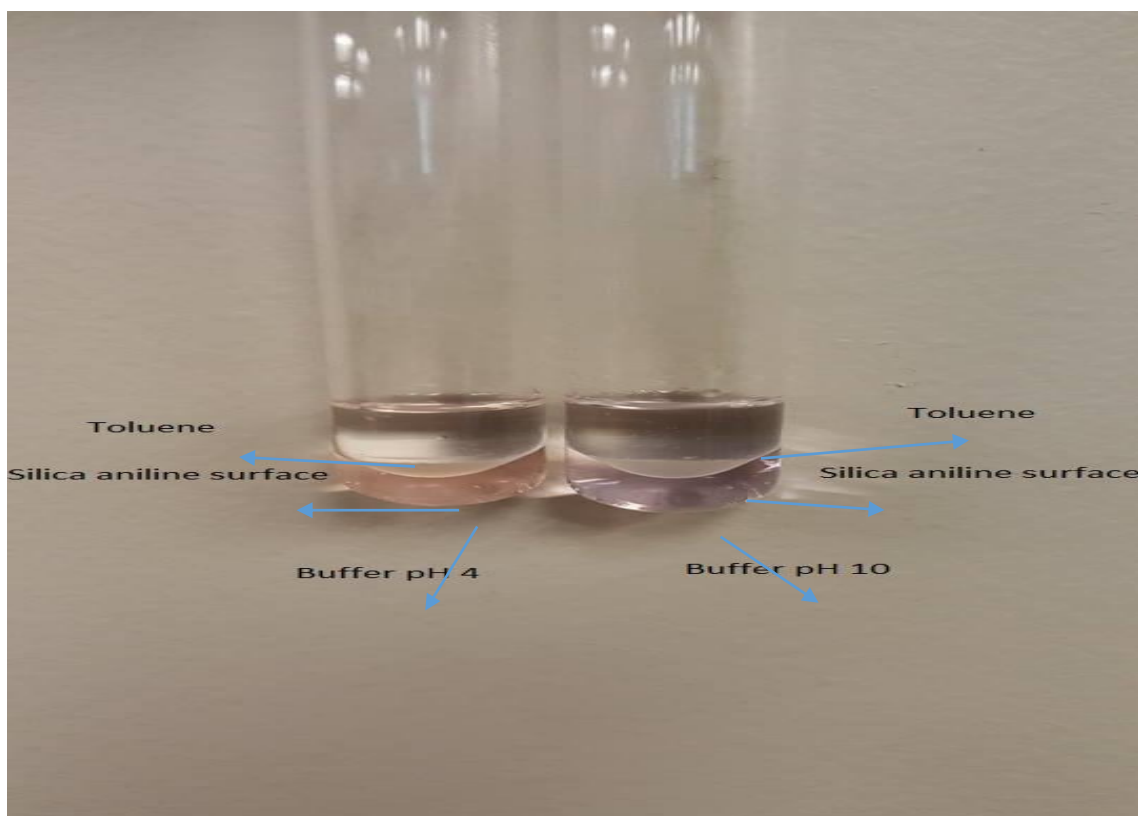


Figure 18. Silica aniline modified surface group in a mixture of buffers and toluene

4.2 Synthesis of the TLC plate surface

Step 1:

Vinyl surface group reaction step [TLC Plates]

Vinyl groups were attached to the Thin-layer chromatography (TLC) plates *via* overnight immersion in trichlorovinylsilane in toluene as shown in Figure 7. After attaching the vinyl group, a FTIR analysis on the TLC plate was performed to determine the existence of the vinyl group on the silica particles. As shown in Figures 19, blank TLC plate was silica based, and 20, after the reaction, the absorption peak 1604 cm^{-1} , the characteristic peak for the vinyl group ($-\text{CH}=\text{CH}_2$), and the absorption peak at 1411 cm^{-1} , the characteristic peak for Si – C vibration, appeared. This confirmed the presence of the Si – CH = CH₂ group.

The True spec CHN Analyzer was also used to measure the percentage of carbon, and hydrogen in the sample. As shown in Figure 21, the amount of carbon was increased to an average of 6.81% which is equal to 5.79 Micromoles per gram silica. This confirmed the existence of the attached vinyl group on the TLC plate.

After the modification of the TLC plate covered with vinyl group, the contact angle was measured to determine the hydrophobicity of the TLC surface. The surface contact angle increased from 22° to 132° , as shown in Figure 24, indicating a changing from hydrophilic to hydrophobic which confirmed the attachment of the vinyl group on the TLC plate surface. Both buffer solutions of pH 4 (hydrophobic) and pH 10 (hydrophilic) were used to measure contact angles.

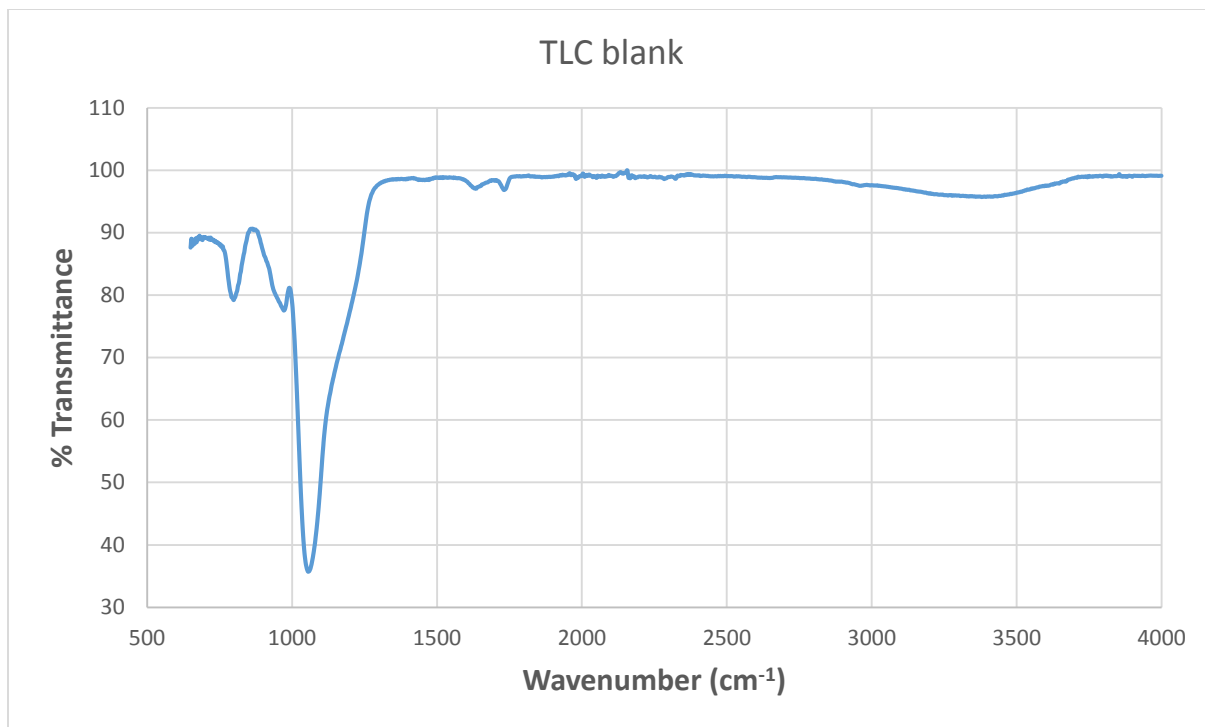


Figure 19. FTIR spectra of the Blank TLC plate

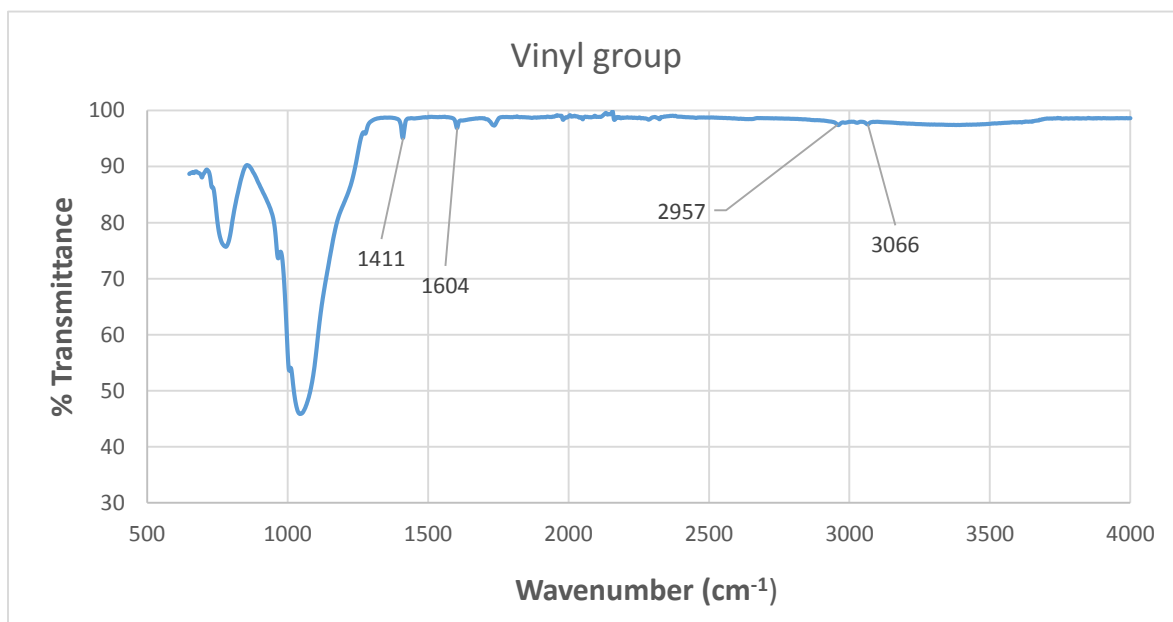


Figure 20. FTIR spectra of the Vinyl surface group TLC plate

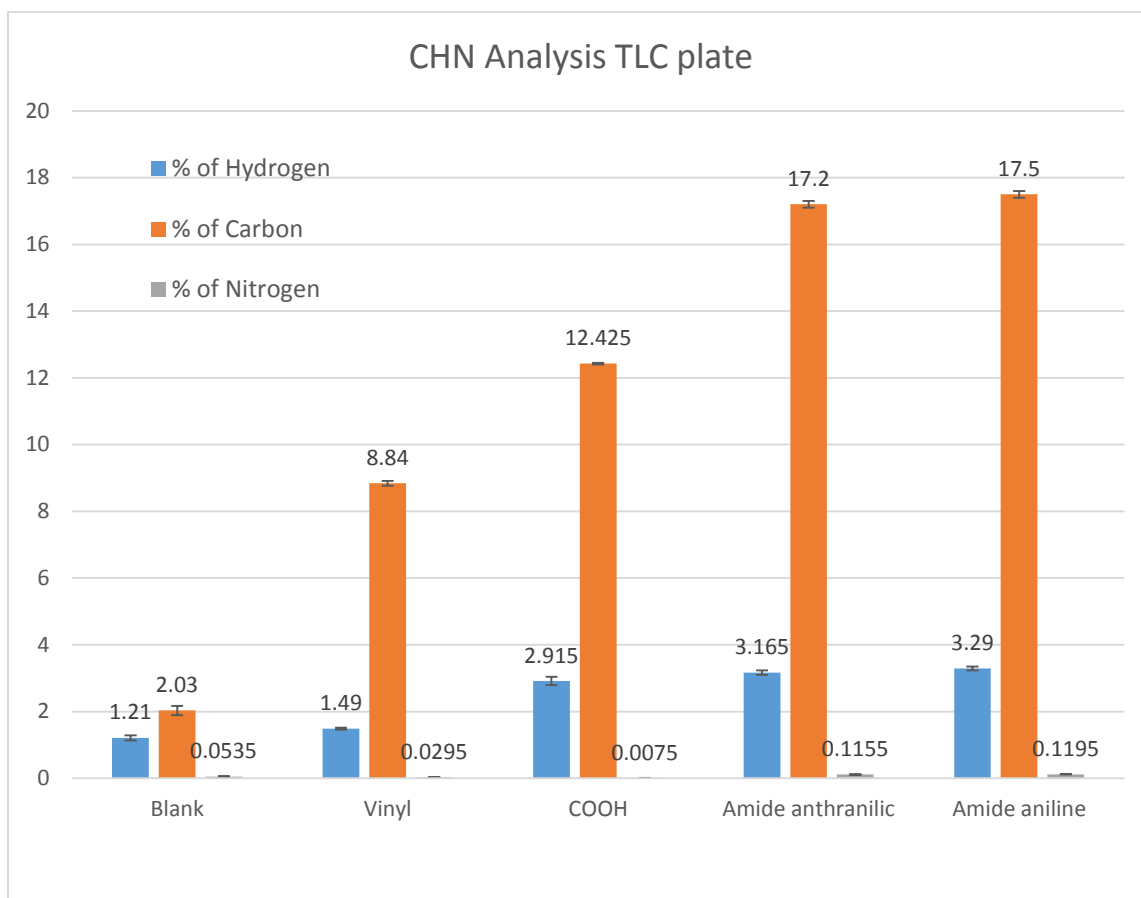


Figure 21. CHN Analysis data TLC plate.

Step 2

Carboxylic acid surface group reaction step [TLC plate]

Previously prepared vinyl functionalized TLC plate was modified with 11-mercaptoundecanoic acid, with a molar ratio of 2:1 (thiol: alkene), through a click reaction between the thiol group and the surface vinyl group and was initiated by AIBN [2, 2-Azobis (2-methyl-propionitrile)]. As shown in Figure 11. AIBN was used to initiate the anti-Markovnikov hydro halogenation of alkenes.

As shown in Figure 22, the appearance of the FTIR peak at 1715 cm^{-1} ($-\text{C}=\text{O}$) supports the successful attachment of carboxyl groups on the silica particle surface as well as the disappearance of the vinyl peaks which were at 878 cm^{-1} and 1603 cm^{-1} .

In addition, the True spec CHN Analyzer was used to measure the percentage of carbon and hydrogen in the sample as shown in Figure 21.

In addition, a Leco SC-432 Sulfur Analyzer was used to measure the percentage of sulfur in the sample. The amount of sulfur was increased to an average of 1.49 micromoles per gram which confirmed the conversion of the vinyl group to carboxylic acid in a 1.49/5.79 mole ratio.

After the modification of the TLC plate covered with carboxylic acid groups, the contact angle was measured to determine the hydrophobicity of the surface. Both buffer solutions of pH 4 and pH 10 were used to measure contact angles. The contact angle was different at different pHs. At lower pH (pH 4) the contact angle was 102° as shown in Figure 24, which is hydrophobic because the carboxylic acid group is protonated COOH rendering surface phenyl groups. However, at higher pH (pH 10) the contact angle was

much lower (36°). This confirmed this material was hydrophilic because the carboxylic acid group becomes the surface carboxylate at this higher pH.

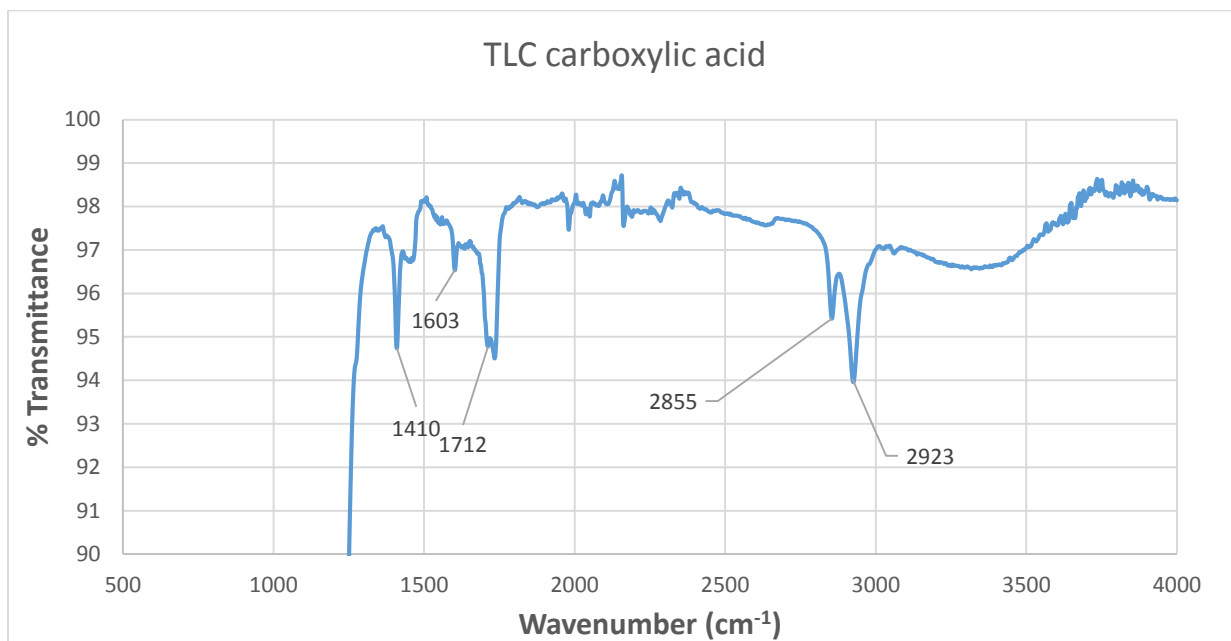


Figure 22. FTIR spectra of the Carboxylic acid modified TLC plate

Step 3

Anthranilic Acid surface group reaction step [TLC plate]

The previously prepared carboxylic functionalized TLC plate was modified with an anthranilic acid moiety through a reaction between the surface carboxyl group and the anthranilic acid amine group (NH_2) with a molar ratio of 2:1 (anthranilic acid: carboxylic acid). This reaction was initiated by EDCl (1-Ethyl-3-(3-dimethylaminopropyl) carbodiimide chloride) and N-Hydroxysuccinimide at 80°C as shown in Figure 13.

As shown in Figure 23, the appearance of the FTIR peaks at 1525 cm^{-1} and 1703 cm^{-1} (peaks for amide I and amide II) support the successful conversion from carboxylic acid to amide. Also, the appearance of the FTIR peaks at 1453 cm^{-1} and 1588 cm^{-1} support the existence of the phenyl ring and the appearance of the peak at 1378 cm^{-1} support the existence of an amide.

A CHN Analyzer was also used to measure the percentage of carbon, hydrogen and nitrogen in the sample. As shown in Figure 21, the amount of nitrogen was increased to an average of 0.1244% which is equal to 0.178 micromoles per gram of silica. This confirmed the conversion of the carboxylic acid to an amide group at a 0.178/1.49 mole ratio.

Contact angles from pH 1 to 13 were measured to determine relative hydrophobicity of the surface of the Anthranilic Acid modified TLC surface. As shown in Figure 24, at low pHs (pH 4), the contact angle is (107°), hydrophobic because the carboxylic acid group is protonated (COOH) and intra-hydrogen bonding between this group and the amide group keeps the phenyl (hydrophobic) moiety exposed to the surface. At pH 10, the contact angle is much lower (13°) as shown in Figure 24, because the carboxylic acid group becomes carboxylate which is charged and hydrophilic.

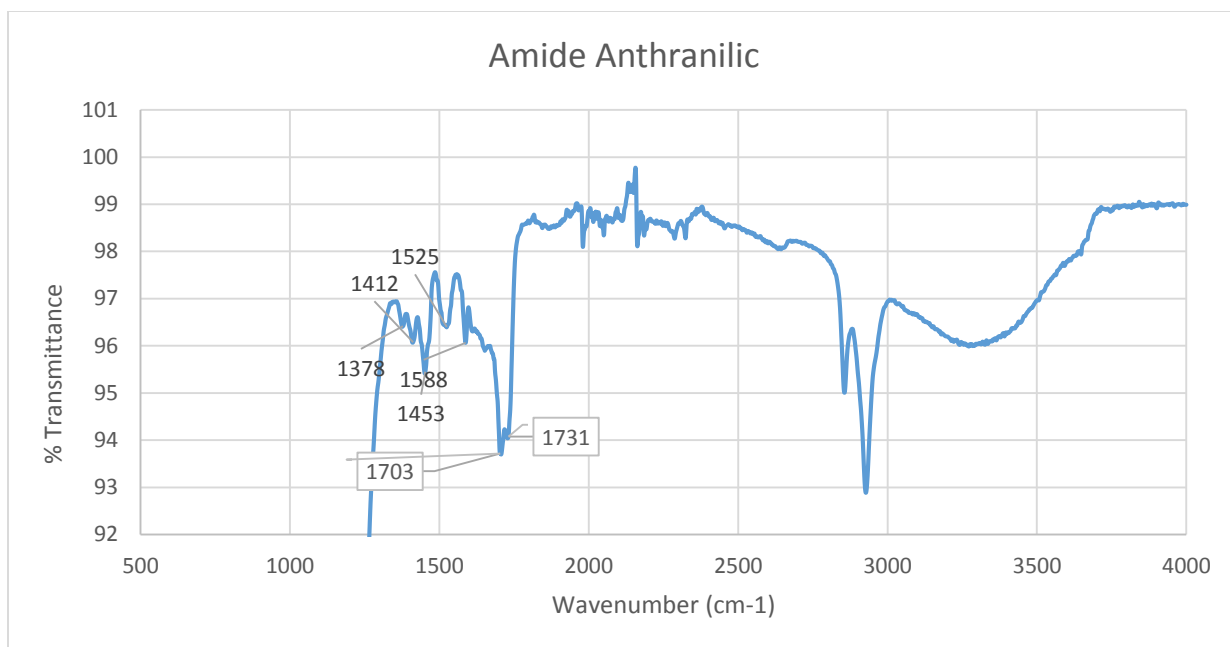


Figure 23. FTIR spectra of the anthranilic acid surface group TLC plate.

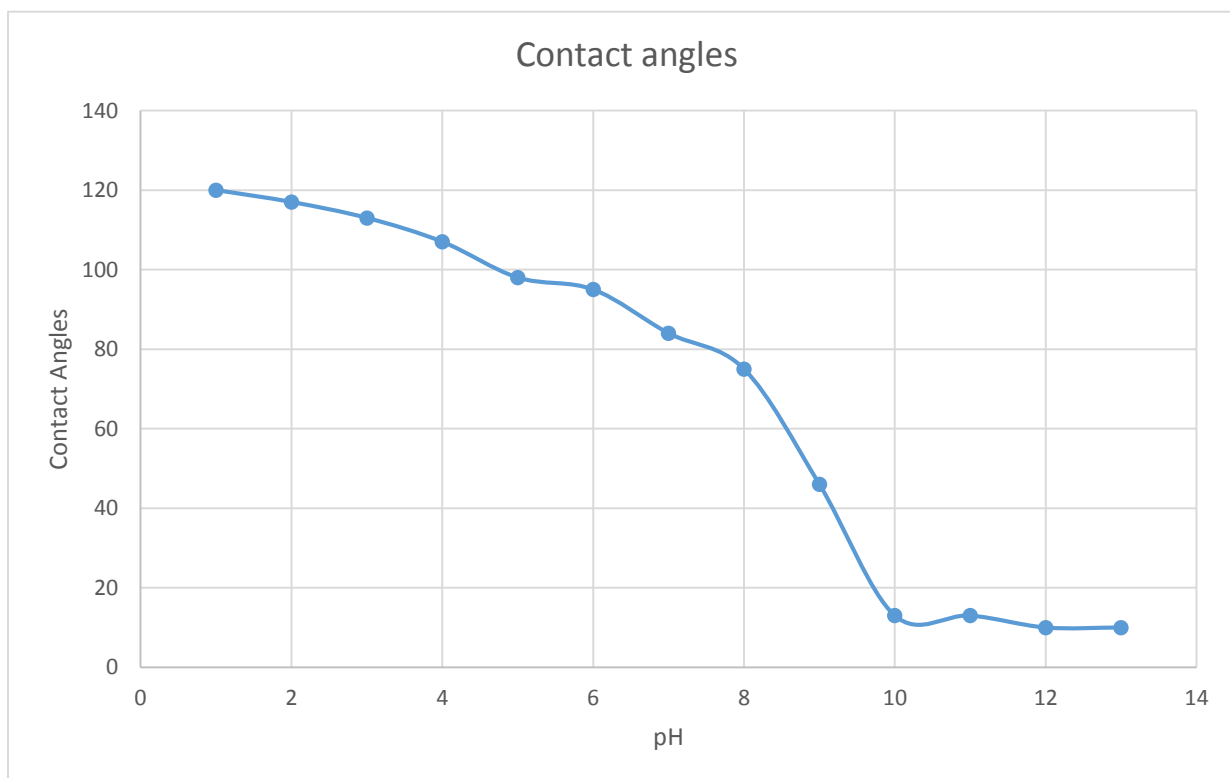


Figure 24. Contact angle measurement for TLC switchable surface at different pHs.

Aniline surface group reaction step [TLC plate]

The previously prepared carboxylic functionalized TLC plate was modified with an aniline moiety through a reaction between the surface carboxyl group and the aniline amine group (NH₂) with a molar ratio of 2:1 (aniline: carboxylic acid). This reaction was initiated by EDCI (1-Ethyl-3-(3-dimethylaminopropyl) carbodiimide chloride) and N-Hydroxysuccinimide at 80 °C as shown in Figure 15.

As shown in Figure 25, the appearance of the FTIR peaks at 1544 cm⁻¹ and 1664 cm⁻¹ (peaks for amide I and amide II) support the successful conversion from carboxylic acid to amide. Also, the appearance of the FTIR peaks at 1444 cm⁻¹ and 1601 cm⁻¹ support the existence of the phenyl ring in addition to the appearance of the C-N peak at 1374 cm⁻¹.

Also, a CHN Analyzer was used to measure the percentage of carbon, hydrogen, and nitrogen in the sample. As shown in Figure 21, the amount of nitrogen was increased to an average of 0.1248% which is equal to 0.178 micromoles per gram silica. This confirmed the conversion of the carboxylic acid to an amide group in a 0.178/1.49 mole ratio.

Contact angles were measured to determine relative hydrophobicity of the surface of the aniline modified TLC surface. Contact angles were measured using both buffer solutions of pH 4 and pH 10. As shown in Figure 26, the contact angle for the aniline group surface remained stable at different pHs as expected because this group does not have acid base properties.

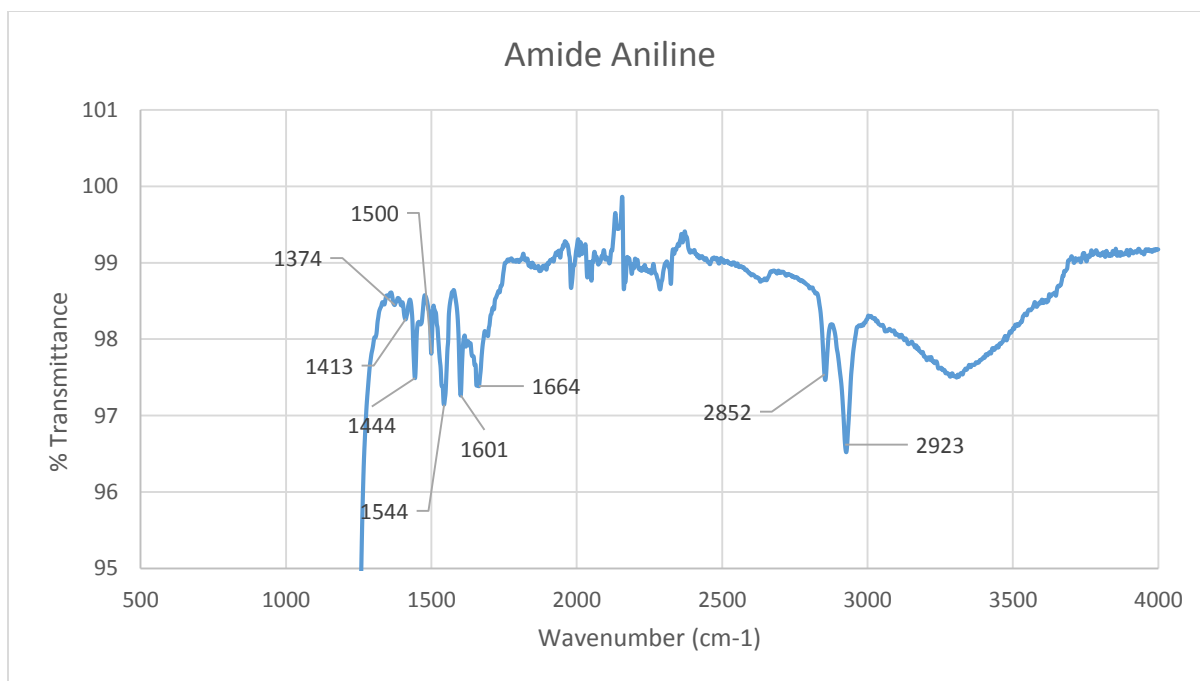


Figure 25. FTIR spectra of the an amide aniline surface group TLC plate

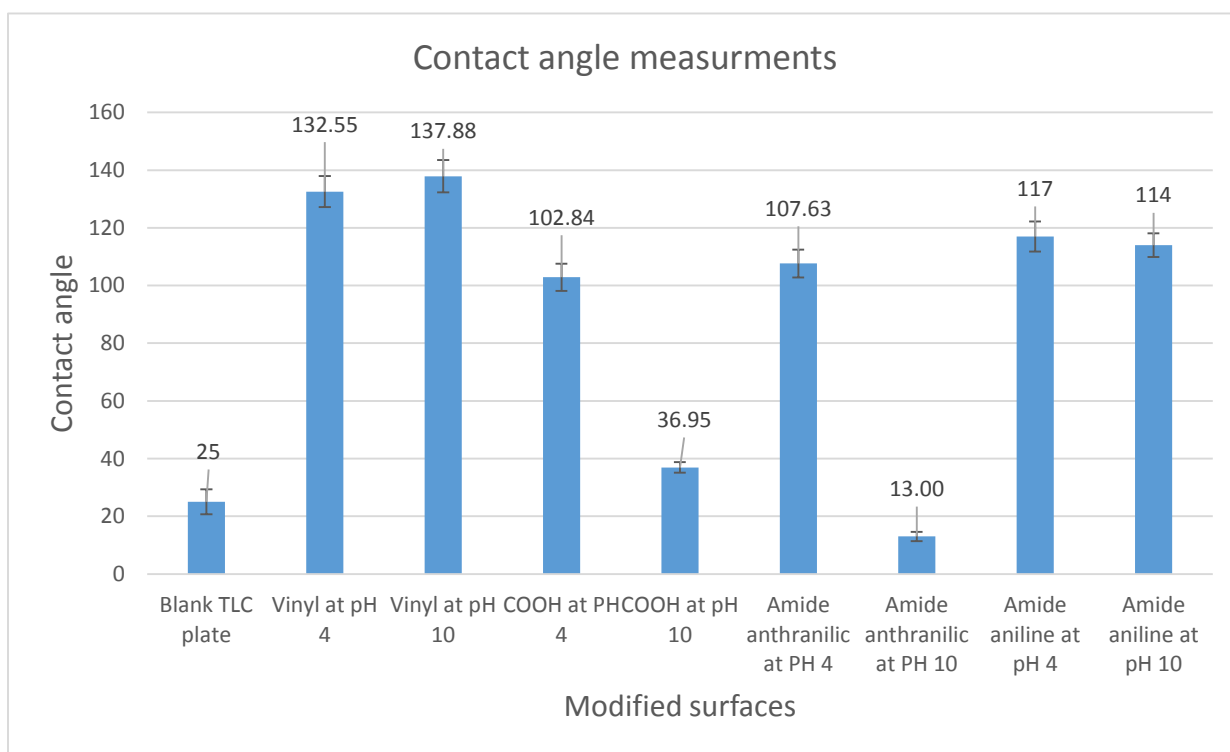


Figure 26. TLC modified plates contact angles

4.3 Synthesis of the Microscope slide surface

Step1

Vinyl surface group reaction step [Microscope slides]

After cleaning the microscope slides, the vinyl group was attached to the surface of the slides via overnight immersion in trichlorovinylsilane in toluene as shown in Figure 7.

The contact angle on a clean microscope slide was measured using water. As shown in Figure 27, the contact angle for the cleaned microscope is 20° which indicates a hydrophilic surface. After the modification of the microscope slides covered with vinyl group, the contact angle was again measured to determine the relative hydrophobicity of the surface. The surface contact angle increased from 20° to 122° , as shown in Figure 27, indicating a changing from hydrophilic to hydrophobic which confirmed the attaching of the vinyl group on the microscope slide surface. Contact angles were measured at both buffer solutions of pH 4 and pH 10. The contact angle for the vinyl group surface remained stable at different pHs as expected because this group does not have acid base properties.

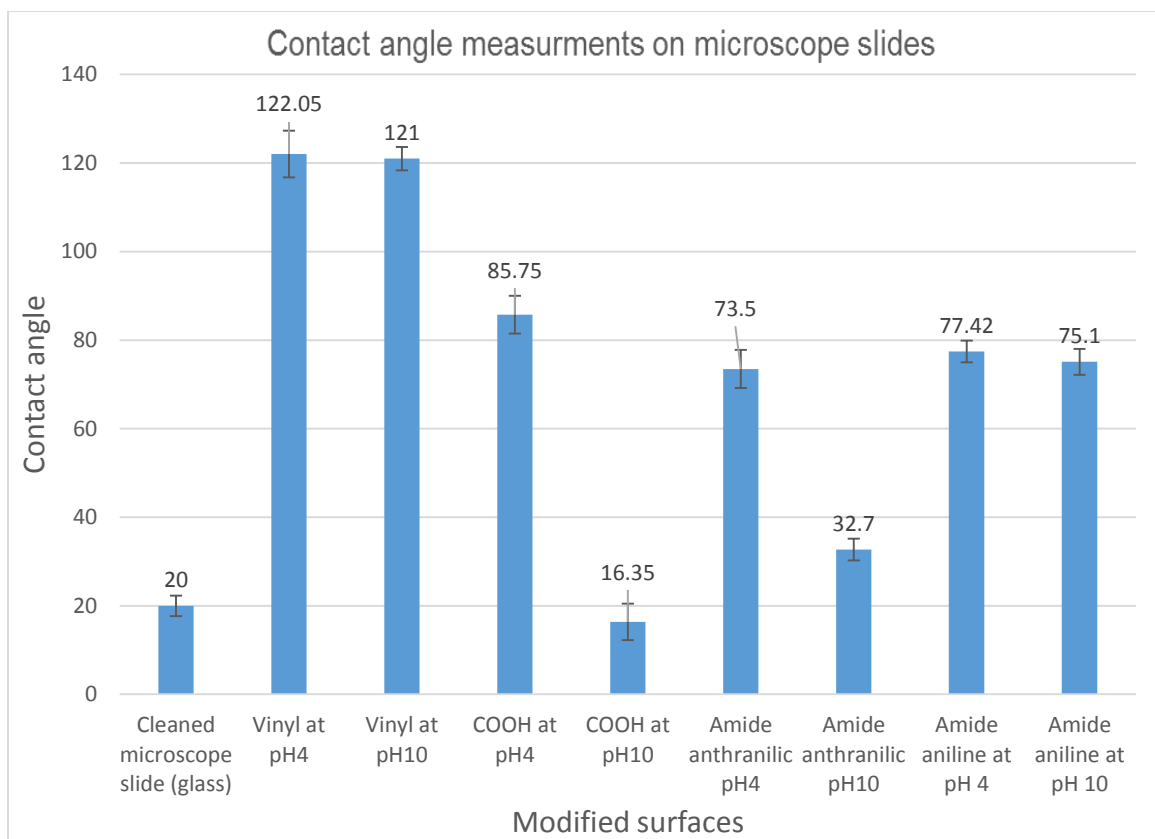


Figure 27. Microscope modified slides contact angles

Step 2

Carboxylic acid surface group reaction step [microscope slide]

Previously prepared vinyl functionalized microscope slide was modified with 11-mercaptopundecanoic acid, with a molar ratio of 2:1 (thiol: alkene), through a click reaction between the thiol group and the surface vinyl group and was initiated by AIBN [2,2-Azobis(2-methyl-propionitrile)] as shown in Figure 11. AIBN was used to initiate the anti-Markovnikov hydro halogenation of alkenes.

Contact angles were measured to determine the relative hydrophobicity of the surface of the carboxylic acid modified microscope slide. Contact angles were measured using both buffer solutions of pH 4 and pH 10. At lower pH(pH 4), the contact angle was

86° as shown in Figure 27, which approaches being hydrophobic because the carboxylic acid group is protonated (COOH). However, at pH 10 the contact angle was much lower (16°) because the carboxylic acid group becomes the surface carboxylate which is charged and hydrophilic.

Step 3

Anthranilic Acid surface group reaction step [microscope slide]

The previously prepared carboxylic functionalized microscope slide was modified with an anthranilic acid moiety, through a reaction between the surface carboxyl group and the anthranilic acid amine group, (NH₂) with a molar ratio of 2:1 (anthranilic acid: carboxylic acid). This reaction was initiated by EDCI (1-Ethyl-3-(3-dimethylaminopropyl) carbodiimide chloride) and N- Hydroxysuccinimide at 80 °C as shown in Figure 13.

Contact angles were measured to determine the relative surface hydrophobicity of the anthranilic acid modified microscope slide. Contact angles were measured using both buffer solutions of pH 4 and pH 10. As shown in Figure 27, at low pHs (pH 4), the contact angle was (73°). The contact angle was not large enough to be called hydrophobic.

At higher pHs, the contact angle is low (33°) because the carboxylic acid group becomes carboxylate which is charged and hydrophilic.

As seen in Figure 27, the contact angle change at pH 4 and 10 was not as great as compared to the same modified TLC plate. The microscope slide (glass) is considered as a smooth surface. The smooth surface has less friction than the rougher TLC surface

which makes it repel a droplet of buffer pH 4 less. On the other hand, the rough surface has more friction than a smooth surface which repels more to the droplet of buffer pH 4 to give it much more of a hydrophobic surface³³.

Aniline surface group reaction step [microscope slide]

The previously prepared carboxylic functionalized microscope slide was modified with an aniline moiety through a reaction between the surface carboxyl group and the aniline amine group (NH₂) with a molar ratio of 2:1 (aniline: carboxylic acid). This reaction was initiated by EDCI (1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide chloride) and N-Hydroxysuccinimide at 80 °C as shown in Figure 15.

After the modification of the microscope slides covered with aniline group, the contact angles were measured to determine the relative hydrophobicity of the surface. Contact angles were measured at both buffer solutions of pH 4 and pH 10. As shown in Figure 27, the contact angle for the aniline group surface remained stable at different pHs as expected because this group does not have acid base properties.

4.4 Anthranilic acid functionalized silica

2-naphthol is an isomer of 1-naphthol. It is a compound that contains two aromatic rings with a hydroxide group at the 2-position. 2-naphthol was used in this study because it has good water solubility (easy to work with in aqueous solutions) and also has a nonpolar portion (2 phenyls) that has attraction to a nonpolar medium. It has a pka of 9.51. A previously prepared surface having terminal anthranilic acid (AA) groups on silica gel particles was used to study the extraction of 2-naphthol. At lower pHs the –COOH surface group on the AA moiety is neutral and intra-hydrogen bonding keeps this group locked with the amine in the 2 position resulting in the phenyl (hydrophobic)

portion exposed to the surface as shown in Figure 28. The aromatic rings in 2-naphthol are attracted to AA through hydrophobic π - π interactions which facilitates its trapping at lower pHs. Hydrophobic substances stick efficiently to a hydrophobic surface (the like dissolves like principle). At higher pHs the AA's carboxylic acid group becomes the charged carboxylate group, rendering the surface hydrophilic as shown in Figure 28. The surface with a terminal anthranilic acid will change from hydrophobic to hydrophilic, with an introduced response (increasing pH change), therefore this will weaken the hydrophobic substance's attractions to this surface which we hypothesize will result in an easier release of the 2-naphthol.

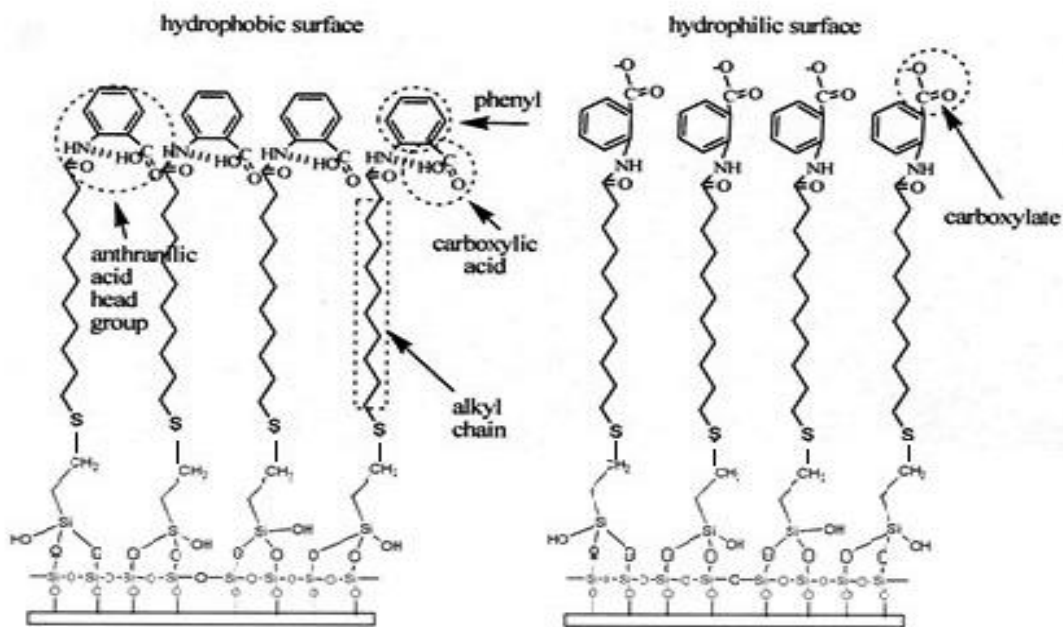


Figure 28. Anthranilic acid surface at low and high pH

4.5 Calibration curve

To measure the amount of 2-naphthol after each experiment, a calibration curve was prepared by injecting 5, 10, 20, 40, and 80 ppm standards of 2-naphthol in 10% methanol. Peak areas and concentration were plotted to get a straight line as shown in Figure 29.

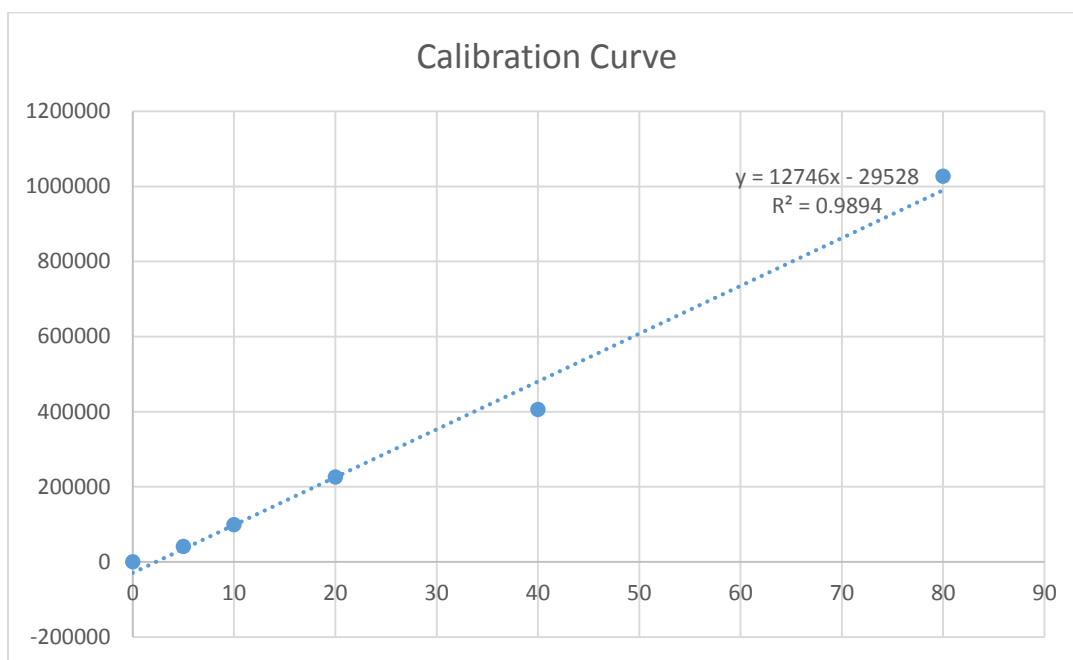


Figure 29. 2-naphthol Calibration curve

4.6 Trapping of 2-naphthol

4.6.1 Trapping of 2-naphthol on the frits

Because the frit that holds the modified silica is a polyethylene polymer and is considered hydrophobic, it is very important to test how much 2-naphthol will be trapped on the frits. Two frits were packed in a solid phase extraction (SPE) column. A solution of 80 ppm 2-naphthol was prepared in a solution of pH 4 using hydrochloric acid (HCl).

Three milliliters of this 80 ppm 2-naphthol solution were passed through this SPE column drop wise (approximately 2 milliliters per minute). The volume of 2-naphthol after passing through the SPE column was an average of 2.1 milliliters. The collected solution was injected into the High Performance Liquid Chromatography (HPLC). The peak area of 2-naphthol was used to calculate the amount of 2-naphthol not trapped on the frits. Based on a calculation using the calibration curve, the average percentage of 2-naphthol that was trapped on the frits was an average of 23% as shown in Figure 30.

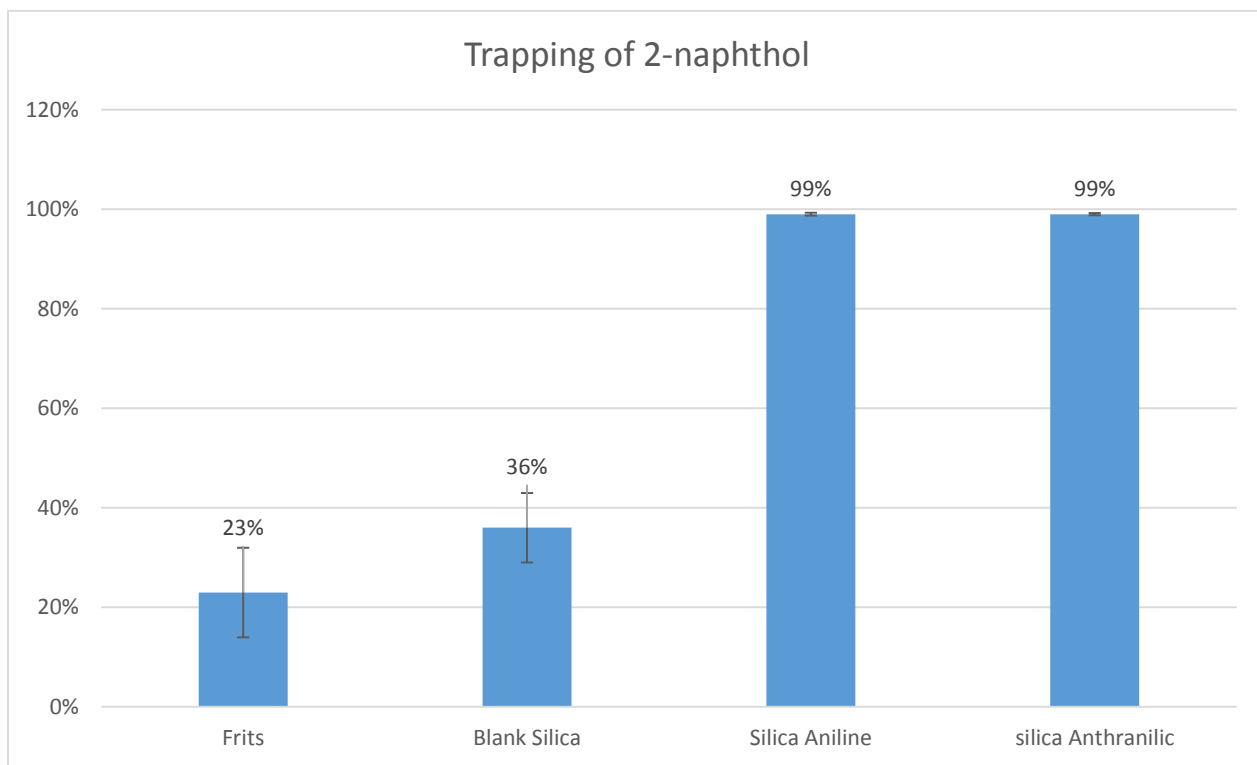


Figure 30. Trapping of 2-naphthol

4.6.2 Trapping of 2-naphthol on the blank silica

Next a control experiment to measure the amount of 2-naphthol trapped on the silica gel was performed. One gram of blank silica was packed between two frits in a solid phase extraction (SPE) column. Three milliliters of the 80 ppm 2-naphthol solution was passed through this SPE column drop wise (approximately 2 milliliters per minute). The volume of 2-naphthol after passing through the SPE column was an average of 2.2 milliliters. This solution was then injected into the HPLC. The peak area of 2-naphthol was used to calculate the amount of 2-naphthol not trapped on the frits. Based on a calculation using the calibration curve, the average percentage of 2-naphthol that was trapped on the blank silica surface and the frits was 36% as shown in Figure 30.

4.6.3 Trapping of 2-naphthol on the aniline functionalized silica

1.00 gram of aniline functionalized silica was packed between two frits in a solid phase extraction (SPE) column. Three milliliters of the 80 ppm 2-naphthol solution was passed through this SPE column drop wise (approximately 2 milliliters per minute). The volume of 2-naphthol after passing through the SPE column was an average of 2.2 milliliters. This collected solution was then injected into the HPLC. The peak area of 2-naphthol was used to calculate the amount of 2-naphthol not trapped on the aniline functionalized silica. Based on a calculation using the calibration curve, the average percentage of 2-naphthol that was trapped on the aniline silica surface and the frits was 99% as shown in Figure 30. The 2-naphthol was essentially completely trapped on the aniline silica surface because it was hydrophobic (the like dissolves like principle).

4.6.4 Trapping of 2-naphthol on the anthranilic acid functionalized silica

1.00 gram of anthranilic acid functionalized silica was packed between two frits in a solid phase extraction (SPE) column. Three milliliters of the 80 ppm 2-naphthol solution was passed through this SPE column drop wise (approximately 2 milliliters per minute). The volume of 2-naphthol after passing through the SPE column was an average of 2.2 milliliters. This collected solution was then injected into the HPLC. The peak area of 2-naphthol was used to calculate the amount of 2-naphthol not trapped on the anthranilic acid functionalized silica. Based on a calculation using the calibration curve, the average percentage of 2-naphthol that was trapped on the anthranilic acid functionalized silica surface and the frits was 99% as shown in Figure 30. The 2-naphthol was essentially completely trapped on the anthranilic acid silica surface because this surface is hydrophobic (the like dissolves like principle).

4.7. The recovery of 2-naphthol from the frits

A solution of pH 10 using sodium hydroxide (NaOH) was prepared in 10% methanol in water. After the 2-naphthol had been trapped on the frits, 20 milliliters of this was passed through the SPE column drop wise (approximately 2 milliliters per minute). The volume of 2-naphthol after passing through the SPE column was an average of 19.2 milliliters. The 2-naphthol was then injected into the HPLC to measure the amount of 2-naphthol that was recovered. The peak area of 2-naphthol was used to calculate the amount of 2-naphthol that was recovered. Based on a calculation using the calibration curve, the average percentage of 2-naphthol that was recovered 8% as shown in Figure 31.

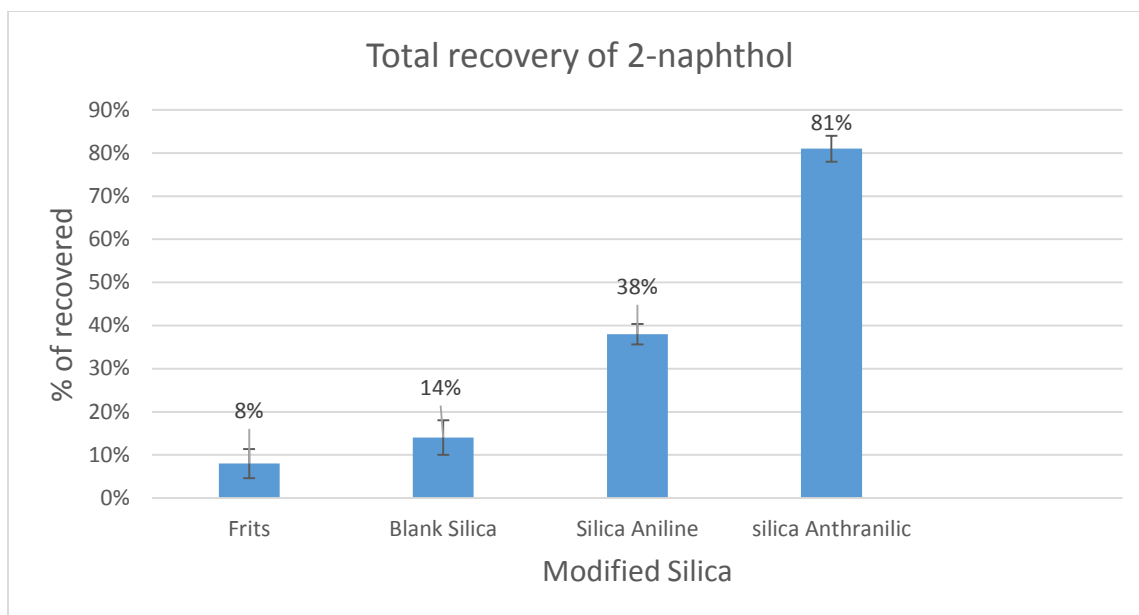


Figure 31. Total recovery of 2-naphthol

After using the same previous procedure, the percentage of 2-naphthol that was recovered from the blank silica, aniline modified silica, and anthranilic acid modified silica was an average of 14%, 38%, 81% respectively as shown in Figure 31.

At pH 10, the 2-naphthol was released easier from the functionalized anthranilic acid silica surface compared to the silica aniline surface. At higher pHs the anthranilic acid's carboxylic acid group becomes the charged carboxylate, changing the surface to hydrophilic, weakening the hydrophobic substance's attraction, and thus resulting in an easier 2-naphthol removal.

4.8 Stability of the functionalized anthranilic acid silica surface

After the 2-naphthol was trapped on the functionalized anthranilic acid silica surface at pH 4 and released at pH 10, functionalized anthranilic acid silica surface was rinsed with methanol and dried. FTIR was used to test the stability of the functionalized anthranilic acid silica. The FTIR spectra of the unused AA modified silica, as shown in Figure 32, and once used AA modified silica as shown in Figure 33, are essentially identical indicating this material can be used at least one time. This materials can be also used two times as shown in Figure 34. However, after using this material several times, the amide AA phase is destroyed from the pH 10 solution as noticed from the disappearance of functional group peaks as seen in Figure 35.

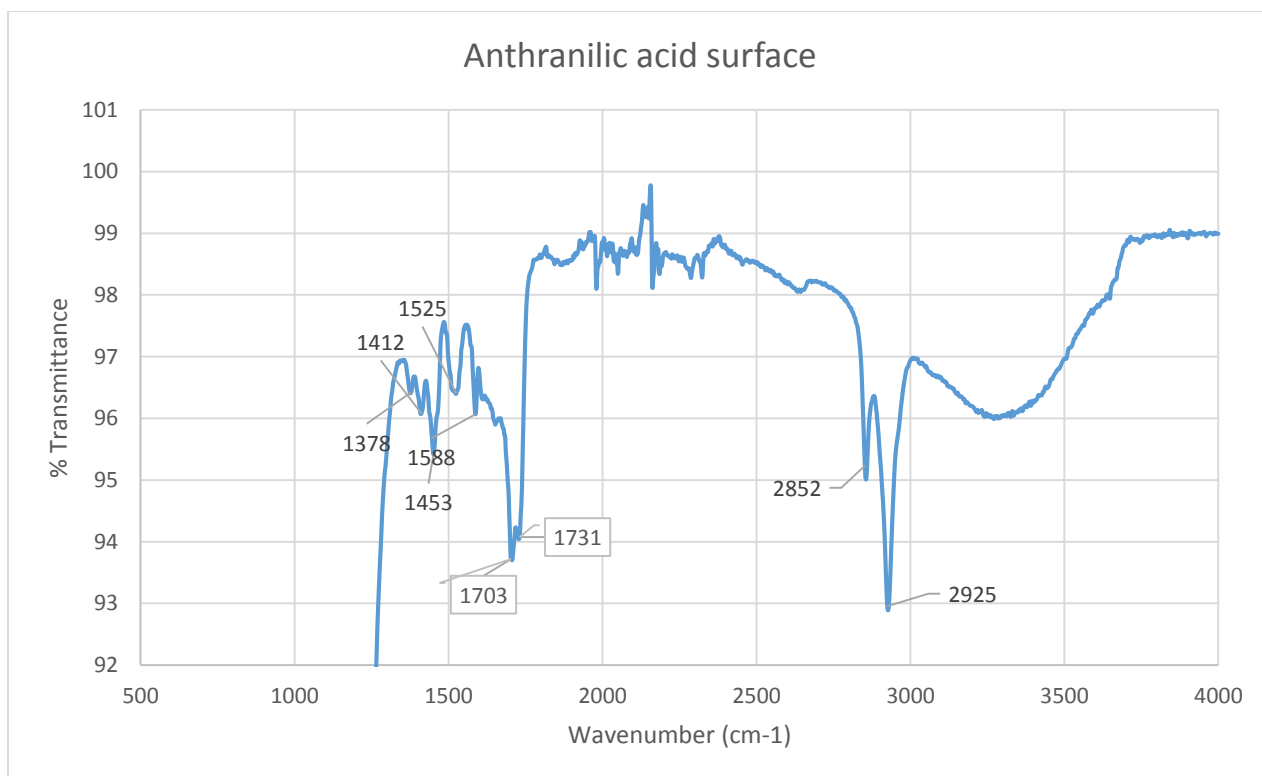


Figure 32. FTIR spectra of the anthranilic acid surface group silica particles

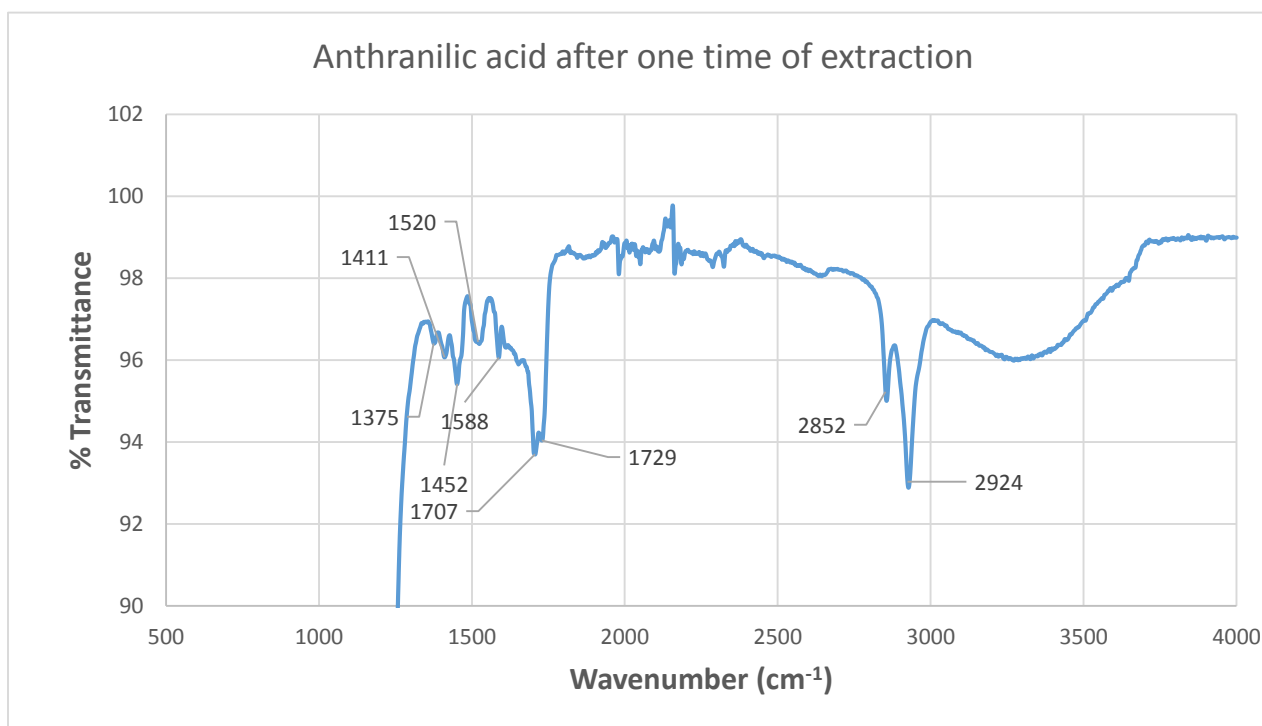


Figure 33. FTIR spectra of the anthranilic acid surface group silica particles after one time of extraction.

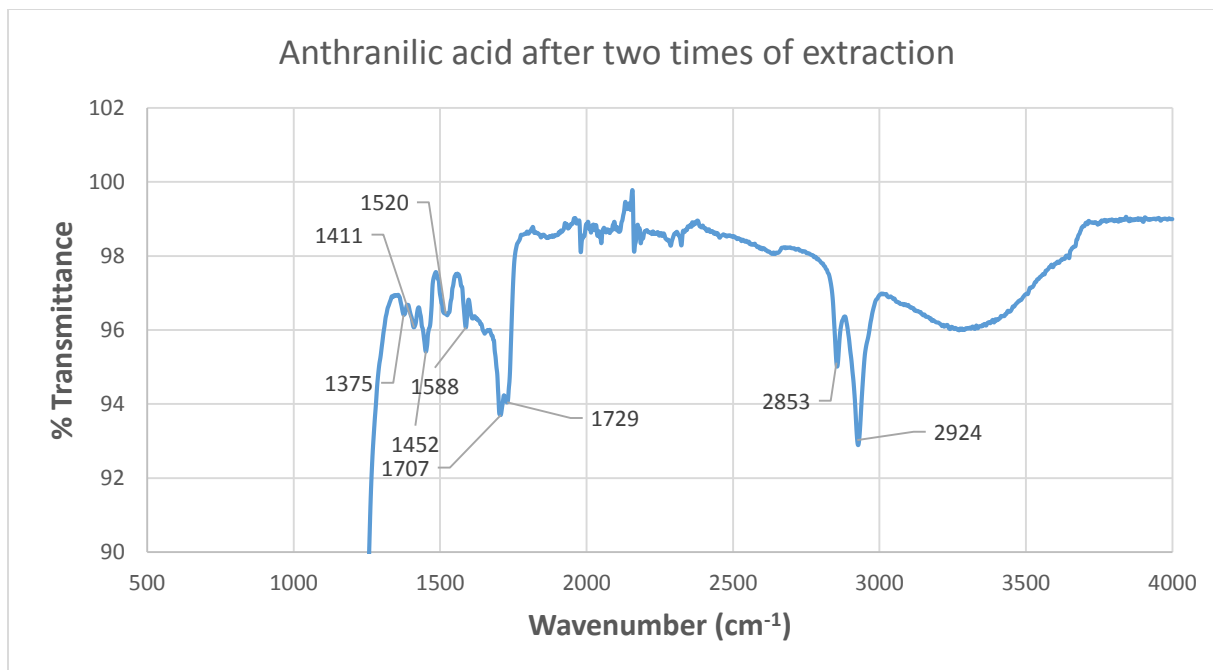


Figure 34. FTIR spectra of the anthranilic acid surface group silica particles after two times of extraction.

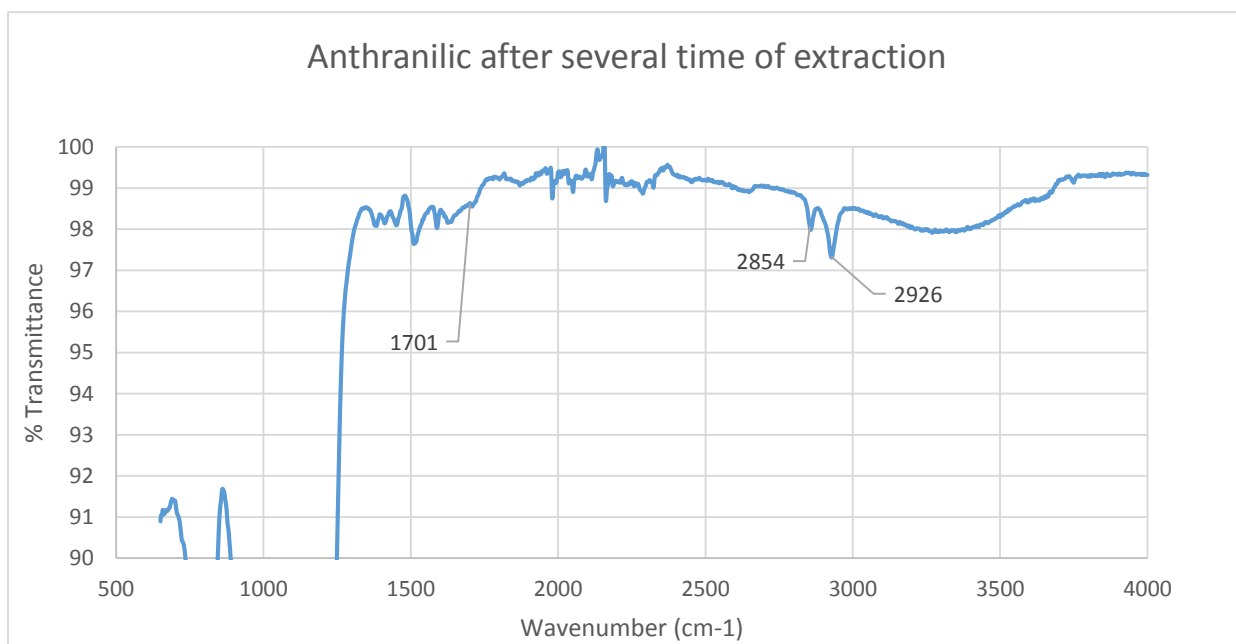


Figure 35. FTIR spectra of the anthranilic acid surface group silica particles after several times of extraction.

Conclusion

In this study, surfaces have been prepared having a terminal anthranilic acid (AA) group on: silica gel particles, microscope slides, and TLC plates. Contact angle measurements, FTIR data, and elemental analysis support the preparation of those surfaces. The contact angle measurements on a surface having a terminal anthranilic acid (AA) group on silica gel particles, and TLC plates are hydrophobic at lower pH and hydrophilic at higher pH. 2-naphthol was used as a hydrophobic molecule and was successfully trapped on the anthranilic acid functionalized silica in its hydrophobic form. 81% of the 2-naphthol that had been trapped was successfully released by rinsing the anthranilic acid functionalized silica with a pH 10 sodium hydroxide solution (in 10 % methanol in water). There was more 2-naphthol released from this now hydrophilic surface compared 38% on an aniline control surface. The result has shown that these materials can be used more than one time; however, it cannot be used several times because the pH 10 solution will destroy the chemically bound surface which is responsible for the switch from hydrophobic surface at lower pH to hydrophilic surface at higher pH.

APPENDIX

Functional group	% of Carbon	% of nitrogen	% of sulfur
Blank	2.03	0.0535	0.027
Vinyl	6.81	0.0295	
Carboxylic acid	10.395	0.0075	2.243
Amide anthranilic	15.17	0.1155	
Amide aniline	15.47	0.1195	

Table 1. CNS Analysis data TLC plate

Functional group	% of Carbon	% of nitrogen	% of sulfur
Blank	1.83	0.004	0.036
Vinyl	6.95	0.0138	
Carboxylic acid	10.34	0.0052	2.382
Amide anthranilic	15.33	0.1184	
Amide aniline	15.67	0.1208	

Table 2. CNS Analysis data silica particles

BIBLIOGRAPHY

- (1) Liu, Y.; Mu, L.; Liu, B.; Kong, J. Controlled Switchable Surface. *Chem. - Eur. J.* **2005**, *11* (9), 2622–2631.
- (2) Bai, D.; Hardwick, C. L.; Berron, B. J.; Jennings, G. K. Kinetics of pH Response for Copolymer Films with Dilute Carboxylate Functionality. *J. Phys. Chem. B* **2007**, *111* (39), 11400–11406.
- (3) Shibuichi, S.; Onda, T.; Satoh, N.; Tsujii, K. Super Water-Repellent Surfaces Resulting from Fractal Structure. *J. Phys. Chem.* **1996**, *100* (50), 19512–19517.
- (4) Sun, T.; Wang, G.; Feng, L.; Liu, B.; Ma, Y.; Jiang, L.; Zhu, D. Reversible Switching between Superhydrophilicity and Superhydrophobicity. *Angew. Chem. Int. Ed.* **2004**, *43* (3), 357–360.
- (5) Atomic World - Lotus effect about:reader?url=http%3A%2F%2Fwww.hk-phy.org%2Fatomic_world%2Flotus%2Flotus02_e.html (accessed Jun 29, 2015).
- (6) Wilson, M. D.; Whitesides, G. M. The Anthranilate Amide of “ Polyethylene Carboxylic Acid” Shows an Exceptionally Large Change with pH in Its Wettability by Water. *J. Am. Chem. Soc.* **1988**, *110* (26), 8718–8719.
- (7) McDonald, P. D.; Bouvier, S.p, E. *Solid Phase Extraction : Applications Guide and Bibliography : A Resource for Sample Preparation Methods Development; Waters Sep-Pak Cartridge Applications Bibliography*; Waters, 1995.
- (8) Ultratrace extraction of persistent organic pollutants about:reader?url=http%3A%2F%2Fwww.sciencedirect.com.libsrv.wku.edu%2Fscience%2Farticle%2Fpii%2FS0165993609001630 (accessed Jun 29, 2015).

- (9) Guide to Protein Purification - Google Books <https://books-google-com.libsrv.wku.edu/books?hl=en&lr=&id=f6Lp4yna4hoC&oi=fnd&pg=PP2&dq=Guide+to+Protein+Purification,+2nd+Edition,+Burgess,+Richard+R.%3B+Deutscher,+Murray+P.%3B+Editors,+Elsevier+Inc.,+2009.&ots=3jITADPjUE&sig=nFmj28N256KAB1cYQUmTGnFKDDo#v=onepage&q&f=false> (accessed Jun 29, 2015).
- (10) Bai, D.; Habersberger, B. M.; Jennings, G. K. pH-Responsive Copolymer Films by Surface-Catalyzed Growth. *J. Am. Chem. Soc.* **2005**, *127* (47), 16486–16493.
- (11) Plastics Surface Energy Wetting Test Methods | Adhesion Bonding
<http://www.adhesionbonding.com/2012/03/19/plastics-surface-energy-wetting-test-methods/> (accessed Jun 29, 2015).
- (12) Roach, P.; Shirtcliffe, N. J.; Newton, M. I. Progress in Superhydrophobic Surface Development. *Soft Matter* **2008**, *4* (2), 224–240.
- (13) RESISTANCE OF SOLID SURFACES TO WETTING BY WATER - Industrial & Engineering Chemistry (ACS Publications)
<http://pubs.acs.org.libsrv.wku.edu/doi/abs/10.1021/ie50320a024> (accessed Jun 29, 2015).
- (14) Marmur, A. The Lotus Effect: Superhydrophobicity and Metastability. *Langmuir* **2004**, *20* (9), 3517–3519.
- (15) Quéré, D.; Lafuma, A.; Bico, J. Slippery and Sticky Microtextured Solids. *Nanotechnology* **2003**, *14* (10), 1109.
- (16) Airiti Library
<http://www.airitilibrary.com/Publication/alDetailedMesh?docid=U0017-2712201410240436> (accessed Jun 29, 2015).

- (17) Akhavan, B.; Jarvis, K.; Majewski, P. Hydrophobic Plasma Polymer Coated Silica Particles for Petroleum Hydrocarbon Removal. *ACS Appl. Mater. Interfaces* **2013**, *5* (17), 8563–8571.
- (18) International Union of Pure and Applied Chemistry
<http://old.iupac.org/publications/books/author/mcnaught.html> (accessed Jun 29, 2015).
- (19) Ganesh, V. A.; Raut, H. K.; Nair, A. S.; Ramakrishna, S. A Review on Self-Cleaning Coatings. *J. Mater. Chem.* **2011**, *21* (41), 16304.
- (20) Surface Roughness and Contact Angle. - The Journal of Physical and Colloid Chemistry (ACS Publications) <http://pubs.acs.org/doi/abs/10.1021/j150474a015> (accessed Jun 29, 2015).
- (21) Xu, L.; Chen, W.; Mulchandani, A.; Yan, Y. Reversible Conversion of Conducting Polymer Films from Superhydrophobic to Superhydrophilic. *Angew. Chem. Int. Ed.* **2005**, *44* (37), 6009–6012.
- (22) UoBLahannetal2003ReverseSwitchingSurface.pdf.
- (23) Shirtcliffe, N. J.; McHale, G.; Newton, M. I.; Perry, C. C.; Roach, P. Porous Materials Show Superhydrophobic to Superhydrophilic Switching. *Chem. Commun.* **2005**, No. 25, 3135.
- (24) Bai, D.; Ibrahim, Z.; Jennings, G. K. pH-Responsive Random Copolymer Films with Amine Side Chains. *J. Phys. Chem. C* **2007**, *111* (1), 461–466.
- (25) Yu, X.; Wang, Z.; Jiang, Y.; Shi, F.; Zhang, X. Reversible pH-Responsive Surface: From Superhydrophobicity to Superhydrophilicity. *Adv. Mater.* **2005**, *17* (10), 1289–1293.

- (26) Xia, F.; Feng, L.; Wang, S.; Sun, T.; Song, W.; Jiang, W.; Jiang, L. Dual-Responsive Surfaces That Switch between Superhydrophilicity and Superhydrophobicity. *Adv. Mater.* **2006**, *18* (4), 432–436.
- (27) Wang, J.; Hu, J.; Wen, Y.; Song, Y.; Jiang, L. Hydrogen-Bonding-Driven Wettability Change of Colloidal Crystal Films: From Superhydrophobicity to Superhydrophilicity. *Chem. Mater.* **2006**, *18* (21), 4984–4986.
- (28) Wang, S.; Liu, H.; Liu, D.; Ma, X.; Fang, X.; Jiang, L. Enthalpy-Driven Three-State Switching of a Superhydrophilic/Superhydrophobic Surface. *Angew. Chem. Int. Ed.* **2007**, *46* (21), 3915–3917.
- (29) Bai, D.; Jennings, G. K. Surface-Catalyzed Growth of Polymethylene-Rich Copolymer Films on Gold. *J. Am. Chem. Soc.* **2005**, *127* (9), 3048–3056.
- (30) Jiang, Y.; Wang, Z.; Xu, H.; Chen, H.; Zhang, X.; Smet, M.; Dehaen, W.; Hirano, Y.; Ozaki, Y. Investigation into pH-Responsive Self-Assembled Monolayers of Acylated Anthranilate-Terminated Alkanethiol on a Gold Surface. *Langmuir* **2006**, *22* (8), 3715–3720.
- (31) Software for ProScope HR & HR2 Digital Microscope Products | ProScope™ <http://www.bodelin.com/proscope/software> (accessed Jul 6, 2015).
- (32) Schirmann, J.-P.; Bourdauducq, P. Hydrazine. *Ullmanns Encycl. Ind. Chem.* **1989**.
- (33) Nosonovsky, M.; Bhushan, B. Roughness Optimization for Biomimetic Superhydrophobic Surfaces. *Microsyst. Technol.* **2005**, *11* (7), 535–549.