

**ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL**

**PREPARATION AND ADSORPTION BEHAVIOUR OF HYDROPHILIC  
ADSORBENTS USING HIGH INTERNAL PHASE EMULSIONS**



**M.Sc. THESIS**

**Bora IŞILGAN**

**Department of Polymer Science and Technology**

**Polymer Science and Technology Programme**

**JUNE 2025**



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**JUNE 2025**



**İSTANBUL TEKNİK ÜNİVERSİTESİ ★ LİSANSÜSTÜ EĞİTİM ENSTİTÜSÜ**

**BOYA ADSORPSİYONU İÇİN YÜKSEK İÇ FAZ EMÜLSİYONLARI İLE  
HİDROFİLİK ADSORBENTLERİN HAZIRLANMASI VE ADSORPSİYON  
ÖZELLİKLERİ**

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*To my dear family,*



## **FOREWORD**

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## **ABBREVIATIONS**

<b>MB</b>	: Methylene Blue
<b>EY</b>	: Eosin Dye
<b>HIPE</b>	: High Internal Phase Emulsion
<b>POPs</b>	: Porous Organic Polymers
<b>SPMA</b>	: 3-Sulfopropyl Methacrylate Potassium Salt
<b>MBAM</b>	: N,N'-Methylenebis(acrylamide)
<b>HLB</b>	: Hydrophilic-lipophilic Balance
<b>APS</b>	: Ammonium Persulfate
<b>TMED</b>	: N,N,N',N'-Tetramethyl Ethylenediamine
<b>METAC</b>	: [2-(Methacryloyloxy)ethyl]trimethylammonium Chloride



## SYMBOLS

$q_e$	: The equilibrium adsorption capacity
$C_e$	: The equilibrium adsorbate concentration
$q_m$	: The maximum adsorption capacity
$K_F, n$	: The Freundlich isotherm constants
$\varepsilon$	: Polanyi Potential
$q_t$	: The amount of adsorbed adsorbate at certain time
$C$	: The diffusion constant
$A_i$	: Water Uptake
$m_D$	: Dry Mass
$m_{sw}$	: Swollen Mass
$k_1, k_2$	: The kinetic rate constants
$K_D$	: The diffusion rate constant
$R^2$	: Coefficient factor
$K_L$	: The Langmuir isotherm constant
$q_{exp}$	: The experimental adsorption capacity
$q_{theoretical}$	: The theoretical adsorption capacity



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## **PREPARATION AND ADSORPTION BEHAVIOUR OF HYDROPHILIC ADSORBENTS USING HIGH INTERNAL PHASE EMULSIONS**

### **SUMMARY**

Water pollution is one of the most major problems for a sustainable life. Especially dyes, which are one of the biggest sources of wastewater, also pollute the environment significantly. The large amounts of dyes produced in industries into water resources causes this problem to arise, for example, about  $7 \times 10^7$  tons of synthetic dyes were produced. At this point, especially textile industries use about 10,000 tons of dyes per year, causing the dye solution to leach into water sources. Another negative impact of wastewater resulting from the dye solution is that discharging as wastewater into aquatic environments poses serious ecotoxicological threats on living organisms. Besides fish, other aquatic organisms such as microalgae are also adversely affected by dye wastes, the consumption of these can cause human health problems such as cramps, fever and hypertension.

Methylene Blue is a cationic dye widely used in various textile fabrics and its chemical structure contains aromatic amines, potentially causing carcinogenic, toxic effects and non-biodegradable can cause a serious threat to human health. In the view of ecological effect, it decreases oxygen solubility, affects the photosynthetic activity of aquatic life, and decreases the diversity inhibits the synthesis of chlorophyll after dye exposure and reduces photosynthetic rate and consequently the photosynthetic activity of aquatic life.

That is why, the removal of methylene blue is essential to the removal of methylene blue is essential to reduce impacts on the environment and living organisms. Adsorption is a suitable method for the removal of dye particles in waste materials. The fact that the structure of the adsorbent has a decisive role on the progress of adsorption makes the synthesis method of adsorbent important. One of the method production of adsorbent is high internal phase emulsion composed of external and internal phase forming 74 % or more of emulsion, which is a versatile technique based on adjusting pore volume, pore size and distribution.

In this thesis, crosslinked highly porous volume polymers were prepared with a high internal phase emulsion method (HIPE). Polymerization of the external aqueous phase composed of monomers with 80% organic internal phase gave a flexible and elastic monolith polyHIPE structure and after extraction of internal phase then powdered. The presence of sulfonic groups in the monomer structure provided no longer need of modification steps and enabled loading of high functionality on pore structures. To evaluate the methylene blue adsorption on based polyhipe adsorbents, a variety of parameters were used to detect its effect on adsorption capacity. As a result of all adsorption experiments, the maximum adsorption capacity of the adsorbent was, found as 1483 mg/g for methylene blue, pseudo second order kinetic and langmuir isotherm were obtained more convenient compared to pseudo first order kinetic and freundlich isotherm.



# BOYA ADSORPSİYONU İÇİN YÜKSEK İÇ FAZ EMÜLSİYONLARI İLE HİDROFİLİK ADSORBENTLERİN HAZIRLANMASI VE ADSORPSİYON ÖZELLİKLERİ

## ÖZET

Günümüzde boyaların kullanım alanları açısından; sanayi boyları, inşaat boyları, otomobil boyları, plastik boyları ve tekstil boyları olmak üzere geniş bir alanı kapsamaktadır. Boyalar temel oluşumları itibariyle genel olarak pigmentler, bağlayıcılar, boyar maddeler ve çözücülerden oluşmaktadır. Bu bağlamda boyların atık olarak çevreye atılması yapısı itibariyle hem çevresel hem de toplumsal problemler ortaya çıkarmaktadır. Özellikle endüstriyel tüketim bakımından değerlendirildiğinde, tekstil sektöründe diğer alanlara kıyasla yüksek miktarlarda boya kullanımı atıksal problemlerin oluşmasında ciddi bir rol oynamaktadır. Oluşan boya atıklarının hem yapısal özellikleri hem de katkı maddeleri sebebiyle çevre üzerinde oluşturdukları olumsuz etkiler sırasıyla şunlardır; su içerisinde bulunan boya pigmentleri güneş ışığının emilmesini ve yansıtılmasını kendisine sağladığı için alglerin fotosentetik aktivitesi azalır ve bu durum besin zincirini olumsuz bir şekilde etkiler. Bu tür boya molekülleri genellikle aromatik yapısı itibariyle, yüksek termal ve foto kararlılık sağlar. Bu durum ise boya moleküllerinin çevrede uzun süre kalmasına yol açabilir. Ayrıca parçalanma ürünleri kanserojen, mutajenik ve toksik yapıda olması biyolojik organizmalar için ciddi bir tehdit oluşturmaktadır.

Tekstil endüstrilerinde yaygın kullanılan bir boya olan metilen mavisinin kimyasal yapısı ve özellikleri aşağıda belirtildiği gibi tanımlanabilir; moleküler ağırlığı 319,85 ve  $\lambda_{max}$  değeri 663 nm olan  $C_{16}H_{18}N_3ClS$  moleküler formülüne sahip aromatik heterosiklik yapıya sahip bir katyonik boyadır. Suda çözünürlüğü çok yüksektir ve bu nedenle oda sıcaklığında suyla kararlı bir çözelti oluşturur. Uluslararası Temel ve Uygulamalı Kimya Birliği'ne (IUPAC) göre kimyasal adı, renk indeksi (CI) 52015 olan [3,7-bis(dimetilamino) fenotiyazin klorür tetra metil tiyonin klorür]dür.

Metilen mavisi, toksik, kanserojen ve biyolojik olarak parçalanmayan bir yapıya sahip olması nedeniyle toksisitesi belirli bir konsantrasyonun üzerinde insan sağlığı üzerinde olumsuz etkilere neden olur. Örneğin, 5 mg/kg'dan fazla dozlarda, MB boyasının monoamin oksitleyici inhibitör özelliklerine sahip olması, su ekosistemlerinde yaşayan faunalar için bir tehdit olmanın yanı sıra, insanda ölümcül serotonin toksisitesine neden olabilir. Bu tür aromatik yapıdaki boyların insan sağlığı üzerinde siyanoz, doku nekrozu, Heinz cisimciği oluşumu, kusma, sarılık, şok, kalp atış hızının artması gibi çeşitli rahatsızlıklara neden olabilir. Ayrıca, MB'nin cilt ile teması, uygunsuz veya işlenmemiş MB yüklü suyun kullanılması sonucu ciltte kızarıklığa ve kaşıntıya ve ayrıca cilt nekrozuna neden olabilir; organ veya dokudaki hücrelerin çoğunun veya tamamının ölümüne neden olan bir durum ortaya çıkarır.

Metiltiyoninyum klorür, genel olarak metilen mavisi olarak adlandırılan bir tuzdur, geniş bir kullanım alanına sahiptir. Özellikle boya sektöründe yaygın olarak kullanılmasının yanı sıra ilaç endüstrisinde de kullanılmaktadır. Örneğin, bu kimyasalın methemoglobinemi tedavisinde kullanılmasının yanı sıra siyanür

zehirlenmesi ve idrar yolu enfeksiyonlarını tedavi etmek için kullanılmıştır. Metilen mavisi, floresan klinik kullanımı gibi tıpta çeşitli amaçlarla kullanılan çok yönlü bir moleküldür. Floresans özelliği sayesinde Metilen Mavisi, cerrahi sırasında daha önce gizlenmiş yapıların görüntülenmesini sağlar. Örneğin , metilen Mavisi paratiroid bezlerinin lokalizasyonunu belirlemek için kullanılmasıyla ilgili çalışma 1971 yılında yapılan raporlamaya dayanmaktadır. Metilen mavisi geleneksel olarak yüksek dozda olarak enjekte edilir ve böylece çıplak gözle büyümüş paratiroid bezlerinin maviiye boyandığı görülebilir. Yüksek dozda insan sağlığını üzerindeki yan etkileri nedeniyle NIR floresan tekniği gibi çeşitli çalışmalar yapılarak daha düşük MB dozları kullanılarak bezlerin tespit edilmesini mümkün kılar. Ayrıca kanser tedavilerinde tümörlerin lokalizasyonunu belirlemek için metilen mavisinin kullanımıyla ilgili çeşitli çalışmalar vardır. Genel olarak metilen mavisinin tıbbi olarak kullanım alanları şu şekilde özetlenebilir; anormal hücrelerin tespitinde kullanılması, sıtma ve tınak mantarı hastalığının tedavisinde ve şok durumunda kan basıncını yükseltmeye yardımcı olması gibi örnekler verilebilir.

Endüstriyel atık sulardan metilen mavisi gibi tekstil boya larını gidermek için çeşitli yöntemler kullanılmaktadır. Bunlara adsorpsiyon/biyosorpsiyon, fitoremediasyon elektrokoagülasyon, sıvı-sıvı ekstraksiyonu, ultrafiltrasyon , nanofiltrasyon, mikrodalga işleme ve biyolojik bozunma yöntemler örnek olarak verilebilir. Termal ve ışık kararlılığı yüksek olması ve biyobozunurluğun düşük olması, metilen mavisi boyasını yaygın yöntemler kullanarak daha küçük inorganik moleküllere parçalamak zordur. Bu arıtma yöntemlerinin her birinin maliyet, uygulanabilirlik ve çevresel etki açısından pozitif ve negatif yönleri vardır. Örneğin, yarı iletken nanopartiküller kullanılarak organik moleküllerin çok bileşenli fotokatalizi, sentetik boyalar gibi tehlikeli kirleticiler içeren atık su arıtımı için uygun maliyetli, herhangi bir tehlikeli yan ürün açığa çıkarmaması açısından da çevre dostu olması nedeniyle artan bir ilgi görmektedir.

Metilen mavisi görünür ışık ışınlaması altında kararlı olması nedeniyle, sadece fotoliz veya katalizle tek başına verimli bir şekilde parçalanamaz. MB boyasının yaklaşık %8' sı 10 saatlik ışınlama süresinden sonra fotoliz yoluyla giderildiği ve ışığa maruz bırakmadan sadece katalizör varlığında 24 saat sonra metilen mavisi'nin yapısal olarak sadece %10'luk bir kısmının parçalanmaya uğradığı bildirilmiştir. Ayrıca, katalizör olmadan görünür ışık altında ayrışma meydana gelmediği de gözlemlenmiştir. Benzer şekilde, herhangi bir katalizör kullanılmadan karanlıkta ve güneş ışığı altında asidik ve nötr ortamda hiçbir bozulma gözlemlenmemiştir. Bu çalışmalar göstermiştir ki metilen mavisinin atık sulardan uzaklaştırılmasında fotodegradasyon yönteminin kullanımı diğer yöntemlere kıyasla ihmal edilebilir.

Atık sularda bulunan boya ların çevreden uzaklaştırılması için biyolojik yöntemler (enzimlerin ve mikroorganizmaların kullanımı), kimyasal yöntemler (gelişmiş oksidasyon süreçlerinin kullanımı) ve fizikokimyasal yöntemler (çoğunlukla adsorpsiyon) dahil olmak üzere farklı arıtma yöntemleri şekilde özetlenebilir. Bu yöntemler arasında adsorpsiyon uygulanabilirliği ve sürdürülebilirliği açısından daha yaygın bir kullanım yöntemidir. Atık sularda boya ların uzaklaştırılması ile ilgili yapılan adsorpsiyon çalışmalarında buz kabuğu, gübre, biyokömür , palmye yağı atıklarından elde edilen aktif karbonlar, muz kabuğu atığı , zeolit , ve aktif karbon , adsorban olarak kullanılmıştır. Metilen mavisi gibi sentetik boya ların giderimi için adsorpsiyon teknolojisinde katı sorbentlerin kullanımı söz konusudur. Bu yöntem, boya ların atık sulardan uzaklaştırılması için yaygın ve etkili bir şekilde kullanılmaktadır. Sulu çözeltilerden boya konsantrasyonlarını azaltmak için araştırılmış ve başarıyla uygulanmış birçok adsorban vardır.

İyi tanımlanmış gözenekliliklere ve yüksek yüzey alanlarına sahip polimerler, ayırma membranları, doku mühendisliğinde yapısal şablon, katalizör ve adsorbent olarak çok çeşitli uygulamalarda kullanılmaktadır. Yüksek iç fazlı emülsiyonlar gözenekli bir şablon oluşturması sayesinde yukarıda açıklanan özelliklere sahip polimerler elde edilebilir. Yüksek iç faz emülsiyon yöntemi, iç fazın %74 veya daha fazla olduğu bir şablon yöntemidir. Bu tür malzemelere kullanılan yöntem temelinde poliHIPE kısaltması kullanılır. Bu yöntemin genel tanımı şu şekilde yapılabilir; emülsiyon sistemine göre organik fazda ya da su fazında bulunan monomerlerin polimerleştirilmesi ve daha sonra damlacık içerisinde bulunan iç fazın uzaklaştırılması sonucu oluşan mikrometre boyutlarında yüksek gözenekliliğe sahip bir polimerik şablon elde edilir. Bu malzemede aynı zamanda, büyük gözeneklerin birbirlerine bağlantısını, iletimini sağlayan ve genellikle pencere olarak adlandırılan daha küçük gözeneklere de sahiptir. Bu yapıda olan poliHIPE malzemeler açık gözenekli morfolojiye sahiptirler. Bu tür gözeneklerin özellikle kütle transfer sürecinde önemli bir fonksiyona sahiptir. Örneğin bu tür düşük yoğunluklu yüksek oranda gözenekliliklere sahip polimerlerin hem organik reaksiyonlarda katalizör olarak hem de adsorpsiyon sürecinde adsorbent olarak kullanılması şu şekilde açıklanabilir; porları birbirine bağlayan pencere olarak adlandırılan küçük gözeneklerin reaktan veya adsorbatın polimer içerisindeki aktif bölgelere ulaşmasını sağlar.

Bu çalışmada düşük oranda çapraz bağlanma derecesine ve hidrofilik yapıya sahip yüksek oranda gözenekli polimerik malzeme yüksek iç faz emülsiyon yöntemi ile hazırlanmıştır. Su fazında bulunan monomerlerin polimerleşmesi sonucu elastik bir monolit yapıda poliHIPE elde edilmiş ve daha sonraki aşamada Soxhlet ekstraktörü kullanılarak %80'lik organik iç faz, reaksiyona girmemiş monomerler ve surfaktant uzaklaştırılmıştır. En son aşamada ise boya adsorpsiyonu deneyinde kullanılmak üzere toz haline getirilmiştir. Monomer yapısındaki sülfonik grupların varlığı, modifikasyon işlemine ihtiyaç kalmamasını ve gözenek yapılarına yüksek oranda fonksiyonel grup yüklenmesini sağlamıştır. Yapıdaki sülfonik grupların varlığı sayesinde katyonik bir boya olan metilen mavisi için uygun bir adsorbent olarak belirlenmiştir.

Bu tezde, metilen mavisi boyasının yüksek gözenek hacmine sahip adsorban tarafından adsorpsiyonu değerlendirilmiştir. Bu amaçla sıcaklık, pH, iyon etkisi, sıcaklık, gibi çeşitli parametrelerin adsorpsiyon kapasitesinin değişimi üzerindeki etkisini belirlemek ve su tutma kapasitesini ölçmek için çeşitli deneysel yöntemler uygulanmıştır. Elde edilen tüm deneysel veriler ele alındığında, adsorbanın maksimum adsorpsiyon kapasitesi metilen mavisi için 1483 mg/g olarak bulunmuş, pseudo ikinci derece kinetik ve langmuir izotermi, pseudo birinci derece kinetik ve freundlich izotermine kıyasla deneysel verilerle daha uygun olduğu gözlemlenmiştir.



## 1. INTRODUCTION

From the last approximately twenty years to today, the regarding problems resulting from environmental pollution e.g., textile industrial effluent have increasingly taken more serious and and troubled. As a given example of this situation, the only textile industry is known to consume 700,000 to 800,000 tons of dye which almost %15 of that could be reused [43, 44]. These large amount of effluents including organic dyes like azo-dye composed of above % 60 among textile of dye are able to impact on human bodies e.g., azo dyes are turned into toxic amino acid by intestinal microflora gusted in the human gut, which diverse tissues are affected in a negative way.

Of the synthetic dyes, methylene blue is widely used in a great many of application such as colorant for papers, cosmetics and interestingly healthcare industry e.g., it is able to be utilized in malaria treatment, heparin treatment as well as the treatment of vasoplegia .Which methylene blue are used up large scales in diverse sectors, however, are required to make necessary treatment processes. This clear reality encourages researchers to investigate the elimination of MB in the wastewater. Hence, there are lots of academic studies about removing MB by using a variety of processes regarding as adsorbent of natural and polymeric materials through porous structure. For the sake of example related to natural adsorbent, the seeds of *Foeniculum vulgare* modified with oxalic acid exhibited high adsorption capacity i.e., maximum value 892.857 mg/g against MB [3].

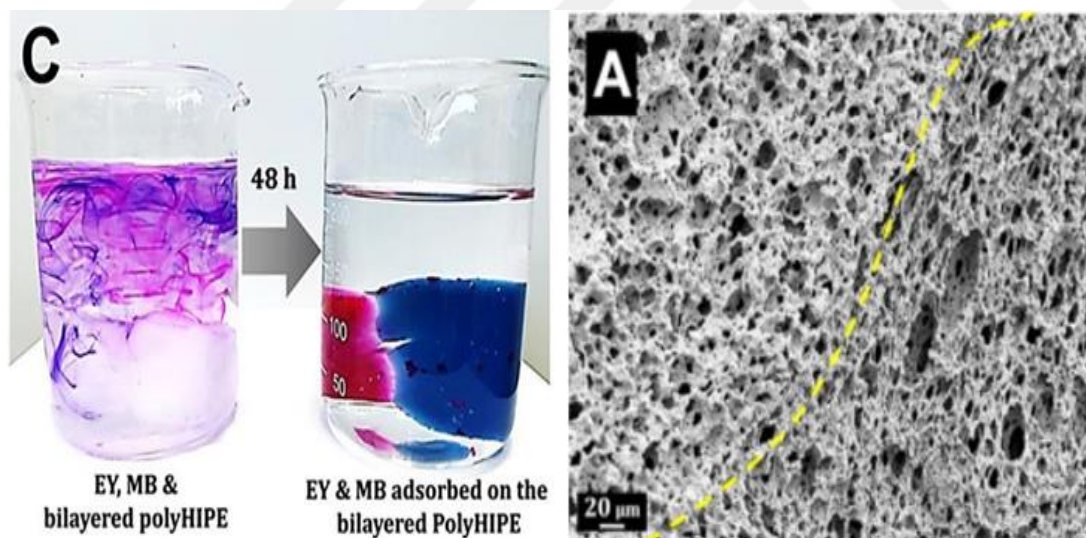
PolyHIPE's composed of at least %74 internal phases, are well-known polymeric monoliths, are generally used as gas storage, heterogeneous catalysts and adsorbents. Thanks to porous structure containing voids and windows, the mass diffusion process makes an enlightening and intriguing polyhipe. Hydrophilic polyHIPE's also impart enhanced adsorption capacity, which incorporates the phenomena of adsorption and absorption so-called 'sorption systems'.

The results of adsorption experiments promise that this material is good candidate for elimination of the methylene blue from aqueous solution.

## 1.1 Literature Review

In this part, a number of academic researches concerning to dye adsorption by means of emulsion templating method based on oil in water emulsion, are summarized to provide preliminary information as follows;

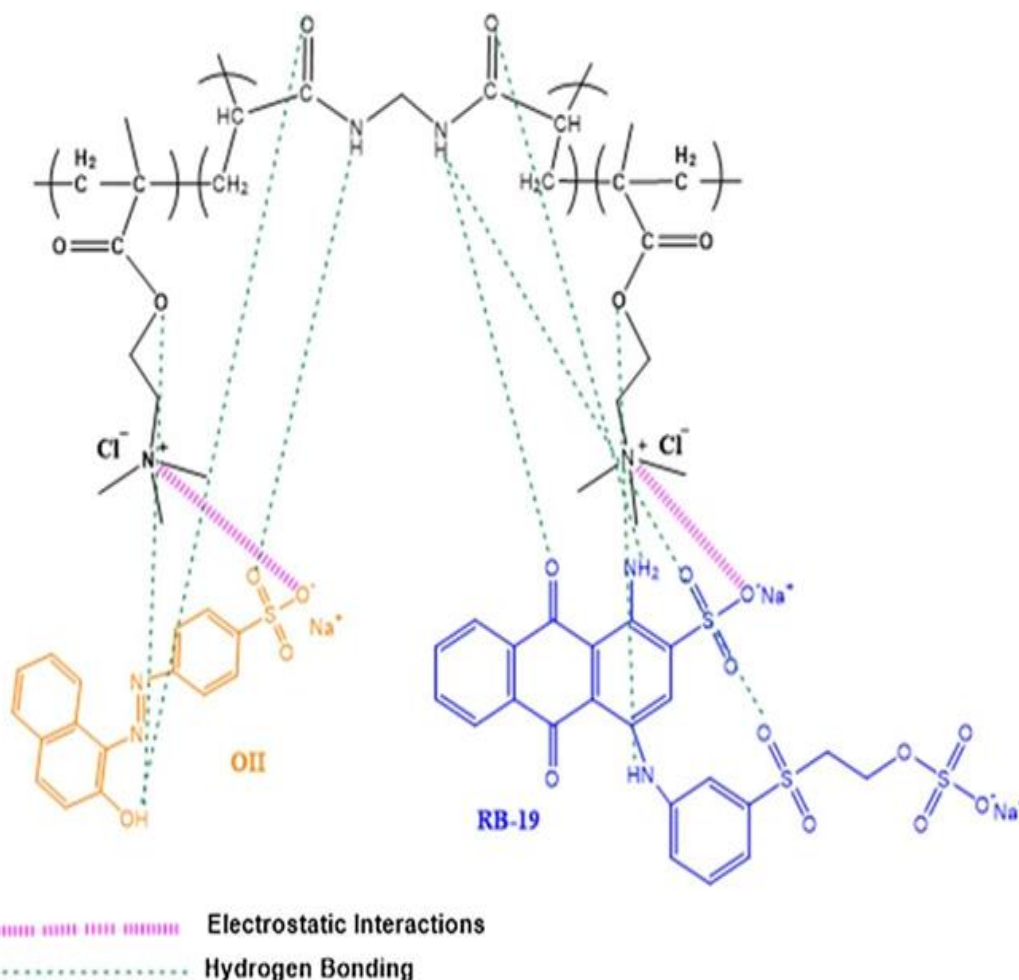
Kovacic and coworkers have made use of amphoteric polyelectrolyte bearing both the anionic and cationic groups to realize the adsorption of two different dyes at the same time. For doing this study, three distinct methods consisting of the copolymerization with cationic and anionic monomers, bilayered-polyHIPE synthesis that cationic HIPE was transferred into the mold and then anionic HIPE was added into the same mold and the last method related to the mixture of two HIPE in the same mold was used. The best result for dye adsorption was obtained with bilayered-polyHIPE due to minimizing anti-polyelectrolyte effect compared to other two techniques. As can be visualized in Figure 1.1, the bilayered-amphoteric polyelectrolyte polyHIPE was used for the adsorption of a mixture of cationic (Methylene Blue) and anionic (Eosin) [37].



**Figure 1. 1 :** Adsorption of MB and EY by the bilayered polyHIPE and their SEM.

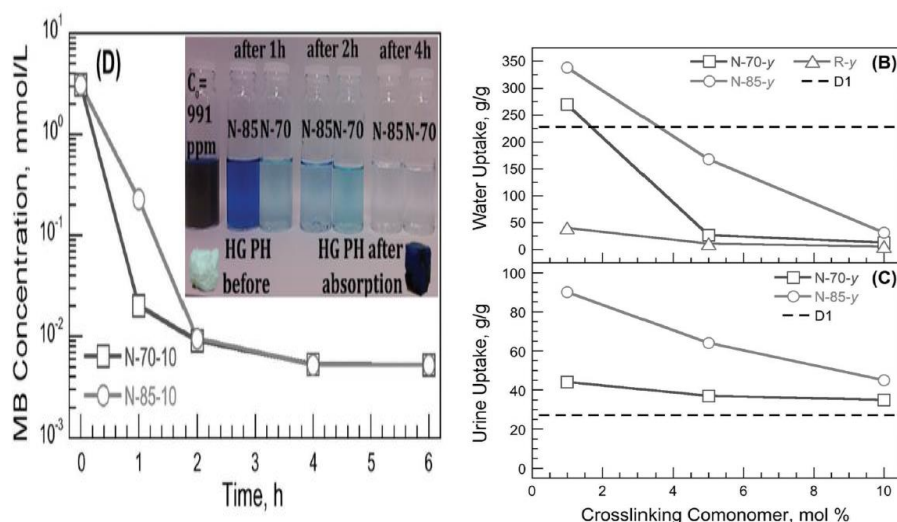
Another study for dye adsorption realized with ammonium based polymers was made by Deimede and co-workers. Ammonium based monoliths produced with oil-in water emulsion were prepared with both %10 and %15 crosslinker ratio. The resulting polyHIPE was assessed for both the adsorption of anionic dyes solution. In Figure 1.2, maximum amount of Orange II adsorbed was reached to 1649 mg/g and adsorbent has

held 1752 mg/g amount of Reactive Blue 19 dye as well. In terms of water uptake, monoliths with %10 and %15 cross-linker captured 18 g and 9,5 g, respectively [36].



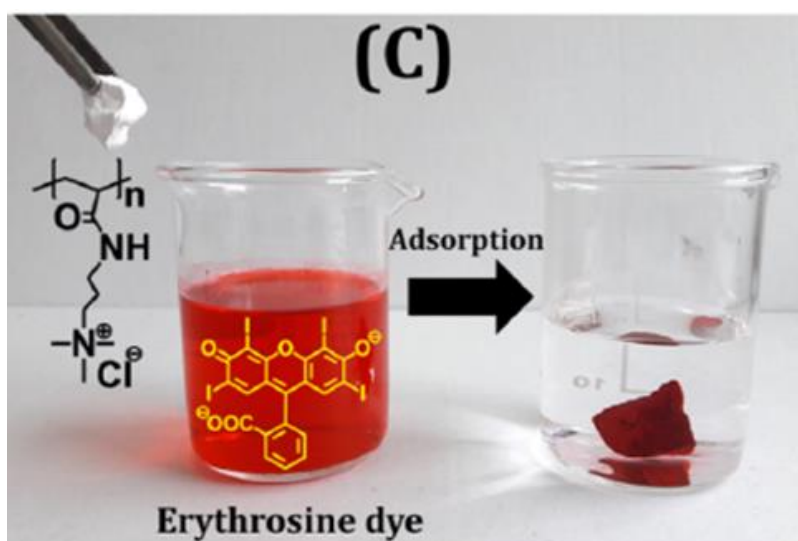
**Figure 1. 2 :** The schematic representation of chemical structure of polyHIPE [36].

Silvestein and kovacic have designed superabsorbent hydrogel polyHIPE for using the emulsion templating. The monolith was prepared based on two parameters, the organic phase ratio adjusted with %70 and %85 and the crosslinking degree ranging from %1 to %10. In Figure 1.3, when the degree of crosslinking was approximately %1, the monolith made from %70 and %85 volume ratio of internal phase, both holds 275 g and 345 g water and 45 g and 90 g artificial urine. Obtained monoliths were evaluated for adsorption performance on methylene blue as well [34].



**Figure 1. 3 :** Change in MB ppm with time and water and artificial urine uptake.

Kovacic and coworkers used cationic monomers for designing the oil-in water high internal phase emulsion. In this study, the N-quaternized functional groups found the polyHIPE structure interact with erythrosine dye including the anionic functional groups, which this interaction is the indicator of chemical adsorption. The photograph in Figure 1.4 proves the strong interaction between the adsorbent and the adsorbate. The resulting polyHIPE possessed swelling properties, i.e., %5 and 10 crosslinking material capturing 95g/g and 50g/g, respectively. The erythrosine dye adsorption takes place between quaternized amine of adsorbent and sodium salt of both carboxylic acid and alkoxy group [35].

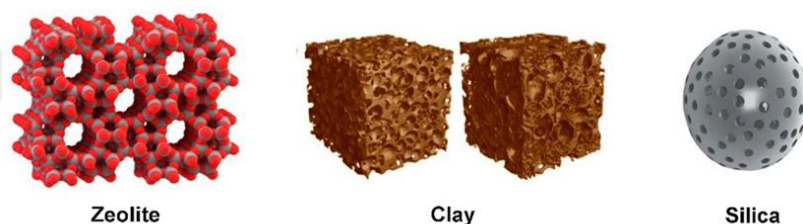


**Figure 1. 4 :** Adsorption behavior of poly(HIPE) toward erythrosine dye [35].

## 2. THEORETICAL PART

### 2.1 Porous Materials

The reason why Porous materials are appealing for scientific studies are ascribed to porosity which is dependent on the number of pores. It can be fundamentally defined as the combination of two different phases in a single structure. Wherein one of them is skeletal portion called as matrix, another fraction composed of liquid or gas phase is pores or voids. As well as various natural porous materials like zeolites, clay and silica shown representatively in Figure 2.1, it can be synthesised by using different methods, provided the size and number of pores to be adjusted.

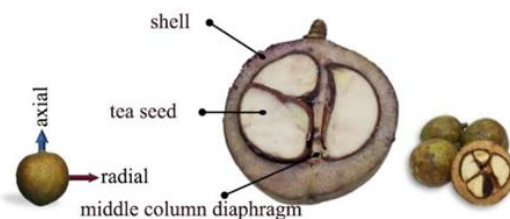


**Figure 2. 1 :** Natural porous substances.

#### 2.1.1 Natural porous materials

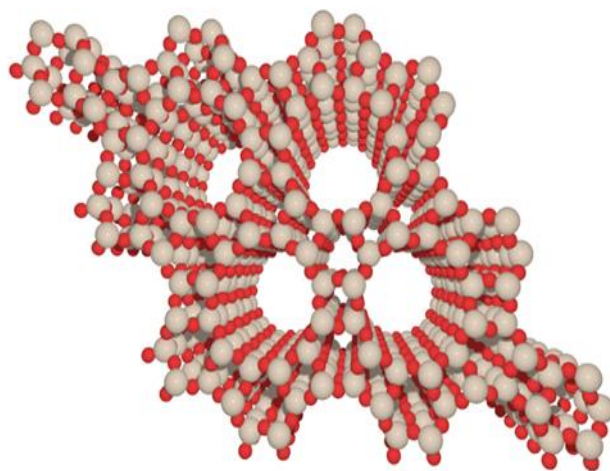
Activated Carbon is a very practical material for adsorption processes of any heavy metals and used to redimination of wastewater. Besides adsorption applications, it is able to be used as a catalyst as well. What reasons the use of activated carbon offers advantageous use of wide-range application is related to possessing pore structure, large surface area and low-cost.

As an example of adsorption study for the use of activated carbon, methylene blue adsorbed on the activated carbon, with the very high surface area '1530,36 mg<sup>2</sup>/g', obtained from tea seed shells was found adsorption capacity to reach 324,7 mg/g[32]. (Figure 2.2)



**Figure 2. 2 :** Tea seed shells [32].

Zeolites generally found in volcanic and sedimentary rocks are the microporous of aluminium silicate with the three-dimensional tetrahedral framework. Thanks to molecular adsorption, it is used in commercial applications such as separation of hydrocarbons, drying of gases and liquids.



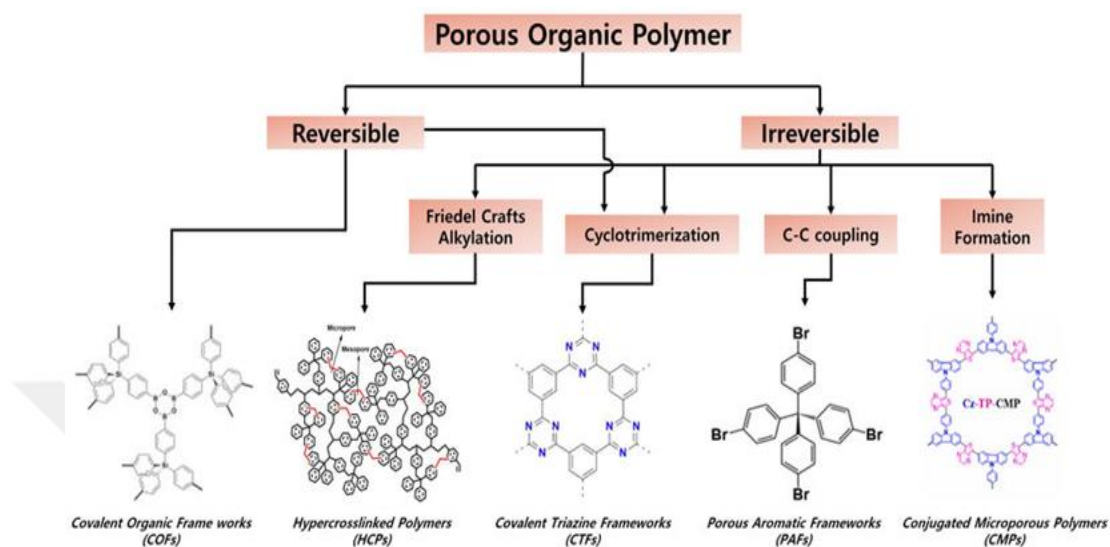
**Figure 2. 3 :** Zeolite representative AFI.

Possessing cage-like structure represented in Figure 2.3 through the network of interconnected tetrahedra, Zeolites can be used in exchange of ions e.g, sodium-containing zeolites trapping calcium and magnesium which of those are involved in hard water release sodium ions to water, so called ‘the softening water process’.

### **2.1.2 Porous organic polymer**

Porous organic polymers are a class of multidimensional porous materials that are mainly composed of three elements, i. e., C, H and O. Due to their inherent porosity, high stability, and designable structure, POPs have enabled their great potential in gas storage/separation, multiphase catalysis, and adsorption. These porosity of POPs can provide channels for the adsorption, transport and release of substances, allowing POPs to be made in membrane separation and solid adsorption useful.

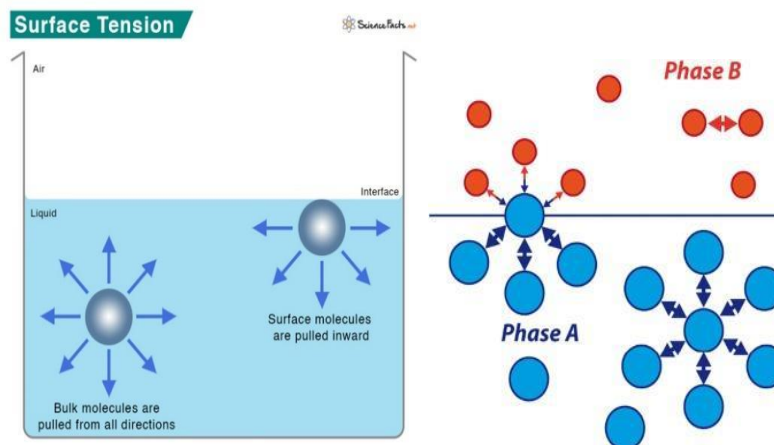
The classification of POPs can generally consist into six types, i. e., covalent triazine frameworks, hypercrosslinked polymers, covalent organic frameworks, polymers of intrinsic microporosity, porous aromatic frameworks and conjugated microporous polymers [33]. (Figure 2.4)



**Figure 2. 4 :** Types of porous organic polymer frameworks [33].

## 2.2 Surface and Interfacial Tension

Surface tension is explained that all molecules in contact with the surface want to make their most stable forms due to idiosyncratic attractive and driving forces, which leading to why the surface tension takes places is associated with attractive forces among the liquid molecules stronger than air molecules [52]. If the air molecules are replaced with liquid, interfacial tension occurs. The summary of this definition is represented with Figure 2.5.

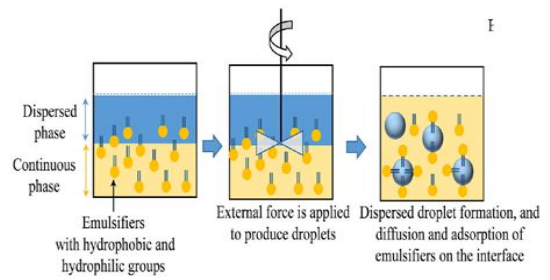


**Figure 2. 5 :** Illustration of surface and interfacial tension [52].

## 2.2.1 Emulsion

Emulsion can be defined as consisting of colloidal dispersion of two immiscible liquids. There are two different phases dispersing each other i.e, corresponding to dispersed phase and continuous phase.

Lots of parameters affect the formation of emulsion and its keeping stable. The most important of them is surfactant, the most crucial point for forming emulsion, with hydrophobic and hydrophilic groups being utilized to reduce interfacial tension. When looked at the Figure 2.6, it is clearly seen how surfactant stabilize the emulsion system.

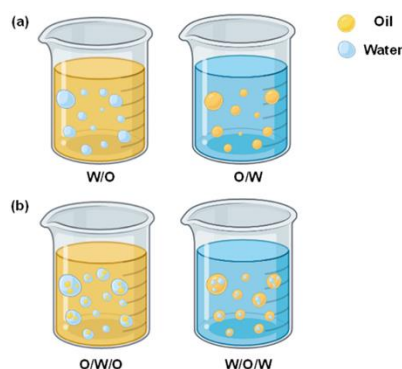


**Figure 2. 6 :** Formation of dispersed droplets in the presence of emulsifiers [23].

### 2.2.1.1 Types of emulsions

Types of emulsion are classified into simple and complex types. Simple emulsions include oil in water or water in oil. When water is the dispersed phase and oil is the continuous phase, the emulsion is termed water-in-oil. Inversely, if oil is dispersed in water, it is called oil-in-water.

Complex emulsions are related to multiple emulsions, known as double emulsions that include both oil-in-water emulsion and inverse emulsion, generally stabilized by surfactants. (Figure 2.7)



**Figure 2. 7 :** Illustration of simple (a) and (b) multiple emulsion systems [41].

### 2.2.1.2 Stability of emulsion system

Emulsions are thermodynamically unstable systems and thus it can be easily separated into layers of oil and water, which means that interfacial tensions have significant effects on stability. Several phenomena such as flocculation, coalescence, sedimentation, Ostwald ripening, creaming and phase inversion are resulted from destabilization of emulsions.

**Coalescence;** Since the emulsifier film among the droplets are broken to a certain extent, the formed smaller droplets merge to form larger droplets. The weaker interfacial film found around two droplets, the higher probability of the happening of coalescence.

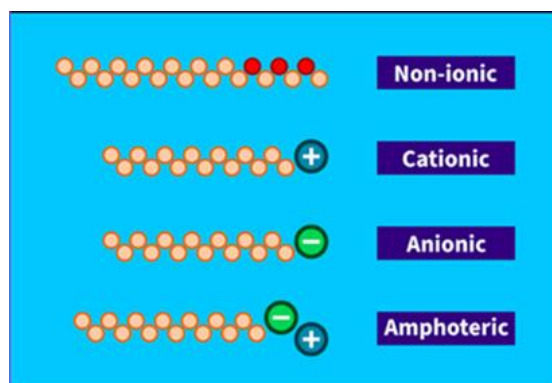
**Creaming;** Due to the droplet with lighter density , it prones to migrate at top of the container, called upward creaming.

**Sedimentation or downward creaming;** Tending to move the bottom of the container, dispersed phase has higher density than continuous phases.

**Flocculation;** It is defined as the aggregation of droplets sticking together. The occurrence of flocculation is based on the interaction of attractive and repulsive forces among droplets.

**Phase inversion:** It occurs due to the change of emulsifier affinity ascribed to the altering volume ratio. In other words, water in oil emulsion can be converted to oil in water.

The choice of the surfactants which is significant for stabilizing the emulsion are critical issues. Generally speaking, there are four types of surfactants represented with Figure 2.8 listed as non-ionic, cationic ,anionic and amphoteric structures.



**Figure 2. 8 :** Schematic representation of four different surfactant types.

Anionic surfactants bearing the negative charge capable of removing dirty laundry can be involved in laundry detergent, shampoo and body soap. The molecular structures of this surfactant include sulfonates, sulfates, or carboxylates salts [50, 51].

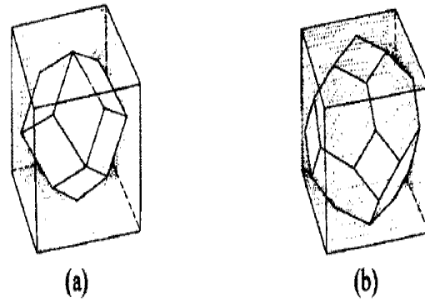
Cationic surfactants positively charged are derived from nitrogen compounds. That they have anti-bacterial and sanitizing properties enable them to get used as disinfectant applications. An example of this type of surfactant is Didecyltrimethylammonium methyl sulfate [50].

Non-ionic surfactants carrying no ions are produced from molecules constituted oxygen-rich components sited at one end and a large molecule accommodated other end sites. The high electron density of oxygen gives partial negative charges, imparting hydrogen bonding with water. Alcohol ethoxylates, nonylphenoxy polyethyleneoxy alcohols, and ethylene oxide/propylene oxide block copolymers are examples of non-ionic surfactants [50].

Amphoteric surfactants refer to surfactants that have the ability to bear both positive and negative charges. They can form two charges based on pH changes. The cationic groups of the surfactants are made of quaternary ammonium groups while phosphate, carboxylate and sulfonate groups comprise the anionic moieties of surfactant. Since they possess two ionizable groups, there can be two or three ionizable stages, e.g; sites where two charges can quench specific pH value bestow to isoelectric point. Such surfactants with properties like compatibility with other surfactants, antibacterial, excellent resistance to hard water and low toxicity found many applications suitable [49, 50].

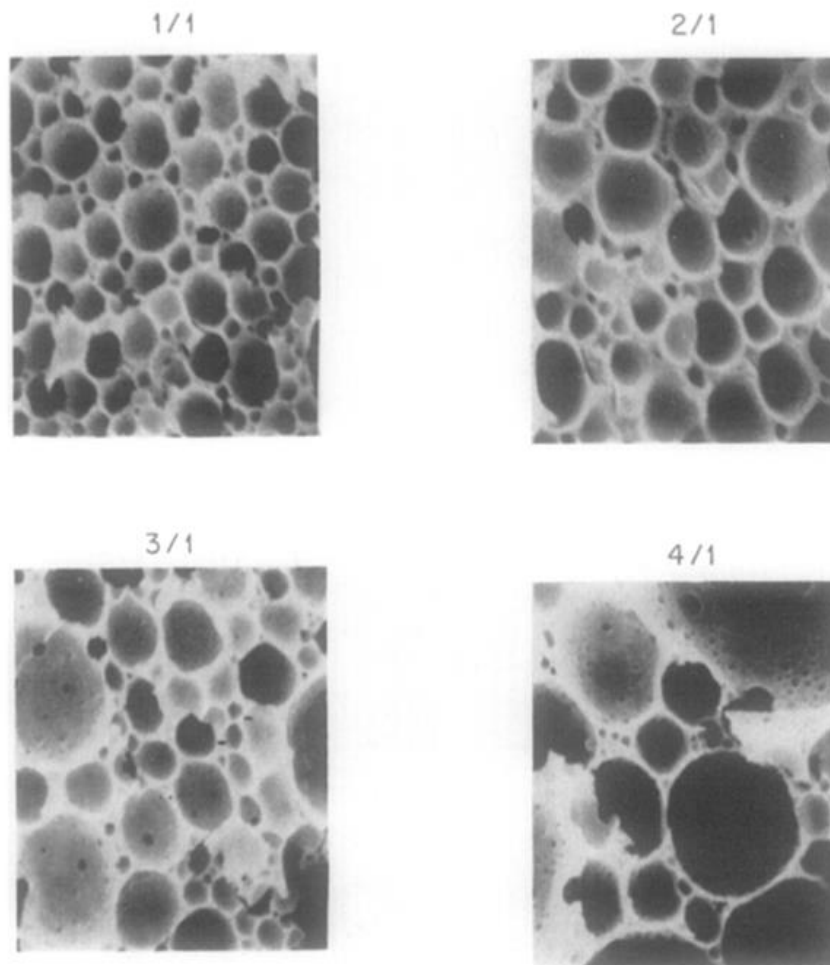
### **2.3 High Internal Phase Emulsion**

High internal phase emulsions are defined as an internal phase volume of at least 74% of the total emulsion and these HIPEs are highly viscous, paste-like properties. If the internal phase volume exceeds 74%, it affects the droplet shape. The dispersed phase droplets composed from 74% to 94% internal phase volume can be assumed a rhomboidal dodecahedron with increasing deformation into polyhedra and above 94%, the packing changes to tetrakaidecahedron [16], which their their representative structures are shown Figure 2.9.



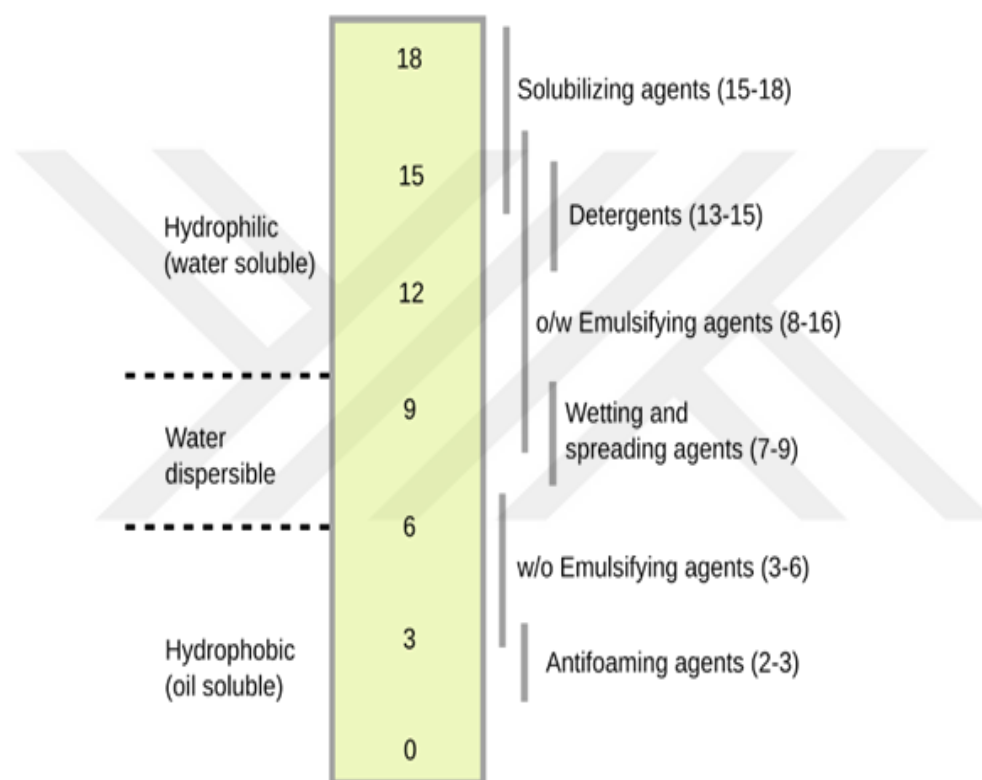
**Figure 2.9 :** Rhomboidal dodecahedron (a) and tetrakaidecahedron (b).

Lissant and Mayhan made a study regarding the effect of water addition on shape geometry of droplets. As clearly shown in Figure 2.10, as increased internal phases, the crowding of the droplets results in polyhedral shapes [19]. The 1/1, 2/1, 3/1, and 4/1 ratios correspond to samples contained 50, 66.6, 75, and 80 % water by volume.



**Figure 2.10 :** Representative micrograph of the 1/1, 2/1, 3/1, and 4/1 fractions.

Another important parameter is surfactant which, generally, diffuses to the interfacial region for supporting the droplet formation and used to be based on hydrophilic-lyophilic balances. The HLB is considered a scale of 0–20 and these values are calculated with the hydrophilic and lipophilic components of surfactant. When surfactants with HLB values of 6–18 are used for formulating oil in water emulsions, 3–6 HLB valued surfactants are used when w/o emulsions are desired, which HLB table are summarized in Figure 2.11 [14].

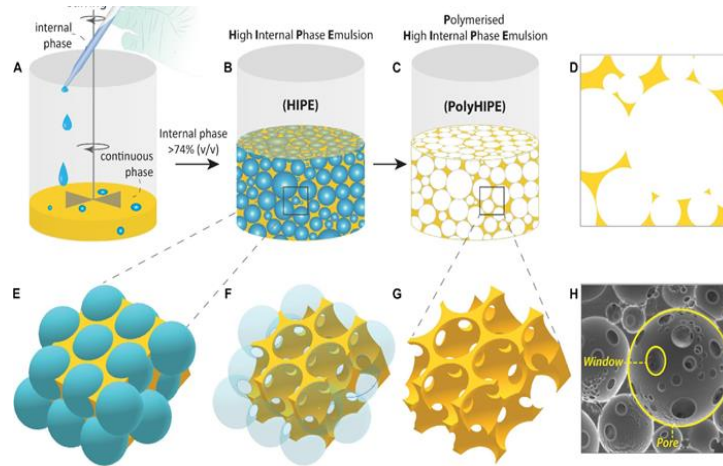


**Figure 2. 11 :** HLB scale representing classification of surfactant types.

## 2.4 The Formation of PolyHIPE

HIPEs are composed of the presence of two immiscible liquids consisting from the continuous and discontinuous phases, corresponding to external and internal phases, respectively. Continuous phase possesses monomers, crosslinker, surfactant and discontinuous phases have liquids. Internal phases are added into continuous phases at constant stirring. After addition of internal phase, resultant emulsion is poured to a plastic container and polymerized with temperature or at a convection oven. In the

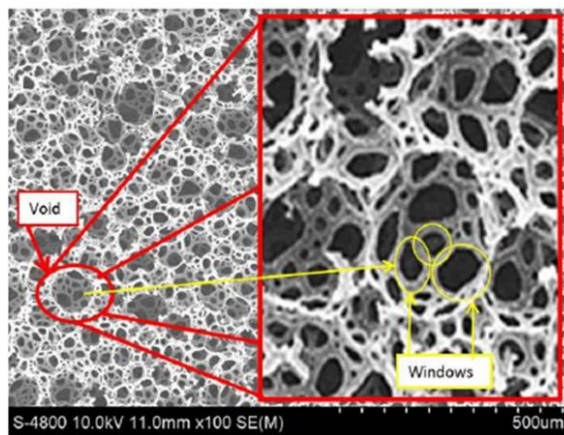
final stage, the resultant polyHIPE is extracted with solvent for removing internal phase. The summarization of polyHIPE formation is illustrated in Figure 2.12 [21].



**Figure 2. 12 :** The preparation of Polymerized High Internal Phase Emulsion.

### 2.4.1 The structure of polyHIPE

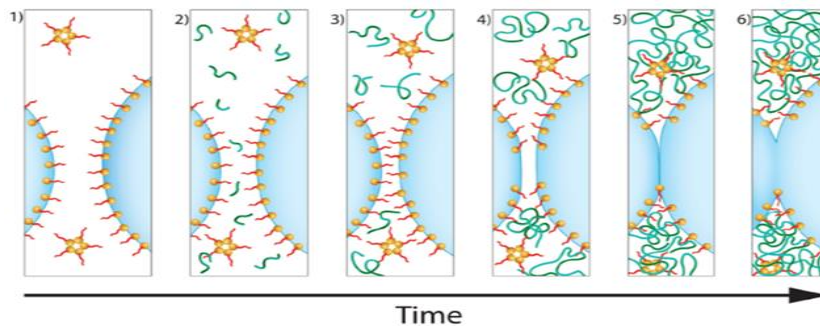
By overviewing the structure of polyHIPE, there are two distinguishing points, the occurrence of pore and window. It is fundamentally explained that as seen in the cavity and window in Figure 2.13, cavities are resulted from removing internal phase, while interconnectivity among pores are associated with the number of windows [42].



**Figure 2. 13 :** SEM micrograph of voids and windows

When evaluated the polyHIPE structure, it is clearly seen that highly porous and interconnected morphology, provides the large void size, which results in moderate low surface area [34], however, values of up to  $700 \text{ m}^2 \text{ g}^{-1}$  can be achieved by means of hyper crosslinking which is method for increasing the surface area or using the porogenic solvent.

Generally, when the polymerization of monomers proceeds in the thermal condition, monomers sited between droplets diffuse or migrate enable them to form flattened areas, which is the case shown in Figure 2.14 how interdroplet structure is obtained [22].



**Figure 2. 14 :** The schematic representation of the pore throat (window) formation.

#### 2.4.2 The effects of some parameters on polyHIPE morphology

Lots of parameters affect emulsion forming, stability and such effects on porosity size and pore distribution. It is elucidated as follow listed;

- The rate of mixture is determinant to achieve how polydispersities are reduced and pore size distribution are uniform. The more rapidly emulsions are mixed, the more unique droplets are attained.
- In the formation of polyHIPE, thermal polymerization is commonly used but the stability of emulsion is sensitive to separated phases.
- While the amount of the surfactants provide emulsion with forming more stability, it leads to take place a great number of window or pore through, reduced mechanical strength. Which in this case is crucial for hydrogel-based polyHIPE because this type of structures have both low crosslink density and acrylate monomer that when polymering, the chains of polymer are getting narrower than styrene or discrete monomer with planar shapes.
- Also, the type of the monomeric structure impacting on the rigidity of structures enables the well-defined locus of pores, is a surprising and intriguing event.
- Another attractive situation is that the location of surfactant might completely alter the texture of polyHIPE. Mostly, if the initiator is found in the internal phase, closed cells are acquired. The other situation is vice versa.

## 2.5 Hydrophilic PolyHIPE's

Hydrophilic polyhipe is based on water soluble monomers used in external phase and organic solvents ascribed in internal phase, called as oil in water emulsion system. This type of polyhipe is not common compared with polyhipe composed of water in oil emulsion due to the fact that many applications necessitate making polyhipe robustness to prevent pores structure to collapse in the course of soxhlet extraction. This circumstance is crucial to be figured out that during polymerization of emulsion imprinted structure should be kept.

Styrene-based polyhipe ,therefore, patterns are more useful to attain durable and stiff scaffolds. It's types monomers are less shranked when polymerizing compared to hydrophilic monomers comprised almost acrylate-based on , e.g; 2-hydroxyethyl acrylate, acrylamide, 3-sulfopropyl methacrylate potassium salts etc, except for sodium styrene sulfonate and (4-vinyl benzyl)trimethylammonium chloride, which is reason why it is shown to more convenient as well [20]. Another notable point is to evaluate that the crosslinking degree with below % 10 relative to mole fraction of monomers possesses effect on polyhipe structure. This lower crosslinking degree affects templating structure in a negative way by taking into account durability. Despite these realities, hydrophilic polyHIPE offers many advantages. First of all, swelling properties can contribute to adsorption methods by taking in lots of water as well as binding the metal and dye particles through the functional groups. Another advantage is based on their pliable structures, promising the use of scaffold for tissue engineering and their hydrophilic characteristic is able to provide for biocompatibility with the body.

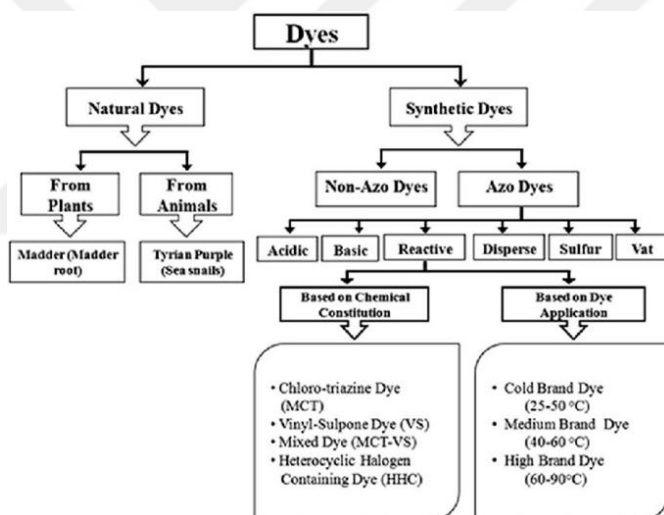
Hydrophilic polyHIPE's are synthesized with two methods aligned with the type of monomers. That water-soluble monomers used in the formation of polyhipe are unstable during the emulsion formation along with the low mechanical strengths which enables them to use other processes ascribed to post-polymerization-functionalization. In this strategy, polyhipe generated with hydrophobic monomers are, generally, converted to the hydrophilic polyHIPE by modifying the functional groups. This approach emerges some drawbacks which the porosity, density and morphology of polyHIPE can alter after modification as well.

## 2.6 Constitution of Dyes

The reason why dyes have specific colours is ascribed to possessing their chemical structures containing conjugated pi bonds. These groups like  $\text{NO}_2$ ,  $\text{N}=\text{O}$  and  $\text{N}=\text{N}$  are regarded as chromophores. Another significant group which is not chromophores themselves and have the ability to give non-pair electrons are made deeping the colour a coloured compound. The groups are named auxochromes. Some examples of common auxochromes are:  $\text{OH}$ ,  $-\text{NH}_2$ ,  $-\text{NHR}$ ,  $-\text{NR}_2$ ,  $-\text{Cl}$ ,  $-\text{CO}_2\text{H}$ , etc.

### 2.6.1 Classification of dyes

Dyes can be sorted into various categories depending on their chemical structure, solubility, application method, and other factors. When looking at flow charts indicating dye classification in Figure 2.15, dyes are most fundamentally divided into two classes as natural and synthetic dyes.



**Figure 2. 15 :** Flow-chart based on chemical constitution and its application.

The classification of dyes can be according to the scope of applications such as textiles, food and cosmetics. These classifications provide the categorization of dyes according to their intended use and suitability. These types of classifications enable industries to choose the most appropriate dyes for specific designs while regulating safety, suitability and durability [38].

Dyes are classified into the following types on the basis of their applications [48].

**Acid Dyes:** The type of azo-dyes found sodium salt of sulfonic acid, carboxylic acid are applied for dyeing the wool, silk and nylon.

**Basic Dyes:** Basic dyes known as cationic dyes are salts of organic colour bases. These are used to dye modified nylons, polyester, wool, cotton, leather, paper. Methylene blue, Rhodamine B, Malachite Green Carbinol, aniline yellow and crystal violet are examples of the basic dyes.

**Direct Dye or Salt Dye :** These dyes are soluble in water and chiefly composed of amines and phenols attached to the fibre thanks to hydrogen bonding. The dye colours often have only fair fastness to light, poor fastness to washing. The common examples of direct dyes are Martius yellow and congo red.

**Disperse Dye:** Disperse dyes, lacking ionizing groups and thus possessing low water solubility, are made useful for dyeing hydrophobic textile such as polyesters, acetates, and polyamides. In the presence of phenol, cresol or benzoic acid found in a soap solution, the dyes are dispersed to provide colour to fiber. Key advantages of disperse dyes are their high temperature resistance, good light fastness, and wide color range.

### **2.6.2 Dye removal techniques**

There are distinct methods to achieve effective dye removal, such as: physical, chemical, electrochemical and biological treatments. They are illustrated with the chart below. Adsorption, one of the different physical methods such as coagulation/flocculation and filtration, is a useful, facile and low-cost method for removing dyes. In this time, both natural and synthetic adsorbent was used for this purpose e.g, clay, fly ash, activated carbon and zeolite, the example of natural adsorbent.

### **2.7 Adsorption**

Adsorption is a phenomenon that attractive forces govern to move a solute (adsorbate) to the surface of an adsorbent until equilibrium in the concentration of the adsorbate where no further net adsorption occurs. Based on the attractive forces adsorption can occur by two kinds of interaction composed of physical or chemical interactions.

In physical adsorption, Van der Waals forces which are weak are effective for bonding between substrate and adsorbent, with no changes of chemical structure for both substrate and sorbent.

Chemisorption can be explained by the chemical bonding like ionic bond or covalent bond resulting from rearrangement of electron density between the adsorbent and substrate.

## 2.8 Adsorption Isotherms

Adsorption isotherms describe how adsorbate from the bulk solution reacts with the surface of adsorbent. It represents a relationship between the amount of adsorbate per unit mass of adsorbent and the adsorbate concentration or pressure in the bulk solution at a fixed temperature.

### 2.8.1 Langmuir isotherm

Langmuir isotherm is defined as the equilibrium system of adsorbate and adsorbent. This model is referred to as monolayer sorption where a single molecule occupying the surface site remains the same. Linear formula of Langmuir isotherm is more useful for utilizing the parameters.

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} * K_L} + \frac{C_e}{q_{\max}} \quad (2.1)$$

In this formula,  $C_e$  ( $\text{mg L}^{-1}$ ), is the equilibrium concentration of adsorbate,  $q_m$  ( $\text{mg/g}$ ) maximum adsorption capacity,  $K_L$  ( $\text{L/mg}$ ) free energy of adsorption and  $q_e$  ( $\text{mg/g}$ ) the equilibrium adsorption capacity. By using this formula, parameters are found by plotting  $C_e$  against  $C_e/q_e$ , i.e., slope and intercept referring to  $q_m$ , and  $K_L$ , respectively [26].

### 2.8.2 Freundlich isotherm

Freundlich isotherm which is an empirical equation is used for the explanation of heterogeneous surface adsorption. The linear Equation 2.2 is as follows:

$$\ln q_e = \ln K_f + 1/n \ln C_e \quad (2.2)$$

In this equation, the Freundlich constants are indicated with  $K_F$  ( $\text{mg/g}$ ) and  $n$  which are the characteristic of the adsorption system. Adsorption capacity and adsorption intensity are shown with  $K_F$  and  $n$ , separately [26].

### 2.8.3 The Dubinin–Radushkevich isotherm

The Dubinin–Radushkevich (D-R) isotherm model presumes that the happening of adsorption processes is ascribed to the volume of adsorbent pores. The description of physical or chemical adsorption processes are generally explained with this model. In Equation 2.3, linear formulation of this model is shown in the formula below.

$$\ln q_e = \ln q_m - K\varepsilon^2 \quad (2.3)$$

In this equation, parameters are expressed that  $q_e$  is the equilibrium amount of the adsorbate;  $K$  is constant,  $q_m$  is the theoretical adsorption capacity and  $\varepsilon$  is the Polanyi potential ( $\text{kJmol}^{-1}$ ) which is calculated with ‘  $RT\ln(1 + (\frac{1}{C_e}))$  ’ as well [27].

## 2.9 Adsorption Kinetics

Adsorption kinetics are defined as the rate of the diffusion process which adsorbates from aqueous move to solid-phase interface. That adsorption take place forms seven important steps

The kinetic adsorption process is based on two step assumptions. The first step is able to clarify that the adsorbate from the bulk solution moves to the surface of the adsorbent. The second step results from diffusing of the adsorbate and arranging its organization within the sorbent pores. The rate-limiting step of adsorption process elucidates the adsorption mechanism

### 2.9.1 Pseudo first order kinetics

Pseudo First Order kinetics suppose that the diffusion of adsorbate into adsorbent controls the adsorption rate. As given Equation 2.4, the linear form of the Lagergren rate equation is as follows.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (2.4)$$

In the pseudo-first-order kinetics, amounts of adsorbate retained per adsorbent ( $\text{mg/g}$ ) at equilibrium and time are expressed with  $q_e$  and  $q_t$ , respectively. By making use of  $\ln(q_e - q_t)$ –time plot, the rate constant and  $q_e$  corresponding to slope and intercept separately were calculated [29].

### 2.9.2 Pseudo second order kinetics

Pseudo second order kinetics model assumes that different adsorption sites located on solid substrate randomly collide with each other during a rate-limiting mechanistic step. The linear form of the this model shown Equation 2.5;

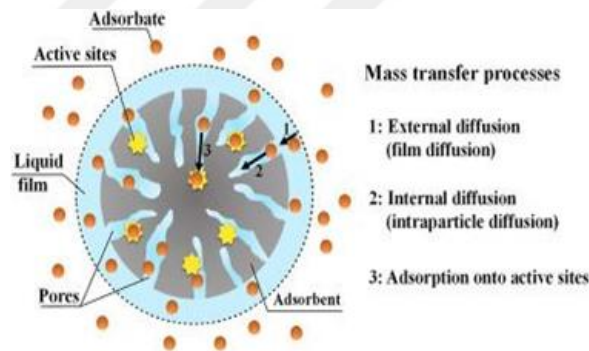
$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} * t \quad (2.5)$$

The pseudo-second-order rate constant and the adsorbent equilibrium adsorbate quantity can be expressed with  $k_2$  and  $q_e$ , respectively [30].

### 2.9.3 Intra-particle diffusion

The intraparticle diffusion model is ascribed to the mass transfer explained that the adsorbate diffuses in the pores inside the adsorbent, which event have three main steps which are summarized with Figure 2.16.

1. Mass transfer to adsorbent surface (external diffusion)
2. Diffusion into pores o adsorbent (pore diffusion)
3. Adsorption onto surface of pores



**Figure 2. 16 :** Mass transfer process inside porous material [24].

$$q_t = K_d t^{0.5} + C \quad (2.6)$$

In Equation 2.6, the intraparticle diffusion rate constant and the boundary layer thickness are denoted with  $k_d$  and  $C$ , separately . Plotting  $q_t$  according to  $t^{0.5}$  gives a multilinear plot composed of two or three steps in which the sudden increase of adsorption capacity results from external surface adsorption, then the increase of adsorption capacity begins to decrease due to the fact that pore diffusion is rate-limited and lastly the increased trend becomes very slow and the equilibrium stage is established [28].

### **3. EXPERIMENTAL**

#### **3.1 Materials and Instruments**

##### **3.1.1 Materials**

All chemicals utilized for the synthesis of adsorbent and adsorption study were used without any pre-purification. 3-Sulfopropyl methacrylate potassium salt, N,N'-Methylenebis(acrylamide), Ammonium persulfate, N,N,N',N'-Tetramethyl ethylenediamine, Toluene, (Pluronic F-127, MW = 12,500 g/mol) provided from Sigma- Aldrich. were used for synthesis of polyhipe. Diethyl ether purchased from Sigma-Aldrich and ethanol with analytical grade were handled for the purpose of soxhlet extraction. Methylene blue, Rhodamine B and Malachite Green Carbinol supplied from Sigma- Aldrich were used to realize the adsorption process.

##### **3.1.2 Instruments**

Fourier Transform Infrared spectroscopy was recorded on a Thermo Scientific. UV-vis spectrophotometer (Perkin Elmer, Lambda 25) was used to determine the remaining dye concentrations in solution after adsorption experiments.

#### **3.2 Preparation of Hydrophilic Adsorbent**

##### **3.2.1 Preparation of polyHIPE**

The emulsion composed of % 80 volume fraction oil droplets was prepared as follow steps. Initially, surfactant Pluronic F-127 (1g), monomer SPMA (6,12g) cross-linker MBAM (0.154 g), and initiator KPS (0.120 g) were dissolved in water in three neck flask. After that toluene was added drop by drop in a slow way. Overhead stirrer mixing the solution at 450 rpm was used to obtain homogenous emulsion. After the addition of toluene, stable emulsion was achieved and with the addition of the catalyst TMED(0,1ml), further mixing with approximately one minute was continued. Subsequently, the emulsion was poured to polypropylene vial and thermal polymerization occurred at 40°C for 24 h. The resulting monolith was washed to

eliminate internal phase, monomer residue and surfactant by using soxhlet extraction with ethanol and diethyl ether, each for 24 h. This polyHIPE was dried under convection oven in the course of 24 h.

### **3.2.2 Acidification of sulfonated based polyHIPE with hydrochloric acid**

The polyHIPE-SO<sub>3</sub>K<sup>+</sup> (1.00 g) was put into a 100 mL beaker. After that HCl (2M, 25 mL) was added to this beaker. The mixture was left at room temperature for 24 h.

## **3.3 Adsorption Experiments**

### **3.3.1 The calculation of optimum adsorbent quantity**

Various amounts of polyHIPE ranging from 25 to 125 mg were used for this experiment. By looking at the experimental results, 25mg polyHIPE is selected with optimum amount of adsorbent.

### **3.3.2 The determination of maximum adsorption capacity of adsorbent**

Polymeric adsorbents (25 mg) were added to 15 mL conical bottom centrifuges and subsequently wetted with water. After this step, 7 mL of dye solutions in the range of 100-10000 ppm were added to the centrifuge tubes to find the maximum dye adsorption capacity of the adsorbent.

### **3.3.3 The determination of the effect of ionic strength on adsorption capacity**

Dye solutions (100 ppm) prepared with sodium chloride ranging from 0,1 to 0,3 molar were used in the adsorption experiment. The 7 ml of this solution and 25 mg polymeric sorbent were mixed at 400 rpm with a magnetic bar during 3h . After this process, the mixture was centrifuged and supernatant was drawn to measure with an uv-vis spectrophotometer how the dye pigments were held from sorbents.

### **3.3.4 Dye sorption kinetics of the adsorbent**

The various dye concentrations ranging from 500 to 5000 ppm were used. Polymeric adsorbent (25 mg) and dye solution were mixed with a magnetic bar and the resulting mixture were centrifuged for detecting the residual amount of methylene blue in the solution.

### **3.3.5 The determination of the effect of buffer solution on adsorption capacity**

Buffer solutions prepared with acetic acid/acetate with pH; 4, 5 and potassium dihydrogen phosphate related to pH; 6, 7, 8 were utilized to obtain dye solution. The adsorption was realized in the 7 ml of dye solution added into a plastic vial including the 25 mg polymeric sorbent. The resulting dye residue was measured with an uv-vis spectrophotometer.

### **3.3.6 The performance of adsorbent on cationic dyes**

The 7 ml of methylene blue, rhodamine B, malachite green carbinol and 25 mg polymeric adsorbent were used for this experiment. Adsorption procedure was aforementioned above.

### **3.4 The swelling kinetics of polymeric adsorbent**

0,2 g polymeric sorbent was put in a glass Filter Crucible kept 24h before the experiment for removing the moisture and the water was added to the polymer for swelling. In the next step, the swollen sorbent was drained at certain intervals for how much water held from the sorbents.



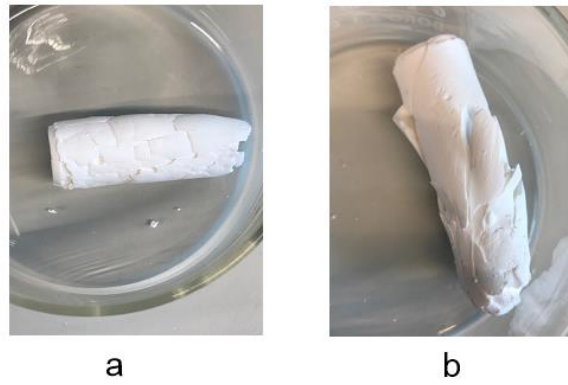
## 4. RESULT AND DISCUSSION

### 4.1 Preparation of Hydrophilic PolyHIPE

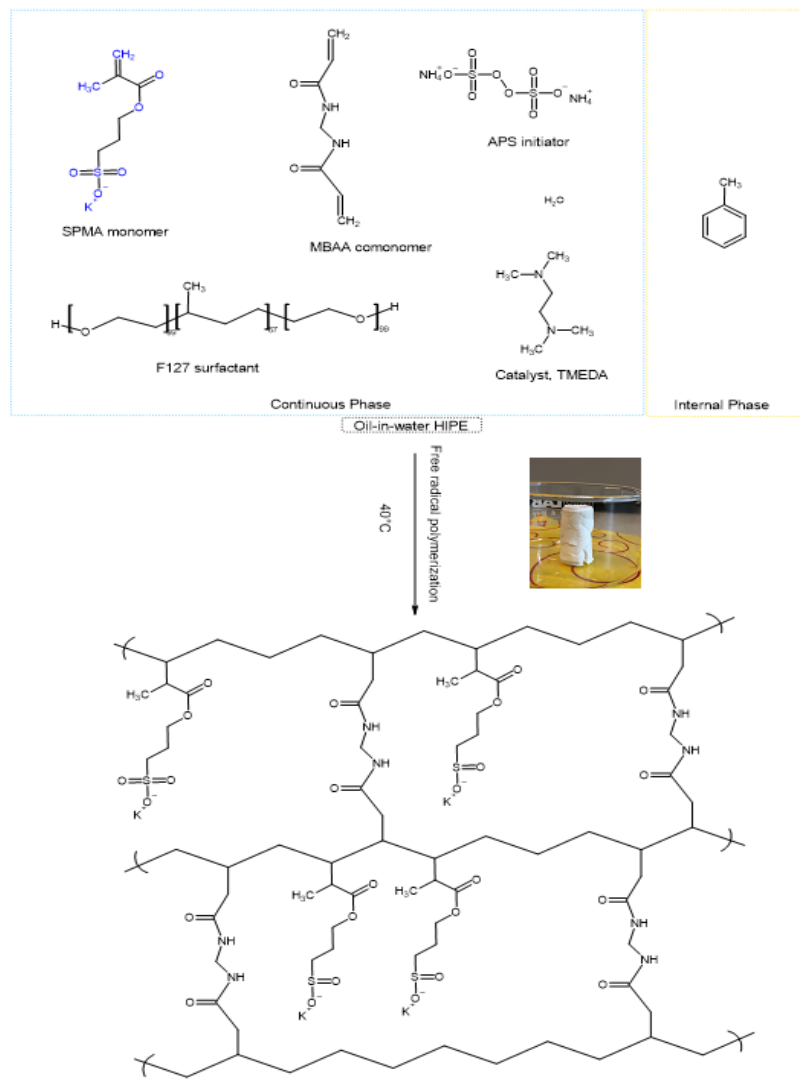
For the formation of a high internal phase emulsion, the external phase: distilled water, 3-sulfopropyl methacrylate potassium salt, N,N'-Methylenebis(acrylamide), ammonium persulfate and surfactant (F127 pluronic) and internal phase (toluene) are handled. The discontinuous phase was added into the continuous phase slowly at constant stirring and a lightly viscous emulsion was obtained. This emulsion was polymerized with convection oven during 24 h and the resulting polymeric scaffold with flexible structure was labeled as PolyHIPE-SO<sub>3</sub>K<sup>+</sup>. Subsequent step is related to imparting polyHIPE permeable and porous structure. For this purpose, in order to remove internal phase, monomer residues and the surfactant, polyHIPE was washed sequentially with both ethanol and diethyl ether by means of soxhlet apparatus. After termination of the extraction process, this material was ground into small particles and weighed to calculate the percentage yield. Since both monomer and comonomer whose structure is similar to each other have a close reactive ratio, the percentage of production yield was found as 85.

An important point in this study is to use a relatively low quantity of surfactant. This circumstance is associated with surfactant quantity which is a crucial effect on open-cell porosity. In this thesis, surfactant F127 was used at 5% of the total weight of the continuous phase. This surfactant stabilizing the emulsion was removed during the extraction process, which contributed to the creation of an interconnected network.

Two different polyHIPE's were synthesized based on cross-link ratios consisting of 4 and 8% of the total mole ratio of monomers. These materials were used as adsorbent for dye adsorption and their swelling properties were investigated as well. Both materials and chemical structures of composition of the resulting polyHIPE's were represented with Figure 4.1 and Figure 4.2, respectively.

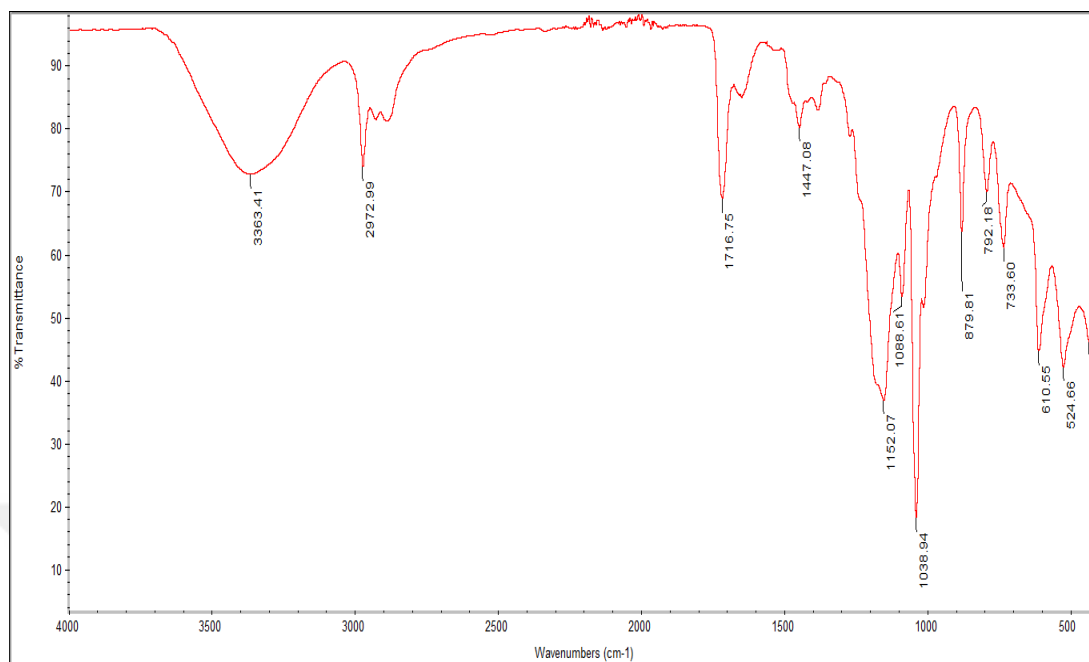


**Figure 4. 1 :** PolyHIPE monoliths including (a = 4%), (b = 8%).



**Figure 4. 2 :** Schematic illustration of the SPMA-based polyHIPE synthesis.

## 4.2 Characterization of Polymeric Adsorbent

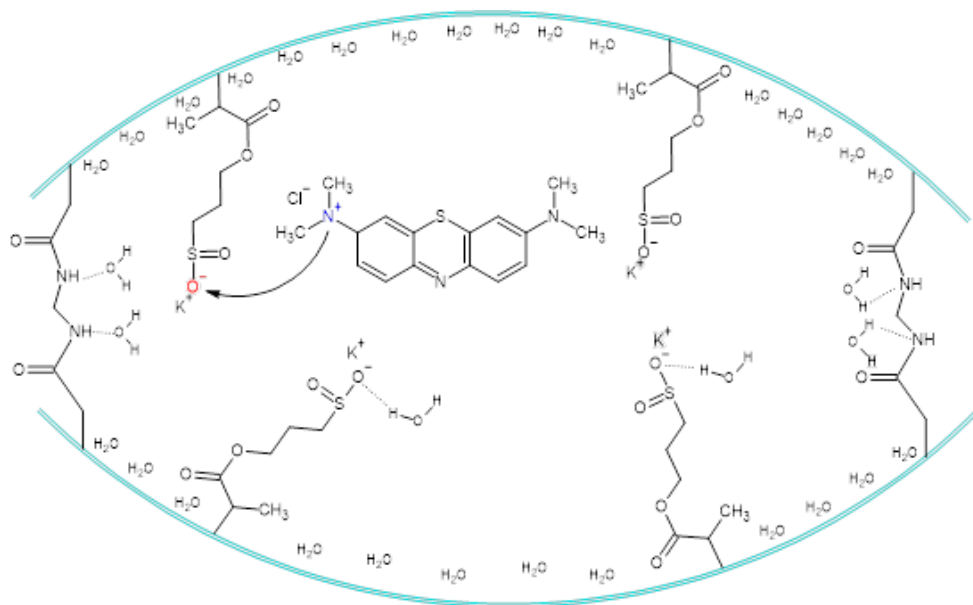


**Figure 4.3 :** FTIR spectrum of SPMA-based polyHIPE.

In Figure 4.3, FTIR spectrum shows that the strong peak at 1716 cm<sup>-1</sup>, which is characteristic of the carbonyl group, is due to the polyHIPE structure made with monomers containing sulfonic and amide functional groups. The strong peak at 1152 cm<sup>-1</sup> and 1038 cm<sup>-1</sup> in the spectrum is due to sulfonyl (S=O) asymmetric and symmetric stretching vibrations, respectively. Also, peaks 2972 and 1447 belong to the alkyl group with separate stretching and bending vibrations, separately. As a result, this FTIR spectrum clearly demonstrates that polymerization has taken place and functional groups have formed.

## 4.3 The Adsorption Results

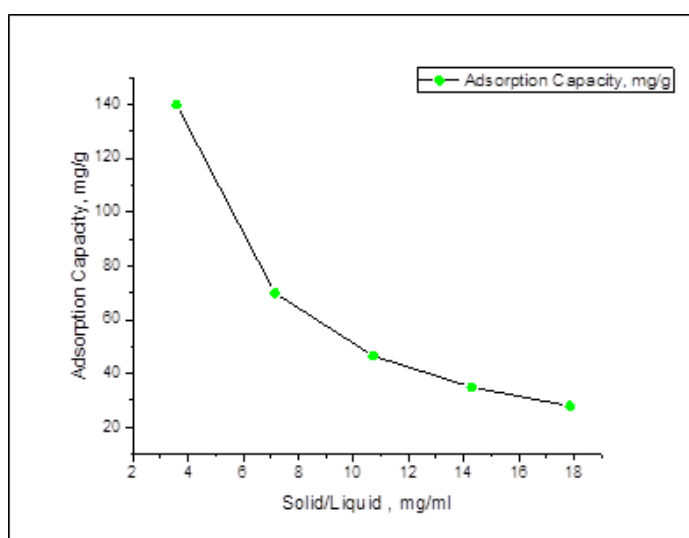
The polyHIPE bearing the sulfonic group provides its to be the highly effective removal of dyes. Thanks to these electrostatic forces between quaternary amine from dye molecules and the sulfonic group of adsorbent, the dye molecules can be binded on the polymer surface. Also, other weak interactions except for hydrogen bonding providing both the water uptake and binding dye molecule are able to be neglected by terms of the contribution to adsorption capacity. In Figure 4.4, the possible interactions between dye molecules and the functional groups of adsorbent can be seen.



**Figure 4. 4 :** Schematic representation of the main adsorption mechanism.

#### 4.3.1 The detecting of optimum amount of adsorbent with solid/liquid ratio

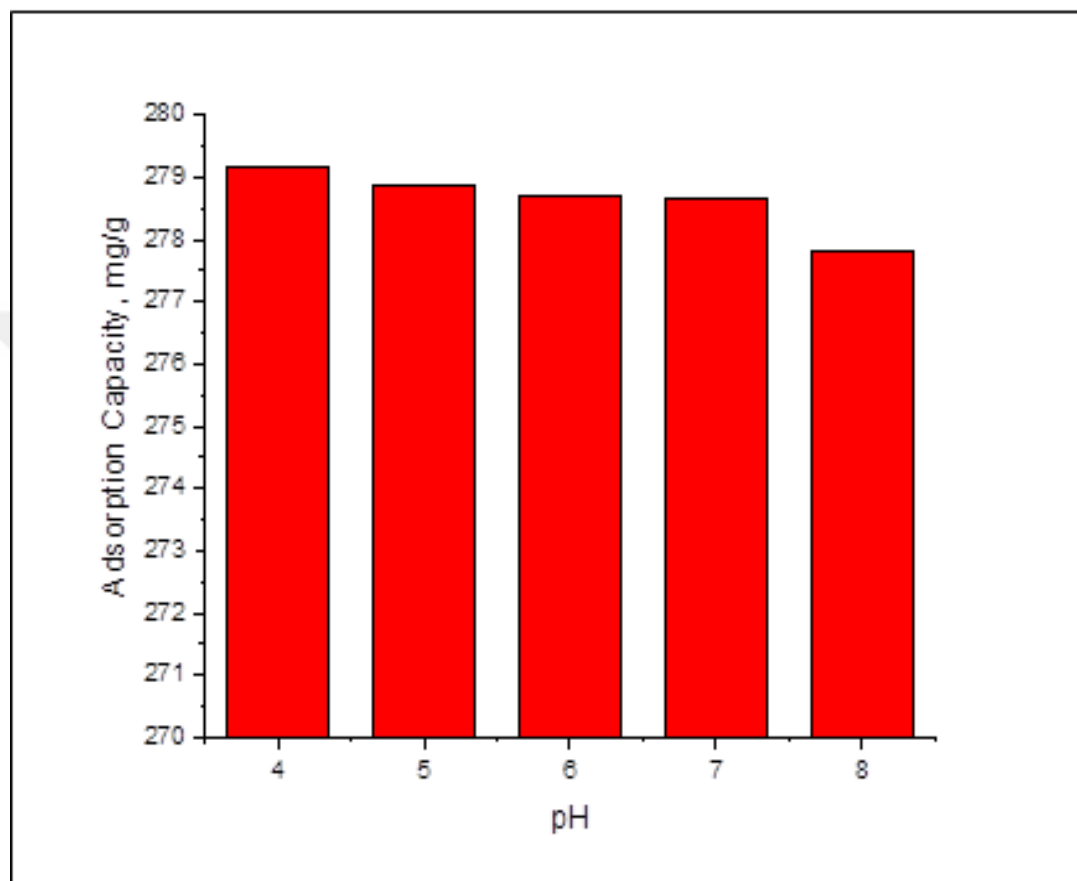
In order to determine the optimum amount of adsorbent, the effect of solid/liquid ratio composed of different adsorbent quantities and the constant volume of dye solution on adsorption capacity of methylene blue was investigated. As observed in Figure 4.5, as the solid/liquid ratio increases, the number of functional groups in the pores increase. However, this resulted in a decrease in adsorption capacity because all adsorbents in different amounts adsorbed almost all of the dye molecules in the solution. According to obtained results, optimum adsorption condition was determined 25 mg adsorbent and 7 ml of dye solution.



**Figure 4. 5 :** The effect of solid-liquid ratio on adsorption capacity.

### 4.3.2 The effect of pH on methylene blue adsorption

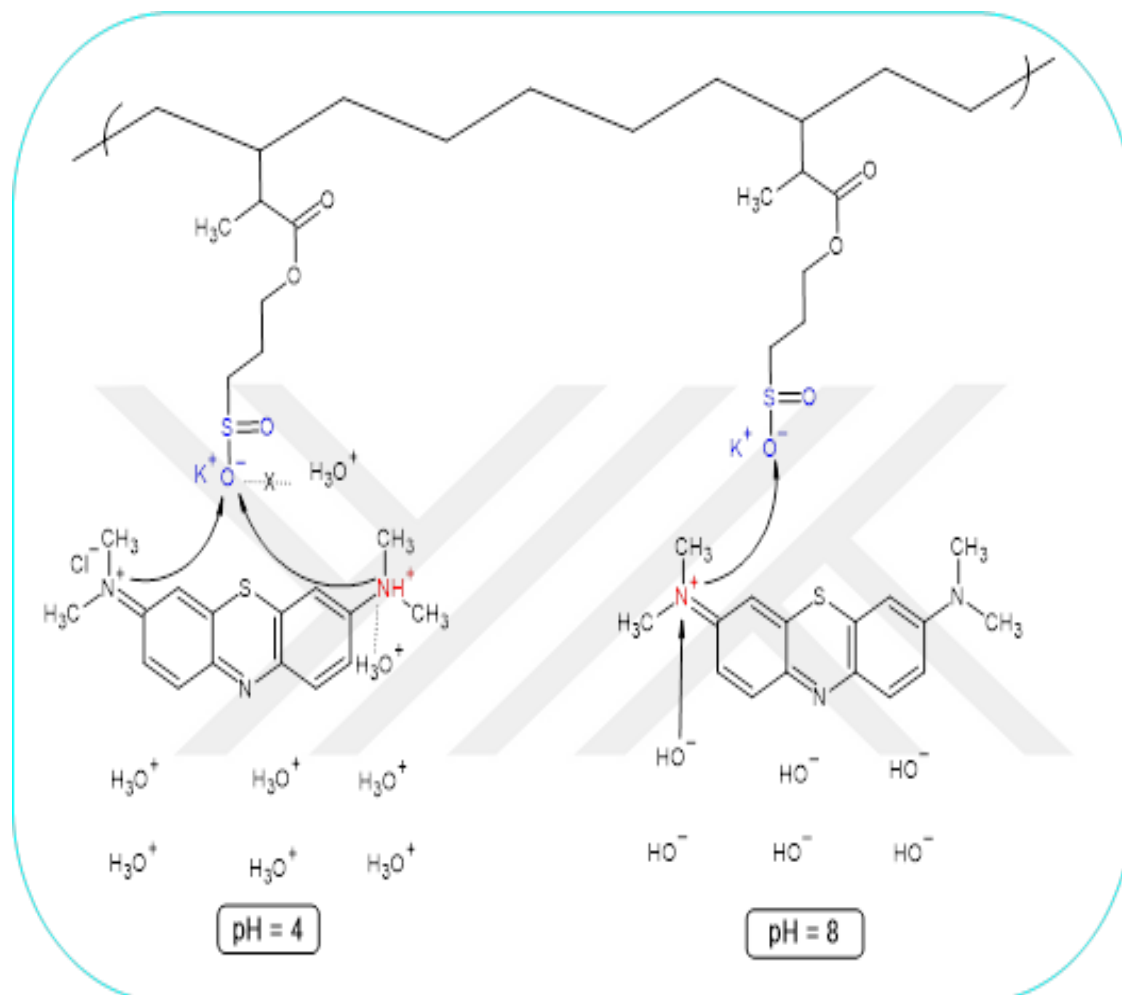
The adsorption of methylene blue on hydrophilic polyHIPE was assessed in a pH range of 4 to 8 and the resultant adsorption capacities were shown in Figure 4.6. As seen from the results, adsorbent performed good adsorption capacities in a broad range of pH.



**Figure 4. 6 :** The effect of buffer solution on adsorption capacity.

Experimental results can be interpreted that at pH = 4, the potassium salt of sulfonic acid with  $pK_a = -7$  groups on the pore structure is not protonated and remained intact but the tertiary amine groups of methylene blue can be protonated by acidic medium. In this perspective, the methylene blue has two quaternary amine and interacts with the oppositely charged polymeric adsorbent, which enables it to reach higher adsorption capacity. At pH = 8, both sulfonate ions located on the polymer surface and the tertiary amine groups found the dye molecules are the same intact. The reason for the declining trend in adsorption capacity can be explained by the excess of hydroxyl ions reducing electrostatic interaction between adsorbent and adsorbate by binding dye molecules. Schematic illustration in Figure 4.7 summarizes what is aforementioned in

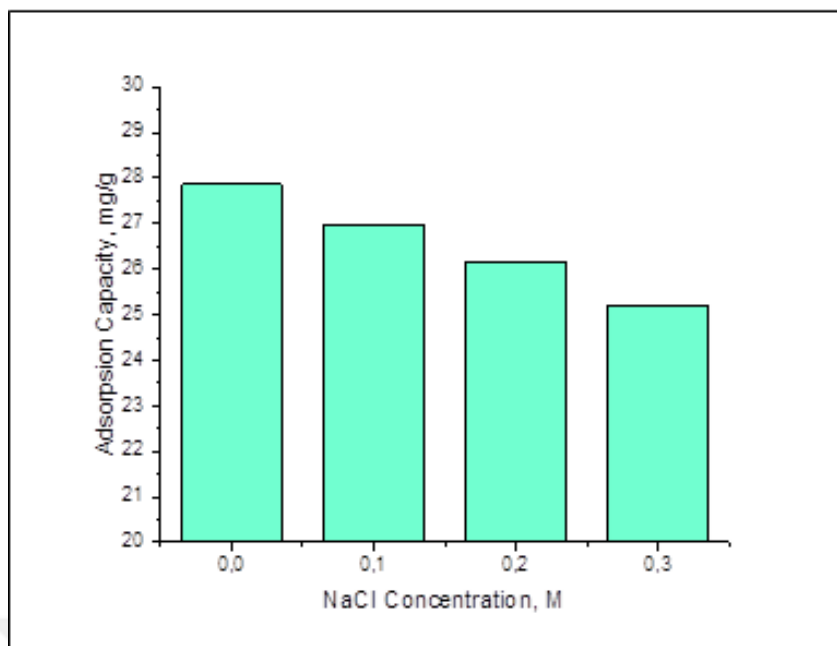
the text above. Looking over the change of adsorption capacity at pH = 5, 6 and 7, it can be clearly seen that adsorption capacity has almost unchanged due to neutral medium at pH = 6 and 7 but also that adsorption capacity at pH = 5 is slightly higher is associated with same event at pH = 4.



**Figure 4. 7 :** The possible adsorption mechanism with the pH-dependent.

#### 4.3.3 The effect of ionic strength on methylene blue adsorption

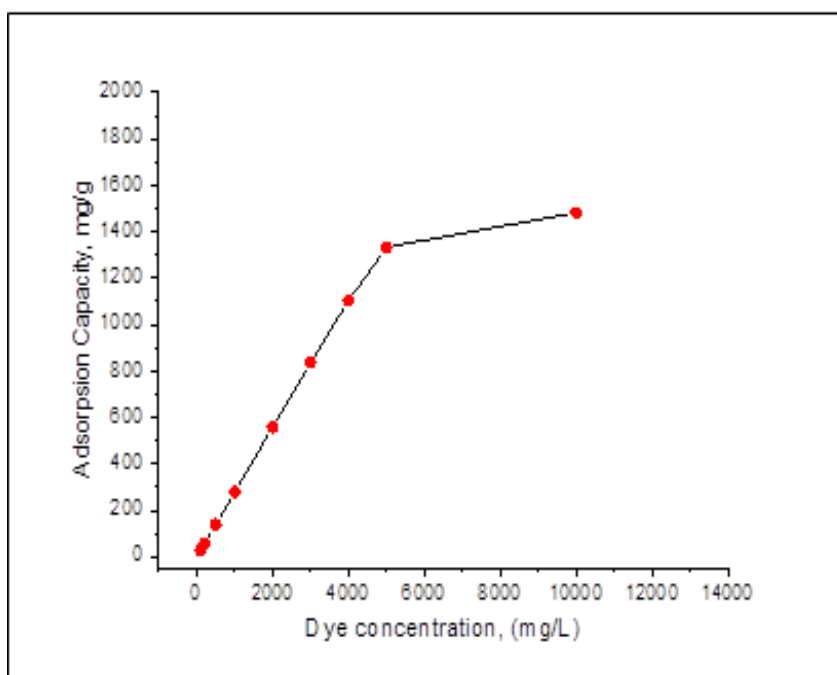
In these experiments, the effect of ionic strength on methylene blue adsorption was studied based on the reduction of electrostatic interaction between adsorbent and dye molecules. For this purpose, dye solutions prepared with ranging from 0.1 M to 0.3 M NaCl were used for determining salt concentration effect on adsorption capacity. Another important point is that the reason for using a maximum of 0.3 M salt for preparing dye solution with 100 ppm is to encounter the solvation problem. Despite this limitation, as can be seen in Figure 4.8, increasing the sodium chloride concentration, decreases the adsorption capacity.



**Figure 4. 8 :** The ionic effect on adsorption capacity.

#### 4.3.4 The determination of maximum adsorption capacity of adsorbent

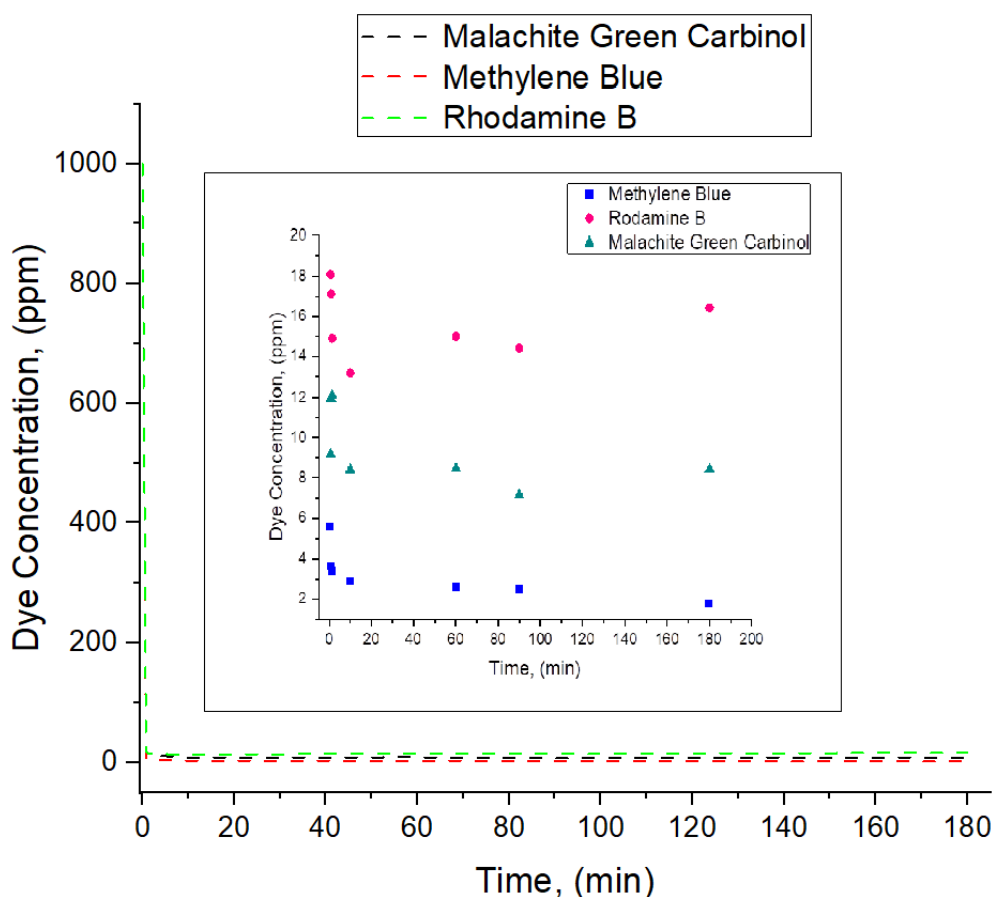
In this assay, various dye concentrations were used together with a fixed amount of adsorbent for determining the maximum adsorption capacity. As dye concentration increases the adsorption capacities of adsorbents increase proportionally and eventually the increase tendency of adsorption capacities slows down sharply, which is which is clearly seen Figure 4.9.



**Figure 4. 9 :** Maximum adsorption capacity of adsorbent.

#### 4.3.5 The adsorption performance of hydrophilic adsorbent on cationic dyes

Methylene blue, rhodamine B and malachite green carbinol whose structure found cationic functional groups were utilized for preparing dye solution. In the adsorption medium, 1000 ppm solution of each of them and 25 mg adsorbent were used. As a result of the experiment, the removal percentage of methylene blue, rhodamine B and malachite green carbinol were 99.82, 98.35 and 99.15 respectively. Considering this result, hydrophilic adsorbent possesses intriguing performance for removing cationic dyes. In figure 4.10, it was shown that a kinetic study in which this graph was created according to the concentration of dye in the reaction medium versus time was carried out.



**Figure 4. 10 :** Adsorption study of hydrophilic adsorbent with other cationic dyes.

The polymeric adsorbent including the sulfonate ion was acidified with 2 M sulfuric acid and then it was evaluated the adsorption capacities of methylene blue, rhodamine B and malachite green carbinol. Compared to results related to selectivity experiment, the remaining dye concentration of three dyes increased. This result can be explained

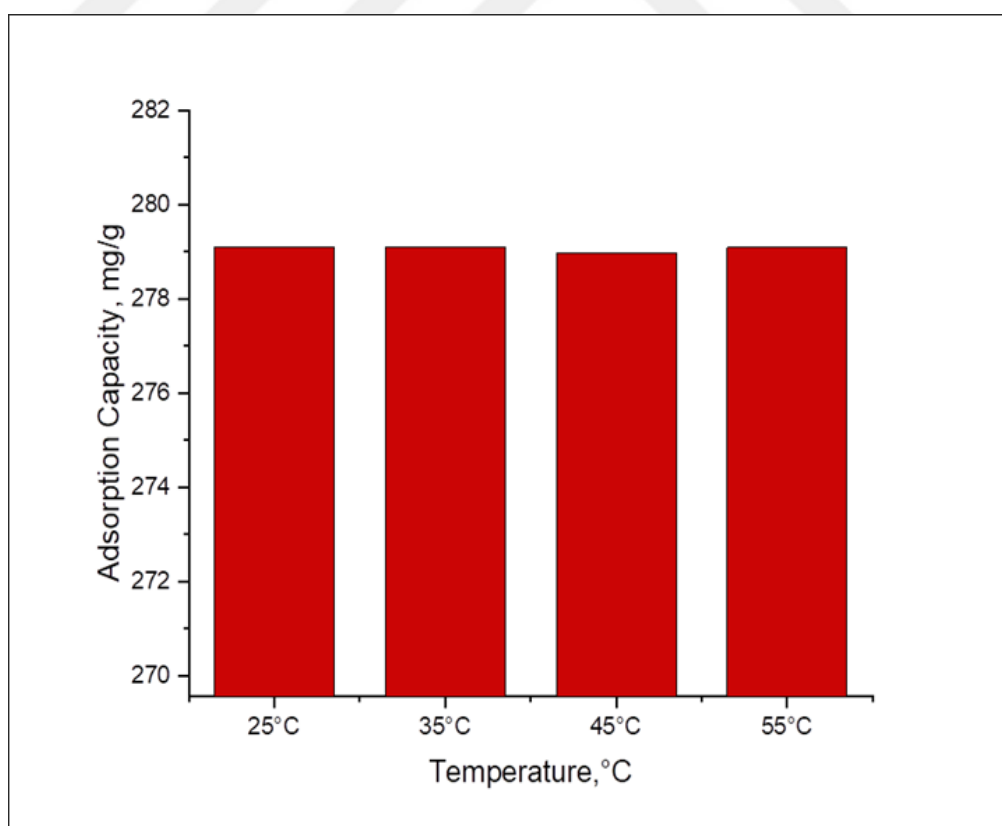
that converting sulfonate group into sulfonic acid may cause ion exchange capacity of adsorbent to decrease. Experimental data of this study was summarized in Table 4.1.

**Table 4. 1 :** Comparison of acidified and neat polyHIPE on adsorption capacities.

1000 ppm dye concentration	The remained dye concentration after adsorption (mg/L)	
	R-SO <sub>3</sub> K <sup>+</sup>	R-SO <sub>3</sub> H
Methylene blue	1.787	31.22
Rhodamine b	16.42	123.28
Malachite green	8.423	345.13

#### 4.3.6 The temperature effect on adsorption

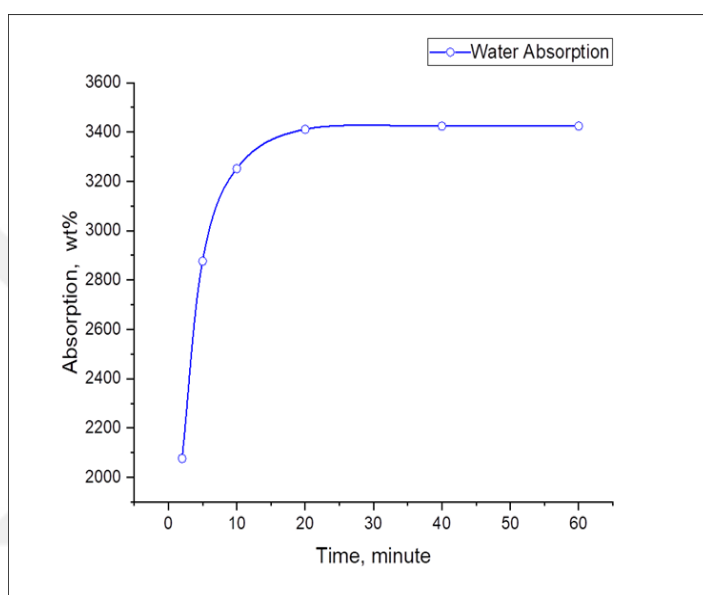
Based on endothermic or exothermic reactions resulting from physical or chemical adsorption, the effect of temperature is an important parameter on assessing the change of adsorption capacity. On the basis of this information, the same condition mentioned in previous assays was used and as result given Figure 4.11 the change of temperature ranges was observed to have minimal effect on adsorption capacity.



**Figure 4. 11 :** Effect of temperature change on adsorption capacity.

### 4.3.7 Swelling behaviour of hydrophilic polyHIPE

In this assay, the water uptake capacity of hydrophilic adsorbent was studied. As observed in figure 1, the obtained result proves that adsorbent reached maximum water retention in a short time. As seen in the maximum point of the graph shown Figure 4.12, adsorbent held approximately 34 grams of water. In other words, the adsorbent kept about 3400 percent of its own weight in water. These results confirmed that adsorbents possess relatively low-crosslinking degree and hydrophilic structures.



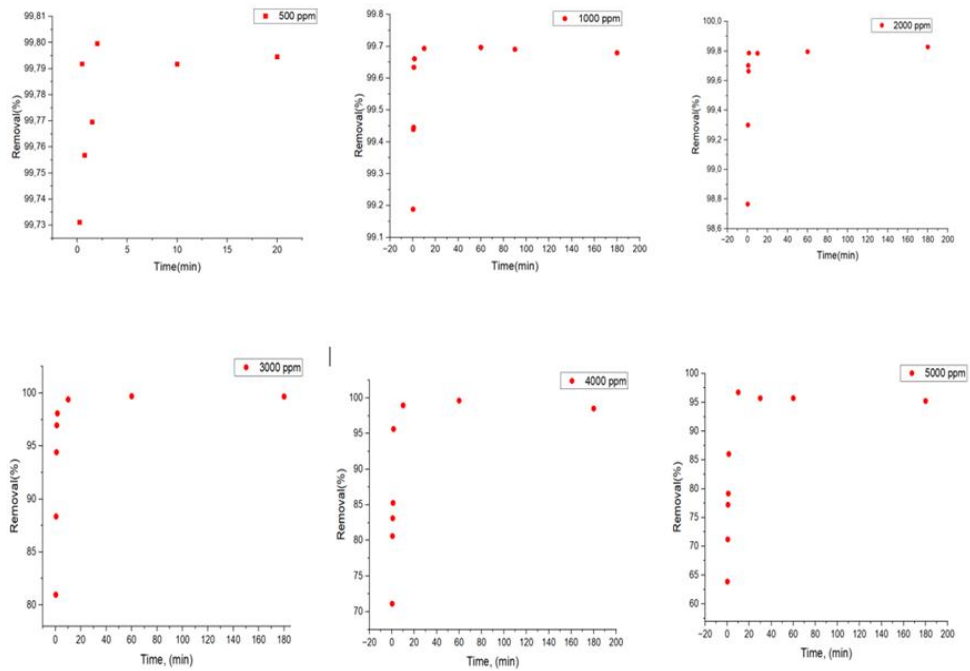
**Figure 4. 12 :** Variation of water absorption with time.

The equilibrium water uptake was calculated according to the formula shown in Equation 4.1. The equilibrium water uptake ( $A_i$ ) was obtained by placing with a known dry mass ( $m_D$ ) into a sintered glass filter funnel filled with the water until a constant swollen mass ( $m_{sw}$ ) was reached.

$$A_i = \frac{m_{sw} - m_D}{m_D} \quad (4.1)$$

### 4.3.8 The kinetic mechanism of dye adsorption

In order to explain the main adsorption mechanism, various dye concentrations ranging from 500 ppm to 5000 ppm with constant adsorbent quantity were utilized in kinetic experiments and  $q_e$ ,  $q_t$  and  $c_e$  which are important parameters used in kinetic models, were determined. All kinetic studies for dye adsorption and value of parameters were represented as graphs in Figure 4.13 and Table 4.2.



**Figure 4. 13 :** The results of kinetic studies for different dye concentration.

First of all, the pseudo-first-order model can be defined by using the Lagergren first-order rate equation. In this model, reaction rates are dependent on concentration of one reactant in bimolecular reaction composed of both concentration of adsorbate and adsorbent in adsorption study. To benefit from this model, the linear form of the Lagergren first-order rate equation shown in Equation 4.2 is used.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (4. 2)$$

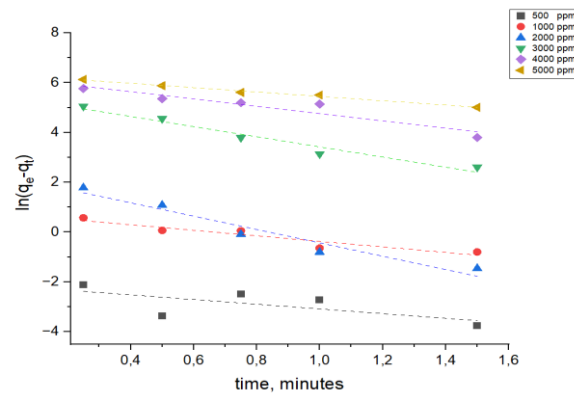
In this equation, the rate constant, the amounts of adsorption equilibrium and at time are shown with  $k_1$ ,  $q_e$  and  $q_t$  ( $\text{mmol g}^{-1}$ ), respectively. By making use of the slope and intercept point of the plot of  $\ln(q_e - q_t)$  versus  $t$ , first-order rate constant  $k_1$  and equilibrium capacity  $q_e$  can be found, separately.

Secondly, the pseudo-second-order model used in this thesis can be defined that adsorption rate is based on the interaction of adsorption sites on the adsorbent surface.

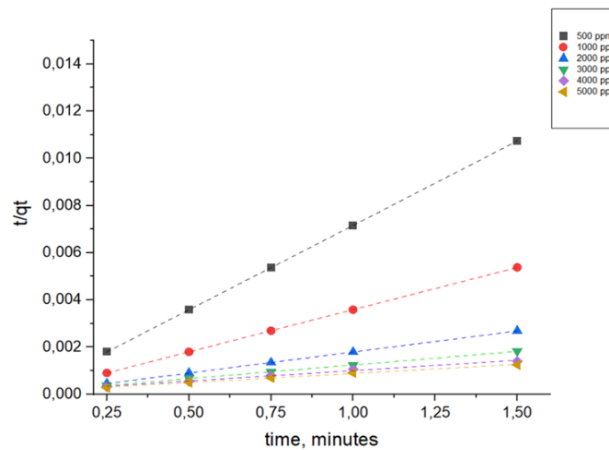
$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e t} \quad (4. 3)$$

The parameters of this formula seen in Equation 4.3 can be explained that  $k_2$  is the pseudo-second-order rate constant of sorption and  $q_e$  is equilibrium capacity.

Adsorption kinetics for methylene blue adsorption on hydrophilic adsorbent are shown in Figure 4.14 and Figure 4.15.



**Figure 4.14 :** The pseudo-first Order kinetics at different dye concentration.



**Figure 4.15 :** The pseudo-second order kinetics at different dye concentration.

The assessment of which model better describes the adsorption process is made by considering the correlation coefficients of the respective plots. By using linear regression obtained kinetic parameters can be seen in Table 4.2. Given that theoretical kinetic data is compatible with experimental data, the adsorption of methylene blue on hydrophilic adsorbent is accepted to obey the second-order kinetics. Also, that correlation coefficients are very close to one is shown that experimental results fit well with the kinetic model. On the other hand, as can be observed in the table, pseudo first order kinetic models are not in good agreement with the experimental data although correlation coefficients are close to one value. The aforementioned results can be inferred that ion exchanges between potassium ions in adsorbent and quaternary amine bulk groups of methylene blue enable them to form strong interaction and thus chemical adsorption takes place.

**Table 4. 2** : The kinetic parameters for dye adsorption on hydrophilic polyHIPE

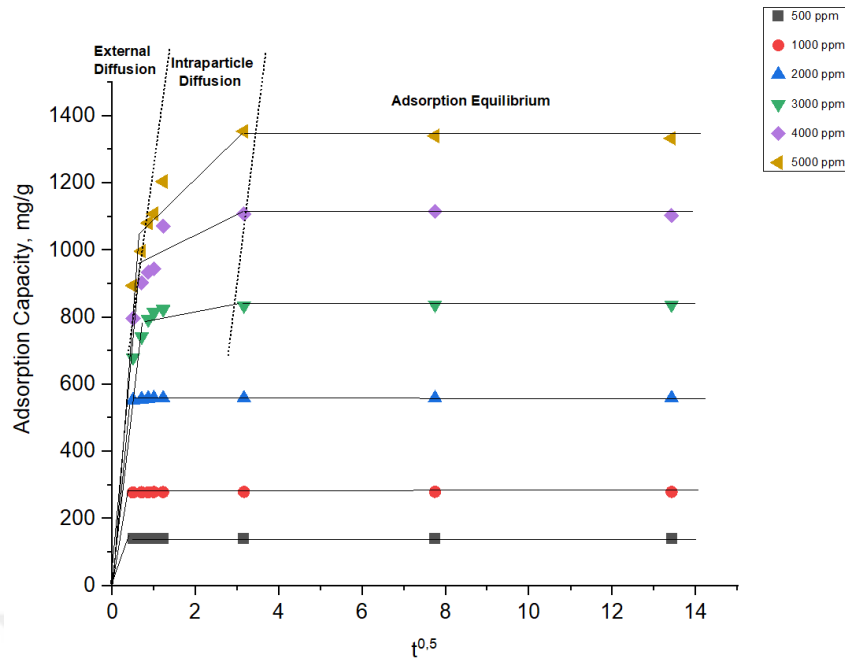
Methylene Blue (mg/L)	The pseudo-first order kinetic				The pseudo-second order kinetic		
	$q_{exp}$ (mg g <sup>-1</sup> )	$k_1 * 10^2$ (min <sup>-1</sup> )	$q_e$ (mg g <sup>-1</sup> )	$R^2$	$k_2$ (g mg <sup>-1</sup> min <sup>-1</sup> )	$q_e$ (mg g <sup>-1</sup> )	$R^2$
500 ppm	139.74	57.5	0.0982	0.3960	36.14	139.66	1
1000 ppm	279.49	110.9	2.07	0.8921	2.29	279.33	1
2000 ppm	559.03	520.2	25.17	0.9491	0.56	561.79	0.999
3000 ppm	837.32	203.7	235.18	0.9441	0.0162	862.06	0.999
4000 ppm	1115.84	146.0	503.70	0.8622	0.0063	1138.85	0.991
5000 ppm	1354.33	87.4	558.91	0.9865	0.0055	1296.84	0.997
20ppm (ref 47)	417.12	22.7	131.61	0.8327	0.0763	405.22	0.996
10 ppm (ref 46)	3.66	26	1.22	0.9843	0.66803	0.461	0.999

Another evaluating model for explaining adsorption mechanism is based on how adsorbate diffuses into hydrophilic adsorbent. This diffusion model is defined by Weber and Morris [37] and it is given as following Equation 4.4:

$$q_t = K_d t^{0.5} + C \quad (4.4)$$

In this model,  $q_t$  is the adsorption capacity at any time,  $k_d$  indicates the intra-particle diffusion rate constant ( $\text{g mmol}^{-1}\text{min}^{-0.5}$ ) and  $C$  is the constant on boundary layer thickness. Drawn the plots  $q_t$  versus  $t^{0.5}$ , multilinearity regions composed of two or more steps occur. In the first step, the occurrence of a sudden increase in the adsorption capacity is associated with the external surface adsorption where this place is the closest point for reaching the adsorbate. In the second part of the plot can be seen a slow adsorption stage, which adsorbate begins to diffuse the inside of pores. In the final portion, due to remaining very low concentrations in the solution, intraparticle diffusion begins to slow and the equilibrium stage establishes.

As observed in Figure 4.16, the graph including dye concentrations of 500, 1000, 2000, 3000, 4000 and 5000 ppm shows that particulate diffusion occurs in two and three stages. At 500, 1000 and 2000 ppm, rapid surface adsorption happens continued by the equilibrium position while in other dye concentrations, it is observed in three stages of the graph. These results offer the approach that all dye molecules with the relatively low concentration are adsorbed with porous structure and dye molecules with higher concentration are held by both the external surface and inside of pores. As a contributions to these results, that hydrophilic adsorbent prepared with 3-Sulfopropyl methacrylate potassium salt found approximately 5 mmol sulfonate group per one gram provide to make external surface adsorption of dye very rapidly and as increased dye concentration, the resistance to mass transfer as pore diffusion emerges, which these results determine how to affected intraparticle diffusion rate constants.



**Figure 4. 16 :** Partial diffusion of adsorbate in the dye adsorption.

#### 4.4 Adsorption Isotherms

Langmuir, Freundlich and Dubinin–Radushkevich isotherms were used to analyze whether experiment results compatibility with theoretical values obtained from isotherm models. Firstly, one of the well known adsorption isotherm is langmuir equation which used for obtaining adsorption data shown in Equation 4.5 :

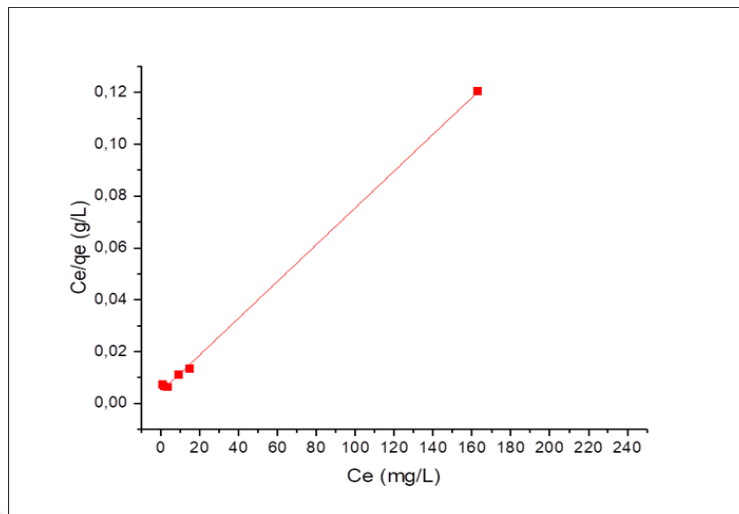
$$q_e = \frac{q_m b c_e}{1 + b c_e} \quad (4. 5)$$

As seen in Equation 4.6 the arrangement of this formula to a linear form is to simplify for evaluating the experimental data.

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} * K_L} + \frac{C_e}{q_{\max}} \quad (4. 6)$$

The demonstration of parameters in this formula are defined that  $C_e$  indicating the equilibrium concentration of dye in solution (mmol/L),  $q_e$  meaning the equilibrium amount of dye adsorbed on the adsorbent at time  $t$ , the maximum adsorption capacity of the adsorbent (mg/g) denoting the  $q_{\max}$ ,  $b$  defined as the adversely of dissociation constant of the ligand/surface interaction,  $K_L$  identifying the energy of adsorption constant are described as mention this text. According to this formula, it is determined

whether adsorbate is strongly adsorbed by assessing  $k_L$  value. In Figure 4.17, langmuir isotherm for methylene blue adsorption on PolyHIPE-SO<sub>3</sub><sup>-</sup>K<sup>+</sup> is shown.

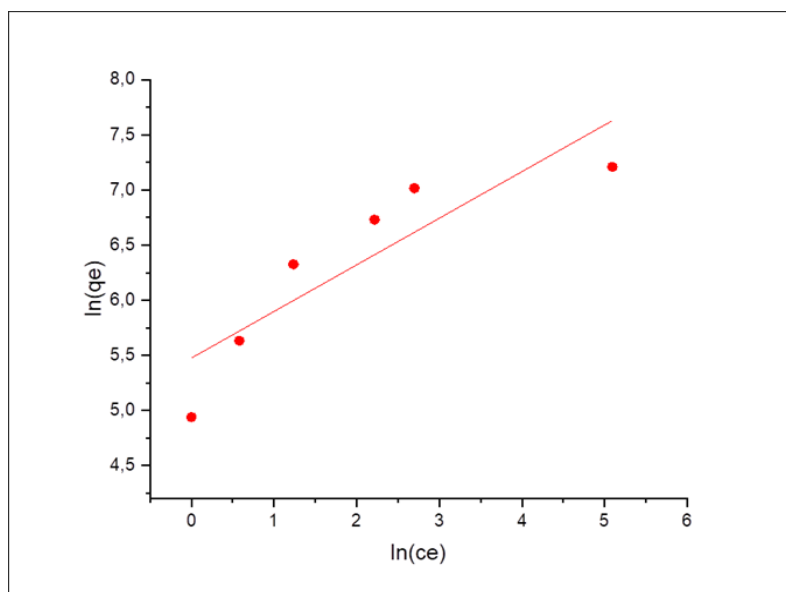


**Figure 4. 17 :** Langmuir isotherm for dye adsorption on hydrophilic polyHIPE.

The second adsorption isotherm used in this study is the Freundlich isotherm. The linear form of the Freundlich Equation 4.7 is generally represented as:

$$\ln q_e = \ln K_f + 1/n \ln C_e \quad (4. 7)$$

By utilizing linear formula Freundlich equation, both  $n$  value can be calculated with the slope of plot and  $K_f$  value can be found with the intercept of plot Figure 4.18, which represents Freundlich isotherm plotted using methylene blue adsorption data for polyHIPE-SO<sub>3</sub><sup>-</sup>K<sup>+</sup>.



**Figure 4. 18 :** Freundlich isotherm related to dye adsorption on polyHIPE.

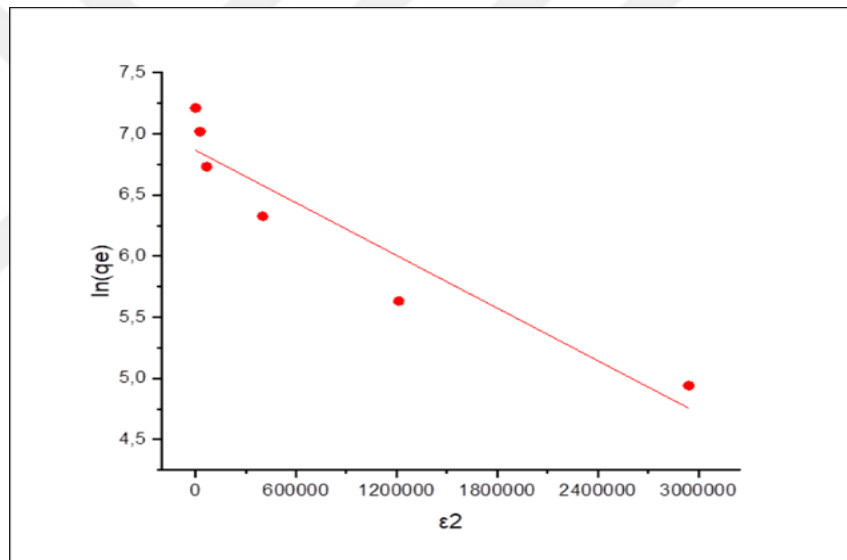
Dubinin–Radushkevich (D-R) is used to explain adsorption mechanisms. Generally, D-R isotherm is used based on some assumption which adsorbate fills pore rather than layer-by-layer surface coverage, thus it can be applied for polymeric adsorbents for substrates with the heterogeneous surface in place of porous polymer possessing homogeneous surface. The following Equation 4.8 is the D–R equation:

$$\ln q_e = \ln q_m - K\varepsilon^2 \quad (4.8)$$

By using the following Equation 4.9, the mean free energy (E) can be calculated.

$$E = (2K)^{-1/2} \quad (4.9)$$

Dubinin–Radushkevich (D–R) isotherms for methylene blue adsorption on polyHIPE adsorbents are represented with Figure 4.19.



**Figure 4. 19 :** D–R isotherm graph related to dye adsorption.

As a result, inferred from both kinetic and isotherm parameters shown with table 4.2 and Table 4.3, respectively, it is being observed that pseudo second order is convenient thanks to correlation coefficient being close to one value and langmuir isotherm gives both the compatibility of  $q_{exp}$  and  $q_m$ (theoretical) values and correlation coefficient close to one. Addressed to these inferences, methylene blue is captured on the adsorbent through chemical adsorption, which academic studies prove that it is a correct deduction as well [35].

**Table 4. 3** : The values of parameters related isotherms.

Langmuir		Freundlich				D-R			
$q_{\text{exp}}$ ( $\text{mg g}^{-1}$ )	$K_d$ ( $\text{mg L}^{-1}$ )	$q_m$ ( $\text{mg g}^{-1}$ )	$R^2$	$K_f$ ( $\text{L g}^{-1}$ )	n	$R^2$	$q_m$ ( $\text{mg g}^{-1}$ )	E ( $\text{kJ mol}^{-1}$ )	$R^2$
1483	0.1562	1409.39	0.999	238.82	2.36	0.7805	957.72	0.8356	0.899
-(ref 46)	1.40	417.12	0.998	15.62	3.108	0.913	418.17	3.352	0.8046

## 5. CONCLUSIONS AND RECOMMENDATIONS

In this thesis to obtain hydrophilic porous material bearing functional groups ( $\text{SO}_3\text{K}^+$ ), high internal phase emulsions (HIPE) were utilized as emulsion templates. The main advantages of this study are based on the contribution of monomer type and swelling property of material. The monomer with inherently functional group, thus, provided to eliminate the modification steps and in this way the high functional group capacity was obtained. Low crosslinked hydrophilic adsorbent showed both high adsorption performance for cationic dye methylene blue and fast water uptake. Also, this adsorbent showed good performances of removal cationic dyes like rhodamine B and malachite green carbinol i.e, the removal of 99% both dyes at 3 hours. The effect of initial dye concentration, pH, ionic strength, temperature, solid/liquid ratio on adsorption capacity of polyHIPE-- $\text{SO}_3\text{K}^+$  were studied. At the same time, adsorbent held approximately 34 grams of water per gram thanks to hydrophilic structure.

Kinetic measurement and isotherm studies were used for explaining the adsorption mechanism. The results demonstrated that, it can be acceptable to occur chemical adsorption between adsorbent and adsorbate. In conclusion, all the data obtained from this thesis make polyHIPE- $\text{SO}_3\text{K}^+$  a good candidate for elimination of cationic dyes from aqueous solutions.



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