MARMARA UNIVERSITY
INSTITUTE FOR GRADUATE STUDIES
IN PURE AND APPLIED SCIENCES

REMOVAL OF MICROPOLLUTANTS USING MOF

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MASTER THESIS

Department of Environmental Engineering

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ISTANBUL, 2022

MARMARA UNIVERSITY
INSTITUTE FOR GRADUATE STUDIES IN PURE AND APPLIED SCIENCES

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ACKNOWLEDGEMENT

I wish to show my appreciation to all of my supervisor Prof. Zehra S. CAN, my Assist.Prof. Seval GENÇ and Dr. Gülenay G. HACIOSMANOĞLU for dedicating their valuable guidance, innovative insights and support throughout the whole study. I would like to thank Assoc. Prof. Neslihan SEMERCİ, also, for her support. To all who have given a hand, I sincerely say thank you very much.

ÖZET

MİKROKİRLETİCİLERİN MOF KULLANILARAK ADSORPSİYON İLE GİDERİMİ

Metal-organik çerçeveler (MOF'ler), üç boyutlu çerçeveler oluşturmak için organik moleküllerle bağlantılı metal iyonları tarafından üretilen bir kristal malzeme sınıfıdır. Geniş yüzey alanı ve gözenek hacmi gibi ilginç özelliklere sahiptirler. MOF'lar, hem organic maddelerin hem de inorganic maddelerin özelliklerinden en iyi şekilde yararlanıldığı yapılardır. MOF'lar, oldukça umut verici, gözenekli adsorbanlardan biri olarak araştırmacıların ilgisini çekmiştir. MIL-101(Cr), özel bir MOF grubudur. MIL kısaltması, ilk sentezlendiği yer olan Lavoisier Enstitüsü Malzemesi'nden gelir. Son zamanlarda, yüksek gözenek hacmi, daha büyük gözenek boyutu ve yüksek termal ve kimyasal kararlılığı nedeniyle birçok araştırmacının büyük ilgisini çekmiştir. Formülü ($C_{13}H_{18}O_2$) olan ibuprofen, geçen yüzyılın ortalarında keşfedilen bir ilaçtır ve o zamandan beri ağrı kesici ve toksisitesi ile ilgili riskleri olan bazı hastalıkları tedavi etmek için ilaç olarak kullanılmaktadır. Diğer yandan, Bisfenol S, tıpta ve endüstride önemli yaygın bir şekilde kullanılan ve canlı organizmalar üzerinde olumsuz sağlık etkilere sebep olduğu düşünülen şüphelenilen Bisfenol sınıfından bir kimyasaldır.

Bu çalışmada, sudaki krom metal-organik çerçeve MIL-101(Cr) üzerine Ibuprofen'in (IBP) ve Bisfenol-S'in (BPS) adsorpsiyonunu araştırdık. Adsorpsiyon mekanizmaları ise FTIR analizi ile belirlenmeye çalışıldı.

Adsorpsiyon deneyleri, 200 rpm sabit hızda sıcaklık kontrollü bir çalkalayıcı (IKA, Almanya) kullanılarak kesikli modda gerçekleştirildi. 40 ml'lik cam şişelerde 10 ml sulu IBP numuneleri hazırlandı. Adsorban dozu 10 g/L ve adsorpsiyon sıcaklığı 25 °C idi. Herhangi bir zamanda adsorbanın birim ağırlığına adsorbe edilen IBP veya BPS miktarı, t, hesaplandı.

Adsorpsiyon öncesi ve sonrası numunelerdeki IBP veya BPS konsantrasyonları bir gaz kromatograf kütle spektrometresi (GCMS-QP2010, Shimadzu, Japonya) ile ölçülmüştür. Kullanılan yöntemin saptama sınırı, enjekte edilen 0,5 nanogram ibuprofen olarak belirlenmiştir.

Anahtar sözcükler: Adsorpsiyon, Ibuprofen (IBP), Bisfenol-S (BPS), Metal-organik kafesler (MOK), MIL-101(Cr), Mikrokirleticiler.

ABSTRACT

REMOVAL OF MICROPOLLUTANTS USING MOF

Metal–organic frameworks (MOFs) are a class of crystalline materials produced by metal ions linked with organic molecules to form three dimensional frameworks. They have interesting properties such as large surface area and pore volume. MOFs rely on making the best of the properties of both organics and inorganics. MOFs have attracted tremendous research interest as one of the most promising porous adsorbents. MIL-101(Cr) is a specific group of MOF. MIL stands for Material of Institute Lavoisier where it was originally synthesized. Recently, it attracted considerable attention of several researchers due to its high pore volume, larger pore size, and high thermal and chemical stability. Ibuprofen with the formula ($C_{13}H_{18}O_2$) is a drug discovered during the mid-decades of last century and has been used since then as a pain killer and as a medicine to treat some diseases with risks related to its toxicity. Bisphenol S is a chemical of the Bisphenol class that plays a significant role in medicine and industry and is suspected to have adverse health impacts on living organisms.

In this study, we investigated the adsorption of each Ibuprofen (IBP) and Bisphenol S (BPS) on chromium metal-organic framework MIL-101(Cr) in water. The adsorption mechanisms were investigated using FTIR analysis.

The adsorption experiments were performed in batch mode in a temperature controlled environment. The amounts of IBP and BPS captured on unit weight of MOF were calculated.

IBP and BPS concentrations in the samples before and after adsorption were measured by a GC-MS device. The detection limit of the method used was 0.5 nanogram ibuprofen injected.

Keywords: Adsorption, Ibuprofen (IBP), Bisphenol S (BPS), Metal-organic framework (MOF), MIL-101(Cr), Micropollutants.

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ABBREVIATIONS

BPS : Bisphenol S

Cr : Chromium

DCM : Dichloromethane

DI : De-ionized

FTIR : Fourier Transform Infrared

GC-MS : Gas Chromatography Mass Spectrometry

IBP : Ibuprofen

MOF : Metal Organic Framework

MP : Micropollutants

SEM : scanning electron microscopy

TPA : Terephthalic acid

XRD : X-ray Diffraction

XRF : Energy Dispersive Isotope-Source X-Ray Fluorescence

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1. INTRODUCTION

1.1. Micropollutants

Micropollutants (MP) are pollutants that seriously impose challenges on the traditional physical methods of extracting them from aqueous media that's only if we assumed that detecting them is possible using the analytical means in hand. Emerging micropollutants are a novel class of pollutants that are being added recently to the environment before having the chance to be analyzed sufficiently in terms of their health, environment and sustainability impacts. Micropollutants are emerging from sources like (pharmaceutical discharge, personal care products and cosmetics and the sanitary wastewaters containing them, drugs, industrial waste, micro plastic and pesticides). [1]

The impacts of micropollutants on the living organisms haven't had the work needed to be inclusively understood enough to lay guidelines for its safe use as a whole since it is practically difficult to track every single chemical being used discovered or manufactured, therefore we have witnessed some adverse interactions of some micropollutants with the living tissues or seen what seems to be attributed to be an influence. It has also been noticed that antibiotics molecules which have found a way to reach natural environments may have a role in raising the resistance in the germs found there against those antibiotics [2][3].

Due to its poor potential of blocking MP, conventional wastewater treatment plants are deemed to be one of the least expected sources of emission [4]. It's nearly impossible to count only on technologies that have been in use during the last few decades in the removing of emerging pollutants for the reason of the widely expanding variety of their

nature, behavior and properties [5].

On the contrary of developing countries that suffer from either insufficient clean water sources or lacking the financial power to access them, developed countries that depend radically on industry to maintain their well-being are in an accelerating manner reaching a worrying condition of heavy contamination [6][7]. Regional conditions of countries are a non-negligible factor to be added to the equation during the study of possible application [5].

MPs sources broadly vary from agriculture to household, traffic points to industries and their mobility makes pathways of their fate in water bodies as broad [8]. (See figure 1.1)

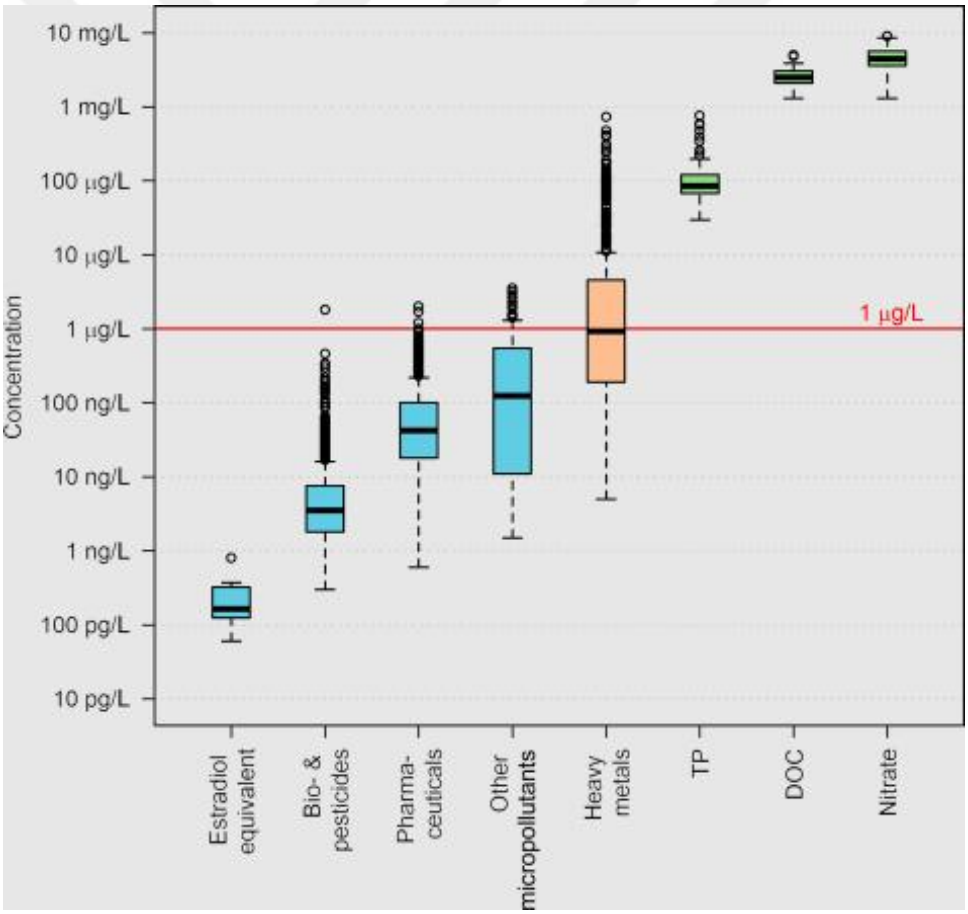

Figure 2.1. Micropollutants' different sources of emission

Pharmaceuticals and personal care products (PPCPs) have been occupying a radical role in our lives for the last one and a half decade. This group of compounds covers a wide

class of chemical contaminants that result from human utilization and disposal from their bodies adding to that veterinary product, such as over-the-counter and prescription drugs, disinfectants and fungicides used in various practices [9].

PPCPs are an environment-threatening emerging concern given the fact that, this class of output consists of not only novel compounds commercially accessible , but also many compounds that were only lately noticed, thanks to the developed technologies alongside analytical strategies that together are able to detect as low as sub-ppt level [10].

Reported examinations of Germany's rivers and wastewater showed concentrations of PPCPs in ppb [11]. The already under operation purifying processes of drinking water and wastewaters have proven ineffective uptake of PPCPs, unlike advanced processes such as activated carbon adsorption, chemical oxidation or ozonation which showed better abatement of PPCPs [12]. The working mechanism of activated carbon technology counts on the presence of some organic functional groups like benzene rings and amino groups. These groups tend to enhance the adsorption affinity of their containing compounds by the active sites of activated carbon granules [9][10]. Not to mention the technology's powerful potentials in removing dyes [15-17], phenols [15][17-19], endocrine disrupting compounds [20][21] and metals [11][12].

One obstacle facing the control of emergence and discard of PPCPs is the inadequate knowledge about those chemicals' long term effects that result from continuous exposure. Thus, the acceptable amounts to be discharged in the habitat haven't had complete regulations [9]. Regardless whether these chemicals have short life times or not non-stopping release still guarantees actual pollution.

1.2. Ibuprofen

Ibuprofen is a drug developed by Dr. *Stewart Adams* (at Boots Pure Drug in Nottingham, UK) during 1960s after a strenuous work that lasted more than a decade to treat inflammation and relieve pain [22]. The credits of the discovery of ibuprofen along other similar compounds were given to both John Nicholson and Stewart Adams in 1963 as a patent. Following studies have shown the effectiveness of Ibuprofen to treat other health conditions such as rheumatoid[1] and juvenile idiopathic arthritis[2].

1) Rheumatoid arthritis, or RA, is an inflammatory disease that causes malfunction in the immune system that makes the latter attack healthy cells. This disease usually affects limbs' joints making them painfully swell as a sign of inflammation. Damage can go further to deform the infected joints. it could also affect other organs such as lungs, hearts and eyes [23].

2) Inflammatory disease that targets joints in children, that appears as fever and pain, rigidness and swelling in the affected joints some of which last only few months, others remain several years. This disease can lead to serious growth complications [24].

Research has been carried on expecting IBP to have an exceptional role in the protection against cancers and Alzheimer disease [25].

It still comes with adverse effects on certain patients such as the ones with abdominal or blood pressure problems, thus they are restricted from using it [26].

IBP drug was the first non-steroidal anti-inflammatory drug (NSAID) licensed for over-the-counter use in 1983 [28].

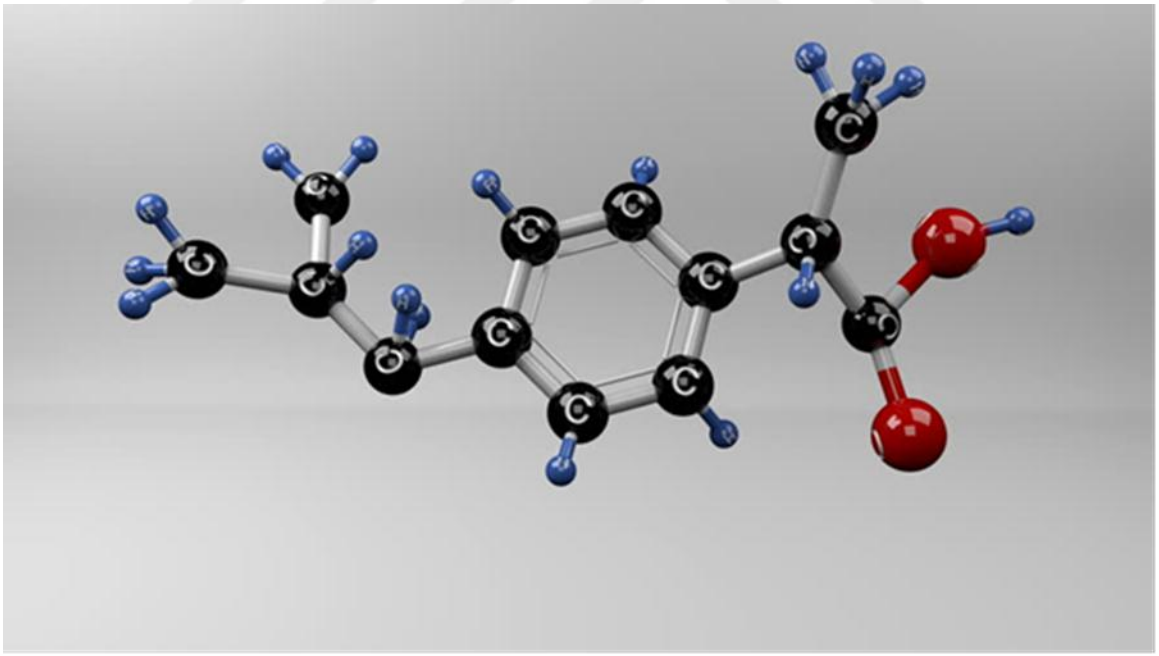

Figure 1.2. Ibuprofen molecule

1.2.1. Chemistry

Here are a few of the physical and chemical properties of Ibuprofen [27]:

Table 1.1. Some properties of Ibuprofen

Chemical formula	$C_{13}H_{18}O_2$	Toxicity	Toxic if swallowed. LD50 is 636 mg/kg in rats.
IUPAC Name	2-[4-(2-methylpropyl)phenyl] propionic acid	Boiling point	157 ºC
Appearance	Solid white crystals	Safety	Irritant, Health Hazard
Molar mass	206.28	Stability in nature	Stable
Solubility in water	21 mg/L	Melting Point	75–77 ºC
Solubility in organics	Readily sol in most organic solvents	Solubility in acetone (g/100 g)	130.63 (25°C)

1.3. Bisphenol S

Bisphenols are a group of organic compounds serving many roles medicine and industry (in plastics production as a medium, dentistry supplies, food reserving, etc.) BPA was the first and until some point the most popular used one before it was banned from usage in the nutrition industry in certain countries due to its negative health impacts. BPA is a *xenoestrogen* which is a term given to chemicals that simulate the functionality of estrogen within the living tissues. BPS was then chosen as the substitution of BPA. Both BPA and BPS are suspected to be a reason for some health concerns one of which was proposed by Boucher et al [29] on the lipid build-up in adipocytic cells motivated by BPS presence within the human tissues. (See figure 1.3)

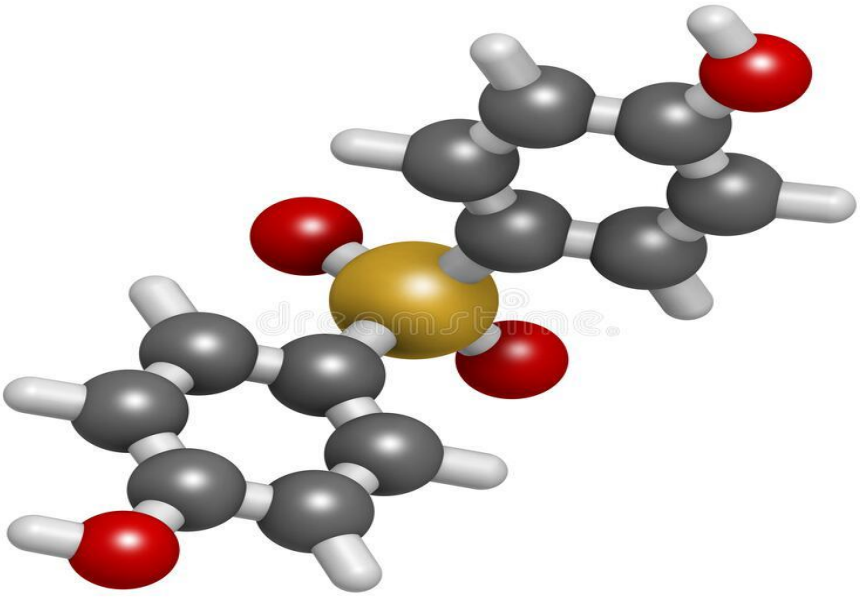

Figure 1.3.BPS molecule

The medicine community first recognized the estrogenicity of BPA about 40 years after it was discovered in the 1891 but the actual awareness of its health and environmental impacts with evidence back-up had not risen until late in the 1990s. Coping with the changes in the view of BPA's safety by communities, BPS was introduced as a substitute to meet industries' needs in the mid-2000s and it was known for being relatively safer depending on the fact that it holds excellent thermal, optical (of how it responds to light exposure), and mechanical properties as polymers. Despite that, evidence emerged afterwards proving the association of BPS with hormones disturbance [30]. Furthermore, reports revealing its presence in human urine were published [31]. Back to Boucher et al [29], BPS showed a connection to obesity through its lipid fixation on adipocyte cells as some previous investigations reported similar provoking impacts of BPA as well on the emergence of adipokines, such as adiponectin that could worsen the metabolic syndrome (combination of diabetes, high blood pressure and obesity) [32][33]. One major point worth mentioning is the significant evidence foun

d on the indisputable endocrine disrupting connection of Bisphenolic compounds.

There seems to be some gaps -in refuting doubts of bisphenols' risks on human health- left that needs to be filled in order to set the ground from which environmental

organizations and human health authorities can count on to lay legislations meeting the goals of sustainability. On top of the challenges standing in the way of banning living entities' exposure to bisphenols is its low-cost production in plastic industries which makes finding a substitute not fairly encouraging. Another aspect of concern is the high amount of bisphenols used in some studies that may not mimic the actual case in reality thus providing insufficiently solid evidence. Due to differentiation in drug movement within the tissues and the corresponding analytically detectable response across species, between sexes of same species alongside some other factors make it difficult to have study conditions that apply on all animals.

Experimentally, the above claims can be addressed by a study example held by three agencies in 2012 under the co-foundation named CLARIT- BPA [34]. On a scale of thousands experimental samples, rats of both sexes were gavage-fed with 5 doses of BPA distributed throughout the day added to that 2 doses of estrogen at the National Center for Toxicological Research at Jefferson, USA. This process began with pregnancy and seized at 2 years of age thoroughly-covering study points of behavior, brain, reproduction, metabolic activity, cardiovascular, and cancer carried out by a total of 12 laboratories across the USA. Academic researchers at universities have been involved in similar matters at their own laboratories.

The main problem lies in the fact that the industry have switched from a harmful chemical to another that haven't sufficiently examined yet which certainly must have the research sector to employ all the possible facilities in the disclosure of the impacts of BPS by conducting applicable experiments.

Notably, in addition to bisphenol A and bisphenol S, other bisphenols, including bisphenol F and BPA diglycidyl ether, also have shown a relation to endocrine-disruption. With all the points mentioned, the following question rises, to which extent should the class of bisphenol compounds be taken into account upon future safety regulations?

1.3.1. Chemistry

Below, there is a table showing a few properties of BPS [27]:

Table 1.2. Some of BPS properties

Chemical formula	$C_{12}H_{10}O_4S$	Toxicity	Toxic if swallowed. LD50 is 4556 mg/kg in rats.
IUPAC Name	4,4'-Sulfonyldiphenol, Bis (4-hydroxyphenyl) sulfone	Boiling point	505.3 °C
Appearance	White, crystalline powder	Safety	irritant, hazardous
Molar mass	250.27	Stability in nature	Stable
Solubility in water	1100 mg/L (Insoluble)	Melting Point	240.5 °C
Solubility in organics	Soluble in ethanol and ether.	Solubility in acetone (g/100 g)	No info in the literature

1.3.2. BPS uses

Uses in industry: used as dyes, ion exchange agents, additives for paints and coating, surface treating agents plating agents, etc.

Uses in commerce: leather and textile production, thermal paper production, etc.

Uses in chemical processes: intermediates, solvents, wash-resistance agents, etc.

1.4. MOF

Reticular chemistry (from the Latin word *reticulum* which means net-shape) is a field of chemistry interested in bonding special chemical bodies (molecules and clusters) by firm links to make structures in coordinated built such as metal-organic frameworks (MOFs).

In MOFs case, metallic molecules join with each other by organic linkers to result in crystalline porous frameworks. MOFs combine the synthetic control exercised in making organic molecules with the numerous geometric and compositional possibilities by using inorganic units [3] (See Figure 1.4).

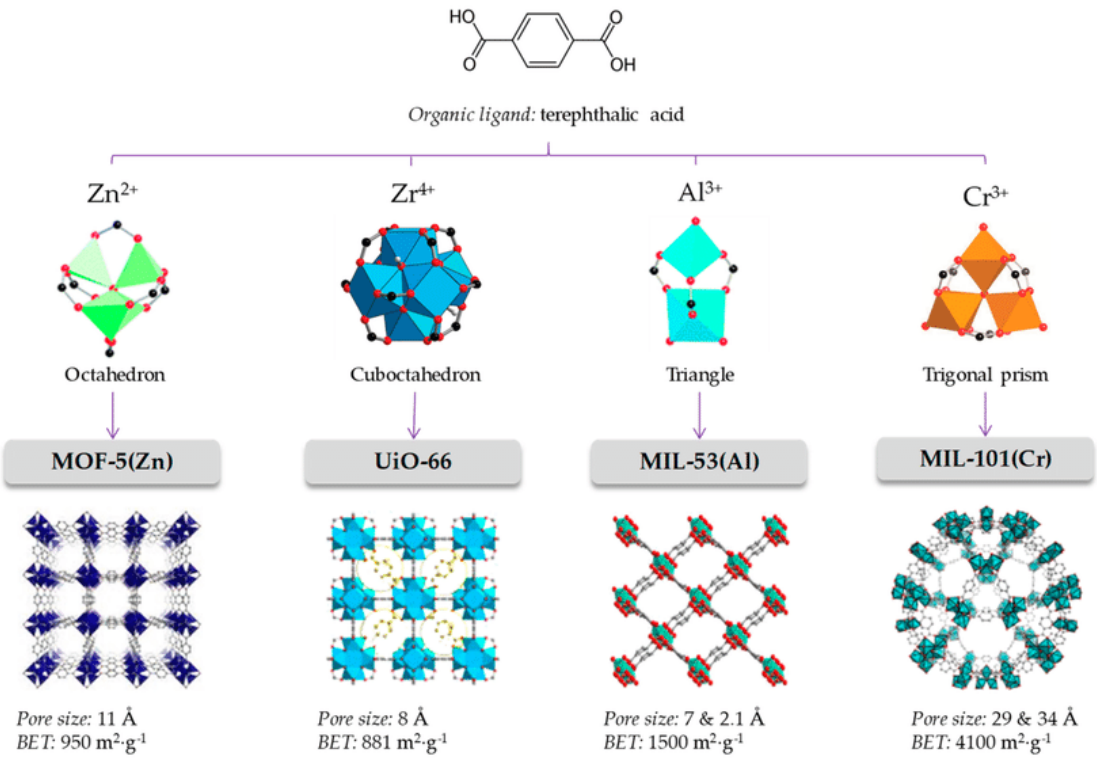

Figure 1.4. Different MOF types and their molecular geometry. Left to right (Zinc, Zirconium, Aluminum and Chromium)

MOFs are simply the connection of two molecules one of which is metal and another is organic rod-like bridge that arrange in a structural form to make a bigger molecule that has proven to have marvelous chemical properties and active sites. MOFs simulate the adsorption mechanism naturally-found in Activated Carbon attributed to the vast surface area and porosity they both carry.

Early findings sharing composition characteristics with what we know as MOF today were developed by coincidence centuries ago. As for the first trace reported, the latter takes us back to the eighteenth century during the work on synthesizing of a pigment named (Prussian or Parisian Blue) in Berlin, Germany [35][36]. According to Georg E. Stahl's book that tells this story, a paint maker named Johann J. Diesback used Johann K.

Dippel's laboratory to develop an organic red paint using *cochineal red* that was given the name (Florentine lake). Diesbach seemed to have had to borrow some potash not knowing that it was polluted with hexacyanoferrate ions [M2Fe(CN)6] (M= Na+, K+) from Dippel's work. Unexpectedly, a blue precipitate resulted having the chemical formula of (Fe^3_4 [$Fe^2(CN)_6]_3 \cdot H_2O$) [37].

The drive to investigate the adsorption possibility of the MPs adopted by this study was inspired by (Tang Y. et al). The latter is a study which has proven over 90% reduction of BPA by TiO2@MIL-101(Cr) after a contact time of 240 minutes[62].

1.4.1. Adsorption kinetics

Adsorption mechanism follows two equations describing the former's kinetics. Kinetics is simply defined as the amount of the solute to be trapped by an adsorbent under specified factors contributing in it. Lagergren's first order and Ho's second order kinetic equations are the one concerned with adsorption processes onto the surface of a solid adsorbent.

Lagergren's first order or pseudo-first order, equation (1.1):

$$\frac{dqt}{dt} = k1(qe-qt) \qquad (1.1)$$

Where; k1 is the pseudo-first order reaction rate constant (1/h); qe is the solute removed (mg/g) at the state of equilibrium; qt is the solute adsorbed at time t.

By substituting equation's variables as t = 0 to t = t and qt = 0 to qt = qt, It can be restructured for linearized data plotting, as shown by equation (1.2):

$$\log(qe-qt) = \log(qe) - \left(\frac{k1}{2.303}\right) t \qquad (1.2)$$

Finding k1 is possible by plotting the data arithmetically then calculating the slope of the line resulting that is the numerical value of k1.

The pseudo-second order equation is presented below, equation (1.3):

$$\frac{dq_t}{dt} = k_2(qe-qt)^2 \qquad (1.3)$$

Where; k2: the pseudo-second order reaction rate constant (g/mg.h); qe: the adsorbate

removal (mg/g) at equilibrium; qt: the adsorbate removal at time t.

By simplifying the Equation above, equation (1.4) is obtained:

$$\frac{dq_t}{(qe-qt)^2} = k_2 dt \qquad (1.4)$$

By integration, using the boundary conditions of t = 0 to t = t and qt = 0 to qt = qt, equation (1.5) results:

$$\frac{t}{qt} = \frac{1}{k_2 qe^2} + \left(\frac{1}{qe}\right)t \qquad (1.5)$$

From plotting (t/qt) versus time, the slope and the intercept give us qe and k_2 values respectively. The product k_2qe^2 represents the initial adsorbate-uptake rate. The half-life time of the target adsorbate which will remain at equilibrium and is usually utilized as a measure of adsorption rate and is obtained by the rearrangement of the above equation to settle in equation (1.6) under the assumption of t = t1/2 and qt = qe/2:

$$t\,1/2 = \frac{1}{k_2 qe} \qquad (1.6)$$

2. AIM AND SIGNIFICANCE

We have considered using our synthesized MOF in the adsorption of dissolved micropollutants from aqueous media in order to study adsorption capacity and decide whether it is feasible and efficient. This could add a cost-efficient and less chemicals-involving purifying technique to handle challenging pollution scenarios caused by MPs that are impossible to stop their emergence either for having an essential role in the human well-being (ex; pharmaceutical MPs) or for playing a radical role in industry and

commerce (ex; cosmetics).

3. MATERIALS AND METHODOLOGY

3.1. MOF Powder Production

3.1.1. Materials

Chromium nitrate salt [Cr $(H_2O)_6$]$(NO_3)_3 3H_2O$ is a green crystal that has a solubility of approximately 80 g/100 ml water at 20^oC which is classified as high solubility. The crystals melt at 60^oC. As for its structure, the chromium molecule is attached to six water-

like group making a three dimensional shape with three nitrate anions and three water extensions responsible for crystallization. Chromium nitrate salt plays a radical role in dyeing industry [38].

Terephthalic acid as a white powder with the chemical formula $C_8H_6O_4$ is an organic acid poorly soluble in water 0.0015 g /100 ml at 20° C. de-ionized water is also needed and last, hydrofluoric acid (5M) which is colorless liquor that is used in the production of fluorine- containing compounds, acidic and corrosive.

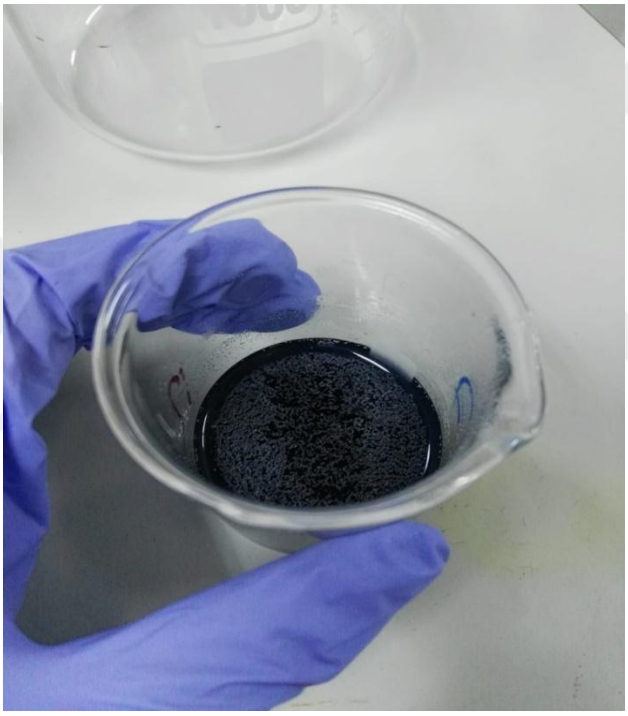

Figure 3.1. Final mixture of reactants before heating up

3.1.2. MOF synthesis

1.205 gram of chromium nitrate salt, 0.5 gram of terephthalic acid powder, 15 ml of de-ionized water and 0.6 ml of hydrofluoric acid were all mixed in a 50 ml glass flask. The sample was then stirred for 24 hours by a magnetic stirrer at 25 ^oC. Then, it was placed into a 50mL Teflon-lined stainless steel autoclave reactor and kept in an oven at 220^0C for 8 hours. (See figure 3.2-a and figure 3.2-b).



Figure 3.1-a. The mixture inside the plastic container



Figure 3.2-b. The reactor used

The reactor was taken out of the oven and let cool down for a few hours (see figure 3.3). The content was moved out of the reactor and put in a jar and sealed. In order to split the supernatant from the green solids, we let it sit for an hour. The split supernatant was carefully disposed using a pipet leaving the solids at the bottom of the jar. This process was followed by purification to obtain the final MOF powder.



Figure 3.3.MOF after heating up process was over

3.1.3. Purification of the synthesized MOF

In the precipitate at the bottom of the jar, white powder was still observed referring to TPA tendency to dissociate in water and settle as a white powder. Thus, cleaning the samples from TPA was needed.

For cleaning, dichloromethane and methanol solvents were poured in sequence in the following manner:

DCM solvent was boiled over a heater and 10 ml of it was poured on the MOF sample that was manually shaken to enhance solvent exposure to white TPA precipitate. The same procedure involving methanol solvent was applied. Using a pipette, the already applied solvents were taken out of the MOF sample making a room for another 2 sets of cleaning courses that were performed as the earlier-mentioned previous course. After finishing cleaning with organic solvents, the sample was put in a 60 ^{o}C oven to dry completely.

The dried sample was then cleaned with DI water a few times to ensure no organic solvents left could interfere with either adsorption or residual concentration detection in

following steps. Finally, our MOF was dried under vacuum to get a final green granule. (See photo 3.4)

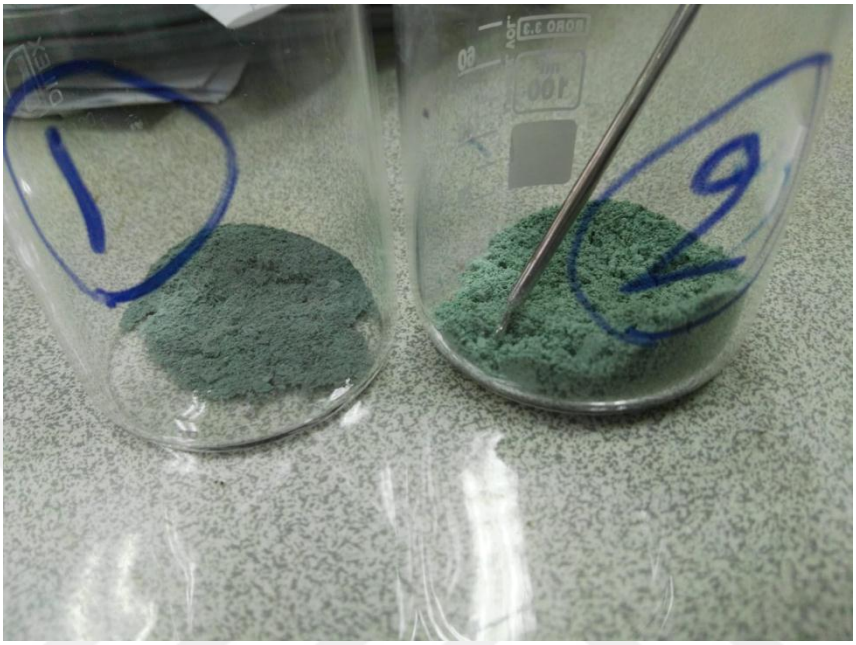

Figure 3.4. The purified final product

3.2. Preparation of Ibuprofen Stock Solution

The chemical properties of IBP make it pretty hard to achieve a significant concentration in water due to the poor solubility of ibuprofen. Thus, we have decided to dissolve it in an organic solvent (acetone) first as described below.

0.01 of IBP powder was spiked with 10 ml of (100% pure) acetone and kept in dark glass amber at 4 ^{o}C for preservation purposes.

3.3. Preparation of Bisphenol S Stock Solution

The production of BPS stock solution followed the exact same manner as described above for IBP:

0.01 of BPS powder was spiked with 10 ml of (100% pure) acetone and kept in dark glass amber at 4 ^{o}C in the freezer.

3.4. Batch Adsorption Experiments

A set of 10 jars (20 ml) were taken and labeled from 1 to 10, 5 of which held the samples numbered (1, 2, 3, 4 and 5) and the other half held their blanks as (6, 7, 8, 9 and 10), respectively. A mass of 0.01 gram of MOF powder was transferred into each of the 5 sample jars leaving the rest of the jars empty. A volume of 5ml of DI water was then poured into each of the 10 jars using a pipette followed by the addition of IBP stock solution (as demonstrated in table 3.3):

Table 3.1. Batch experiment (IBP)

Jar no.	IBP poured (µl)	Jar no.	IBP poured (µl)
1	100	6	100
2	200	7	200
3	300	8	300
4	400	9	400
5	500	10	500

At last the final volume inside each jar was completed to 10 ml using DI water. The openings of jars were sealed with para-film then closed with matching caps.

The 10 jars were placed into a shaker at 25 ^{o}C and 220 rpm for 24 hours.

Separately, the same procedure as above was performed for the adsorption of BPS experiment giving the following table:

Table 3.2. Batch experiment (BPS)

Jar no.	BPS poured (µl)	Jar no.	BPS poured (µl)
1	100	6	100
2	200	7	200
3	300	8	300
4	400	9	400
5	500	10	500

These experiments were carried out five times to ensure accuracy.

3.5. Concentration Detection

3.5.1. Detection methodology

The residual concentrations of IBP and BPS that were not captured by MOF had to be detected to assess adsorption performance of the synthesized adsorbent. The analytical instrument used was Gas Chromatography Mass Spectroscopy (GC-MS).

GC-MS Instrument

Gas chromatography mass spectrometry is an analytical method to measure concentrations of organics in the micro or nanosize. It basically consists of two parts; GC and MS. The results are displayed by a computer as numerical data and chromatograms.

1. *GC Technique*

By applying high temperature, the introduced sample evaporates inside a metallic column where it flows through until it finds the exit. The column contains an inert, solid support material coated with a liquid stationary phase. While flowing through the column the analyte interacts with the stationary phase within the column. The driving force that moves the analyte forward in the column, is the mobile phase, which is an inert gas such as helium. While flowing through the column, the analytes either adsorb on the inside wall of the column (the ions in the liquid or stationary phase) or continue flowing in the gas phase, and thus, separation occurs. What cause the separation are the differences in nature of the analytes which we can summarize as (boiling points, molecular weights, polarity and partially column temperature). Samples of lower boiling points remain in the gas form, which eventually travel faster than the captured samples, therefore, reach the detector or exit first. The longer the path of travel the better the samples are separated.

To help the smooth flowing of the sample, an inert carrier specific gas is pumped to push the evaporated sample into the column. This gas is chosen in a way to ensure that it does not react or interfere with the sample or separation of samples.

This still cannot identify the sample. A known sample, that will work as the reference needs to be introduced to the instrument first (needs to be registered) so that the instrument can measure the next sample according to the mentioned reference qualitatively.

As for quantitative identification, the area under the curves or graphs is proportional to the amount of sample detected but it is not possible to exactly identify an organic molecule using Gas Chromatography alone. Another analytical technique is typically coupled with the GC called Mass Spectroscopy.

2. *MS Technique*

Mass Spectroscopy is simply a tool to identify organic compounds based on their molecular weight. The mechanism is described as following:

A sample is introduced to the instrument and heated until it turns into a vapor. Then, by using a beam of electrons equipped within the instrument, the atoms are bombarded in order to ionize them (the beam strikes an atom and eject an electron from the outer orbit). The ionized atoms are dragged towards a magnetic field which makes the atoms line up in order according to the lightest to the heaviest. Then, it displays them in the mentioned order on the display panel.

Just like the GC technique, the instrument needs to be calibrated with reference chemicals so that it can compare the matching of further samples to them.



Figure 3.5. Shimadzu's GC-MS instrument

3.5.2. Residual concentration

After shaking for 24 hours, our jars were taken out. The jars containing MOF were filtered from the green particles with 0.45 micron filtration papers into different new jars.

10 vials (1.5 ml) were labeled from 1 to 10 to hold the samples. 1 ml of each sample and blank were poured into corresponding vial using a pipette. 100 micro liter of surrogate (Anthracene D10) was also poured into all ten vials. The samples had to dry out; therefore the vials were placed in an oven at 60 ^{o}C until completely dried.

Acetone was the solvent used for the dissolution of the dried sample. For that reason, 100 micro liters was added into each of the 10 vials and sonicated for 10 minutes (intensity of 10% at room temperature). The sonicated samples were then transferred into different 10 glass inserts placed into numbered used vials (as the inserts along with their content will not be contaminated) sealed with caps and at last introduced to the GC-MS auto-sampler in order to be analyzed.

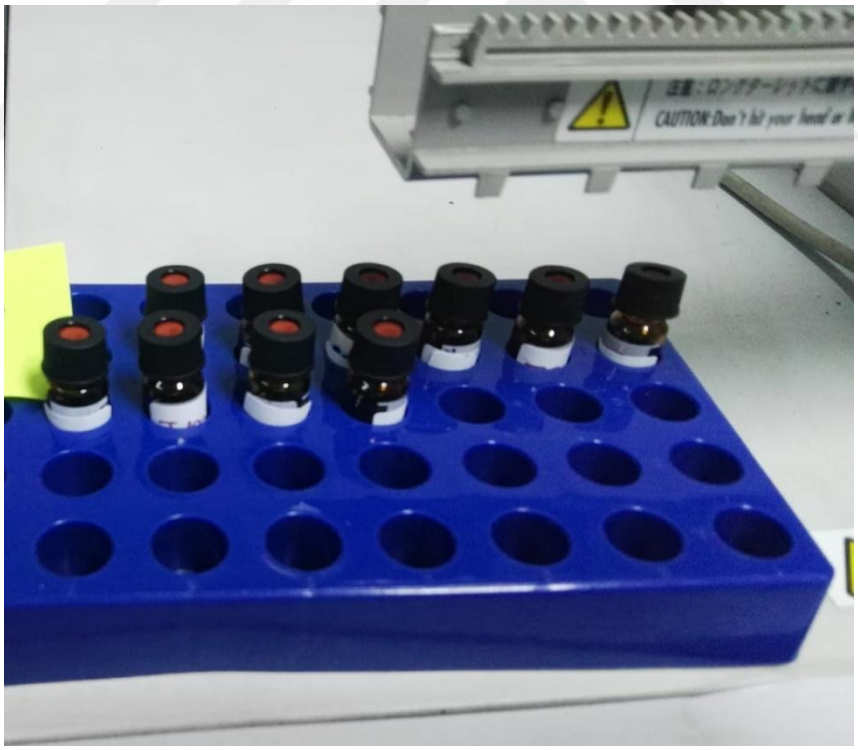

Figure 3.6. Samples placed inside of glass vials, getting ready to be introduced to GC-MS instrument

3.6. Characterization of Synthesized MOF

Scanning electron microscopy (SEM) was employed to monitor the morphologic

characters of the synthesized MOF surface. SEM images were obtained using a Zeiss Evo 10 electron microscope (Germany).

The X-ray diffraction (XRD) pattern of the synthesized MOF was determined at Marmara University Metallurgical and Materials Engineering Department laboratory using Rigaku XRD apparatus (Rigaku Ltd., Japan). The samples were scanned in the 2θ range of 5° – 105°.

The Cr content of the synthesized MIL-101(Cr) was determined by X-Ray Fluorescence using Niton XL Thermo Scientific XRF at Marmara University Metallurgical and Materials Engineering Department laboratory .To perform the XRF analysis, samples were vacuum dried for 24 hours at (105° C) and under 75 mmHg before they were taken to be analyzed.

Fourier-transform infrared spectroscopy (FTIR) analysis technique was used to identify the functional groups present in TPA, the organic linker used in MIL-101(Cr) production, organic micropollutant IBP or BPS, MIL-101(Cr) and MIL-101(Cr) after IBP or BPS adsorption. FTIR spectra were obtained using a Jasco FT/IR-4700 spectrometer (Jasco, Japan) in the spectral range of 4000-450 cm^{-1}.

For the FTIR analysis a total of four samples were prepared. One was taken from the micropollutant studied as clean powder, the second one was taken from TPA powder, the third was taken from a pure non-used MOF powder after vacuum-drying for 24 hours at (105^{0} C) and under 75 mmHg and the last was taken from MOF after it had been used in an adsorption experiment which followed the manner described below:

100 mg of MOF was added to 20 mL of de-ionized water containing the MP studied of a concentration of 50 mg/L. the mixture was allowed to stay in the shaker for 24 hours (25°C and 220 rpm). later, the mixture was eventually taken out, filtered using filtration papers (0.22 micron) and dried in the oven for 24 hours at (105° C) and under 75 mmHg following the same drying procedure as the third sample mentioned above. The dried powder was then scraped from the filtration paper and sent to the FTIR along with the three others.

4. RESULTS AND DISCUSSIONS

4.1. Characterization of the Synthesized Adsorbent

The adsorbent material synthesized in this study was characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), X-ray fluorescence (XRF) analyses, and

Fourier transform infrared (FTIR) spectroscopy,

4.1.1. SEM analysis

Scanning electron microscopy is a powerful instrument for investigation of materials' size and morphology. SEM images of MOF particles synthesized in this study are given in Figures 4.1-a and 4.1-b.

The study of MOF structure by SEM led us to the addition of a purification step to the MOF production method.

Figures 4.1-a and 4.1-b show the SEM image of the green product obtained before purification step was applied. In these figures, the octahedral crystals of synthesized MOF are visible with a diameter in the range of 500 nm to 1 micron. However, rod-like crystals are also visible in these figures. We assumed that the rod-like crystals were the precipitates of the unreacted, excess TPA, and could be eliminated with purifying by appropriate solvents.

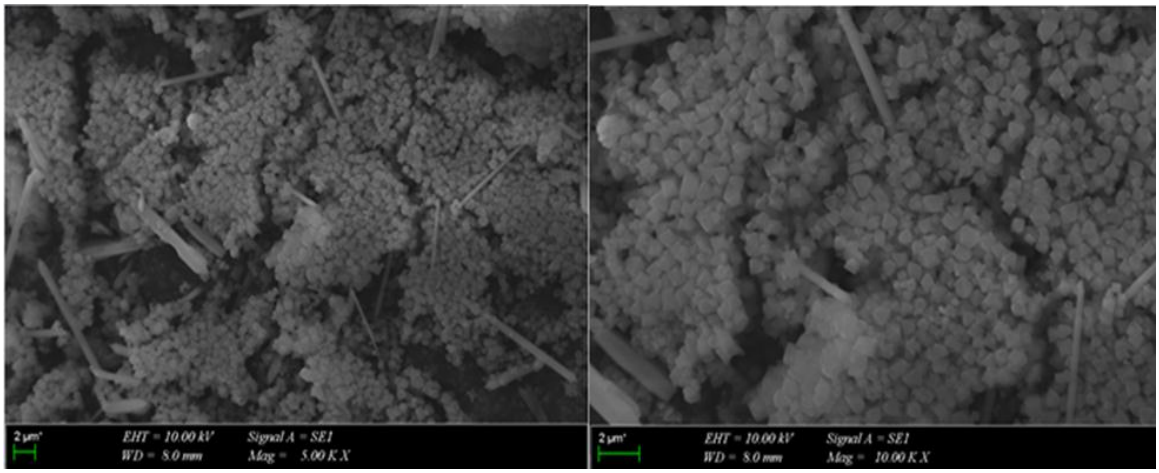

Figure 4.1.SEM images of the green precipitate obtained before purification was applied. (a)5.00X (b)10.00X Magnification

SEM images in Fig 4.2 clearly demonstrated that a purification procedure was required to remove the unreacted, excess TPA before the synthesized MOF could be used as an

adsorbent. Based on this finding, a purification procedure was developed and added to the MOF production method as described in Section 3.1.3.

Figure 4.2 presents the SEM images of the purified final product. The absence of rod-like crystals in each of Figure 4.2-a and Figure 4.2-b clearly shows that the purification step dissolves and removes the unreacted TPA.

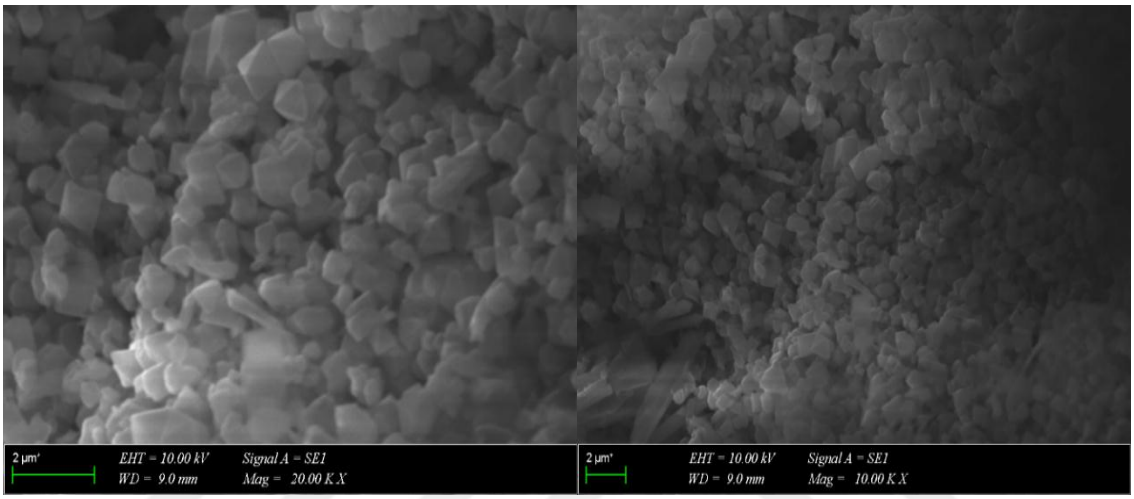

Figure 4.2.SEM images of the final MOF product after purification was applied. (a)20.00X (b)10.00X Magnification

4.1.2. XRD analysis

X-ray diffraction (XRD) is a nondestructive technique employed to determine detailed information about the crystallographic structure of a material. It enables verification of crystallinity. It works by irradiating a material with incident X-rays. Then, the X-rays returning from the sample surface are analyzed in terms of their intensities and scattering angles.

Figure 4.2 displays the XRD analysis of synthesized MOF using Rigaku XRD apparatus (Rigaku Ltd., Japan). The instrument settings were in the 2θ range of 5° – 105°. The XRD patterns of MIL-101(Cr) mainly shows the characteristic peaks of the two phases, which are the characteristic diffraction peaks of MIL-101 (Cr) between 2θ=6°-14° and the characteristic diffraction peaks of terephthalic acid between 2θ=15°- 31°, respectively. There is a good agreement between reported XRD pattern for MIL-101(Cr) and the one

obtained here. The obtained XRD patterns depicted in the figure confirm the highly crystalline nature of the synthesized MIL-101 (Cr)

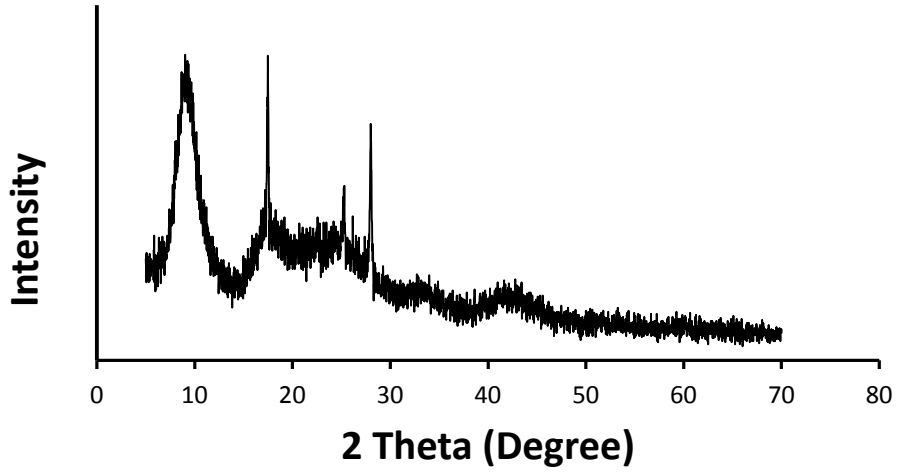

Figure 4.3.XRD analysis of the produced MOF

4.1.3. XRF results

The basis for XRF technique is the generation of characteristic X-rays from a sample irradiated by an energetic beam. In principle, the concentration of the element giving rise to the characteristic X-rays can be determined directly. Therefore, using this technique, we were able to determine mass percentages of the elements making up the MOF sample. Table 4.1 shows the mass percentages of the elements determined by XRF. As can be seen in Table 4.1, XRF analysis of MOF, clearly shows the chromium loading into the synthesized MIL-101 (Cr).

Table 4.1. Mass percentages of the elements found in the synthesized MOF sample

Element Name	**Percentage of Element (%)**
Cr	93,191
Fe	3,584
Si	0,735
Nb	1,259

Others	1,231

4.1.4. FTIR results

Fourier-transform infrared spectroscopy (FTIR) analysis technique was used to identify the functional groups present in TPA, the organic linker used in MIL-101(Cr) production, organic micropollutant IBP or BPS, MIL-101(Cr) and MIL-101(Cr) after IBP or BPS adsorption. The spectra are presented in Figure 4.4 and Figure 4.5.

Figure 4.4 shows the FTIR spectra for TPA, IBP, MOF before adsorption and MOF after IBP adsorption. TPA is a dicarboxylic acid. IBP is also a carboxylic acid. Carboxylic acid molecules have C=O, O-C-O, C–O, and O-H bonds, giving them several diagnostically useful FTIR bands. The strong bands observed in Fig.4.4-a and Fig.4.4-b at around 1700 cm^{-1} correspond to C=O stretching of carboxylic acid groups. This band is wider in Fig.4.4-a, because TPA has two carboxylic acid groups. The band observed at around 1400 cm^{-1} corresponds to symmetric (O-C-O) vibrations of carboxylic acid group. This band is also stronger and wider in Fig.4.4-a, which represents the spectrum for TPA. The band at around 1500 cm^{-1} is the result of asymmetric stretching vibrations of the bond C=O. C–O stretching vibration is seen at around 1270 cm^{-1}. The bands observed between 400 and 1400 cm^{-1} are due to benzene ring, such as bending vibrations of C=C at around 1270 cm^{-1} and deformation vibrations of C-H between 700 and 800 cm^{-1}. As can be seen in Fig.4.4-c, several characteristic bands of TPA are also observed in MIL-101(Cr), such as the band at 1700 cm^{-1}, 1500 cm^{-1}, 1400 cm^{-1}, 800 cm^{-1} and 700 cm^{-1}. These bands confirm the presence of TPA linker in the MIL-101(Cr)[39]. Fig.4.4-d, represents the spectra of MIL-101(Cr) after IBP adsorption. The broad band at 33360 cm^{-1} corresponds to the O-H stretching vibrations that are due to the adsorbed water MIL-101(Cr). After IBP adsorption, intensities of the bands at 1660, 1253, 1100, 746, 657, 582 and 400 cm^{-1} are decreased. These decreases suggest that the adsorption mechanism involves interactions with the carboxyl groups such as hydrogen bonding.

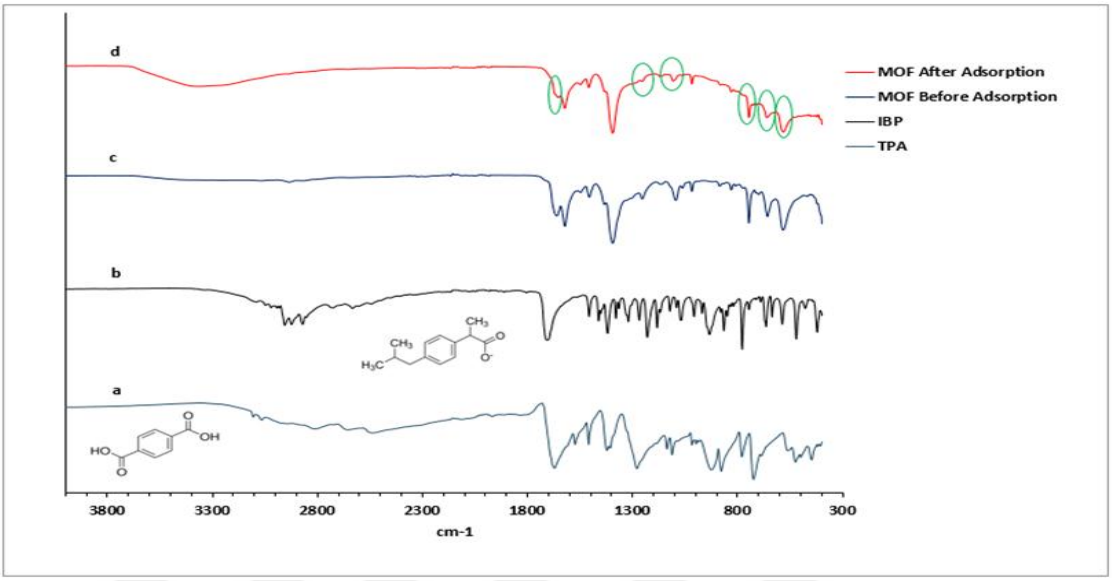

Figure 4.4.FTIR Spectra for a) TPA b) IBP c) MOF before adsorption d) MOF after IBP adsorption

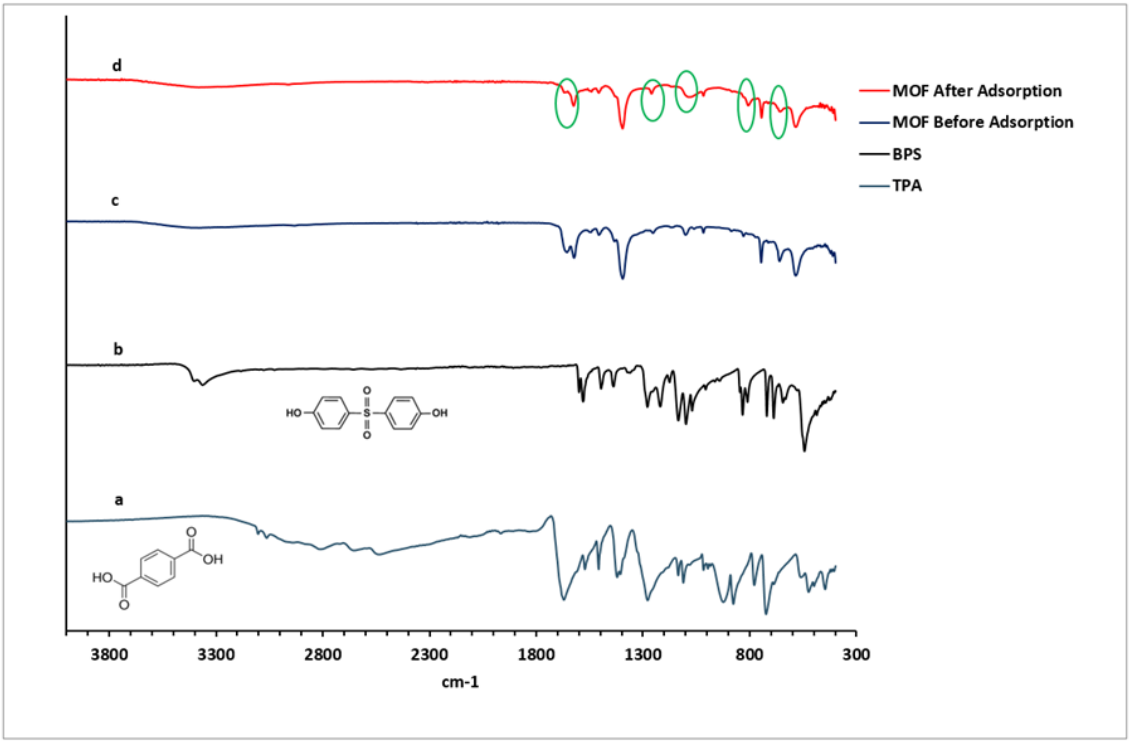

Figure 4.5.FTIR Spectra for a) TPA b) BPS c) MOF before adsorption d) MOF after BPS adsorption

4.2. Adsorption Equilibria

4.2.1. Adsorption isotherms

Adsorption mechanism is usually demonstrated using isotherms (a line showing the change of a certain measurable factor corresponding to another both of which are at the same temperature). Each of the six isotherms shown below (figure 5.1) manifests a different adsorption behavior that depends on the nature of both adsorbent and the target compound. Including these, there are many more isotherms already in use.

Isotherms are acquired by plotting the amount of the target compound adsorbed versus an adsorption capacity representative known as q. The latter is defined as the mass adsorbed (mg) in unit mass adsorbent (g) and is calculated from the formula below:

$$qe = \frac{(ci-ce)*V}{m} \qquad (4.1)$$

Where qt: the amount of a specific micropollutant (IBP or BPS) adsorbed (mg/g) at time t; Ci: the pre-adsorption concentration of the micropollutant in (mg/L); Ct: the concentration of the micropollutant at time t in (mg/L); V: the volume of solution in liters (L) and finally m is the weight of adsorbent in the solution (g).

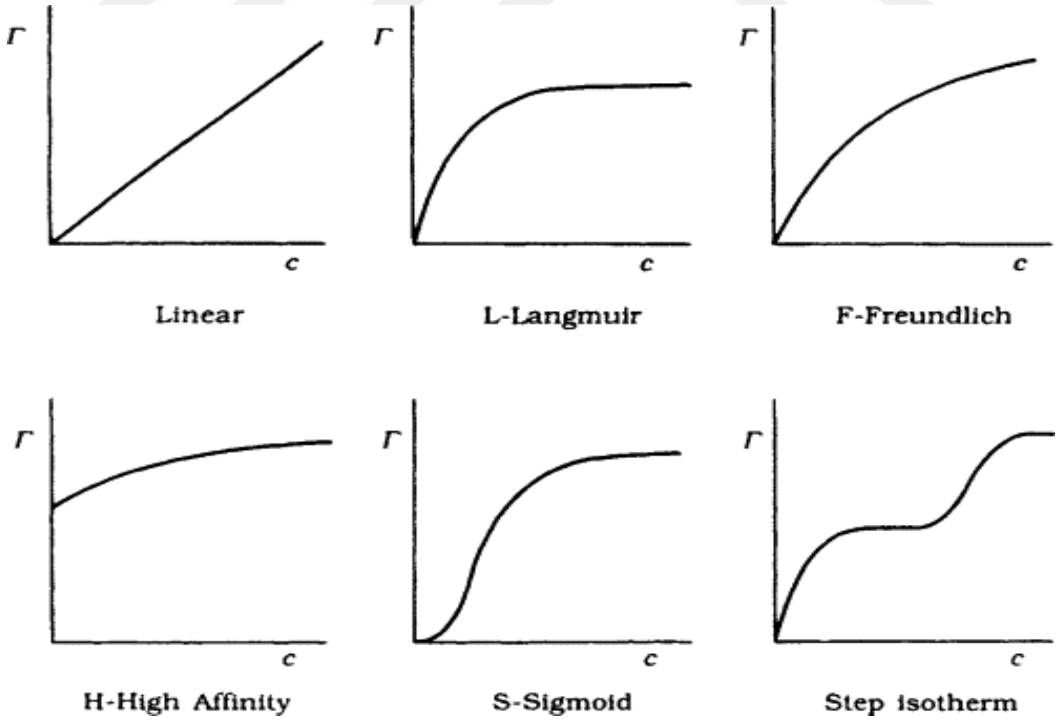

Figure 4.6. Typical adsorption isotherms

Experimentally, two significant isotherms have shown abundance among chemical adsorption processes out of the rest, these are Freundlich isotherm (F) and Langmuir

Isotherm (L). Despite that, we have decided to expand our fitting study to cover two more isotherms presented as Sips and Dubinin-Astakhov in order for our result examination to be more inclusive.

4.2.2. Adsorption isotherm for IBP

Isotherm studies were conducted at 25°C by the synthesized using MIL-101(Cr) as the adsorbent for the removal of IBP. The obtained results are given in Figure 5.2.

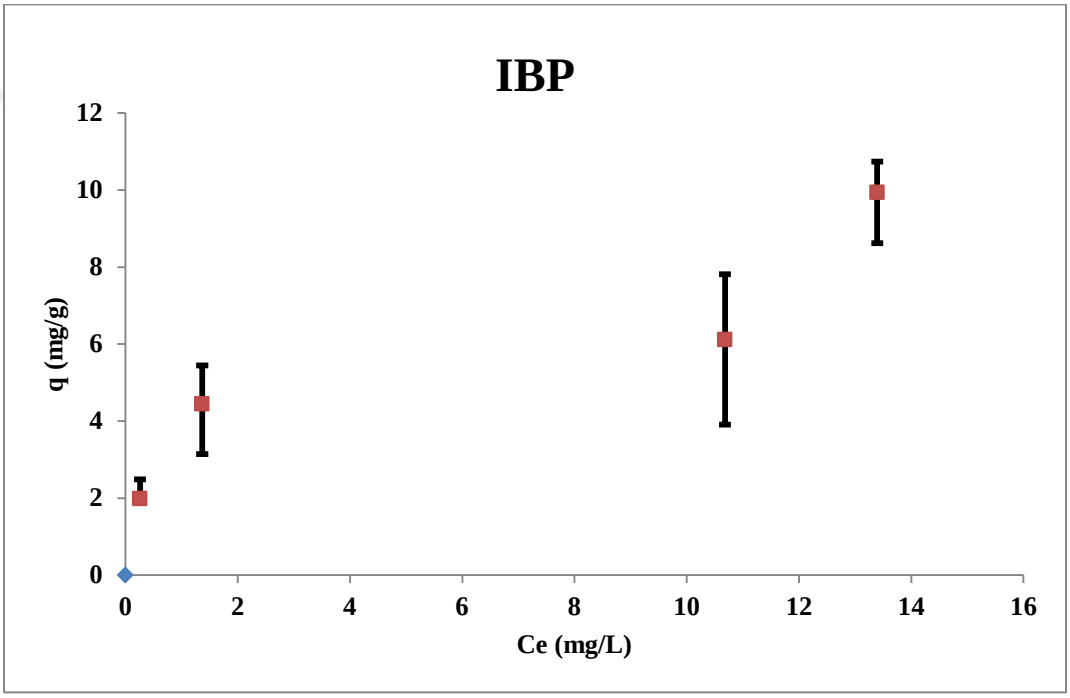

Figure 4.7. Isotherm (Equilibrium) data for IBP adsorption by synthesized MIL-101(Cr).

In order to understand the behavior of IBP adsorption on the surface of synthesized MIL-101(Cr) the above-mentioned isotherm models of adsorption were applied on the collected data.

The isotherm models studied in this research along with their calculated variables are listed in Table 5.2.

Table 4.2. The isotherm models and their calculated parameters for IBP

Type	Formula	Variables	Fitting
Langmuir	$Qe = Q_{max}.K_L.Ce /(1+K_L.Ce)$	Q_{max} (mg/g) = 8.9 K_L (L/mg) = 0.772	R^2= 0.793 X^2 = 0,998 NRMSE = 0,148

Freundlich	$Qe = K_F.Ce^n$	K_F ((mg/g)/(mg/L)^n) = 3.4891 n = 0.3435	R^2= 0.836 X^2 = 0,735 NRMSE = 0,132
Sips	$Qe = (Q_m^s.K_S.Ce^{1/nS})/(1+K_S.Ce^{1/nS})$	0 < 1/nS ≤ 1 Q_m^s (mg/g)= 140,0 K_S = 0,026 $1/n_S$ = 0,356	R^2 = 0.834 X^2 = 0,736 NRMSE = 0,132
Dubinin-Astakhov	$Qe = Q_{DA\ (max)}.\ exp\{-K_{DA}[R.T\ .ln(Cs/Ce)]^{nDA}\}$	$Q_{DA\ (max)}$ = 469,706 K_{DA} = 2,9376 n_{DA} = 0,124 R (L.atm/mol.K) = 0,0821 T (K) = 293 Cs (mg/L) = 21	R^2= 0.886 X^2= 0,749 NRMSE = 0,110

Where Qe is the adsorption capacity of IBP at equilibrium; $Q_{(max)}$ is the maximum capacity according to Langmuir's; Q_m^s is the maximum capacity according to Sips's; $Q_{DA(max)}$ is the maximum capacity according to Dubinin-Astakhov's; Ce is the post-adsorption concentration; K_L is Langmuir's constant; K_F is Freundlich's constant; K_S is Sips's constant; K_{DA} is Dubinin-Astakhov's constant; n is Freundlich intensity parameter; $1/n_S$ is Sips's heterogeneity constant; Cs is the solubility of IBP in water at a specific temperature; nDA is Dubinin-Astakhov's heterogeneity factor. NRMSE is the short for "normalized root mean squared error" which is a statistical error indicator. X^2 is a statistical measure called chi-square.

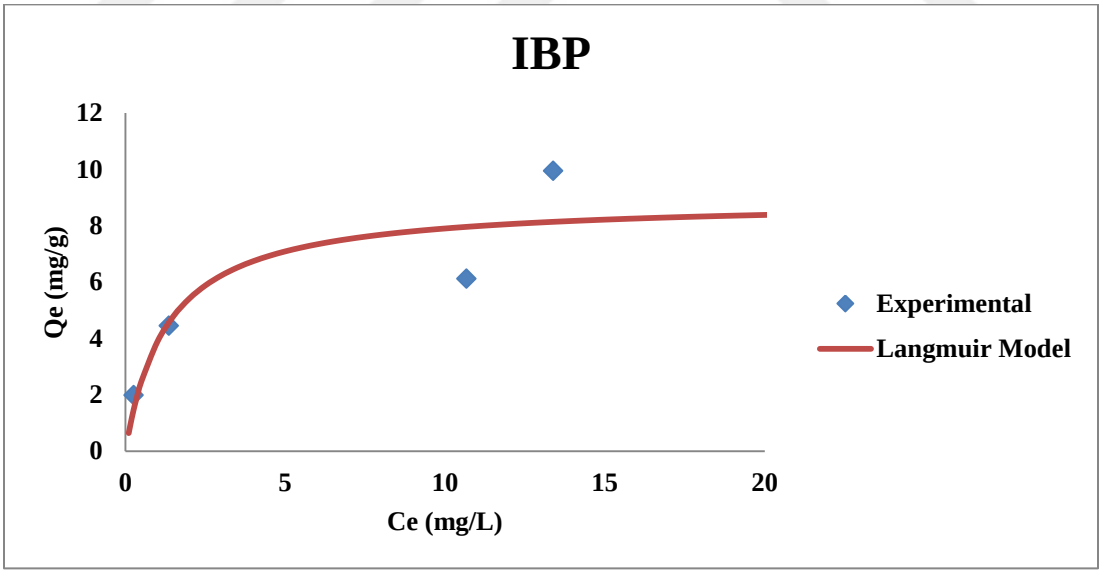

Figure 4.8. Langmuir Model

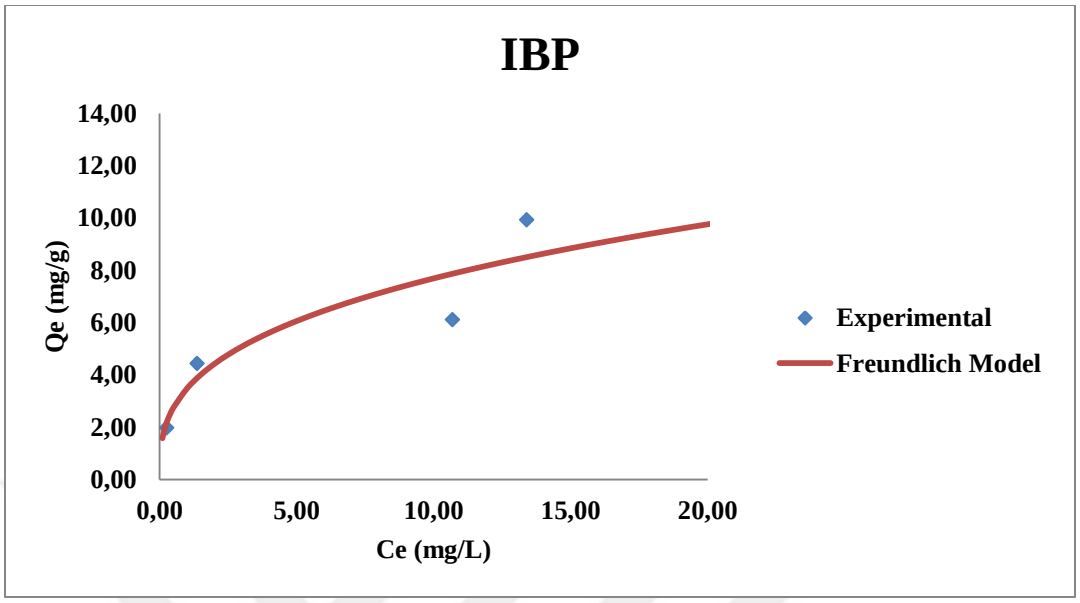

Figure 4.9. Freundlich Model

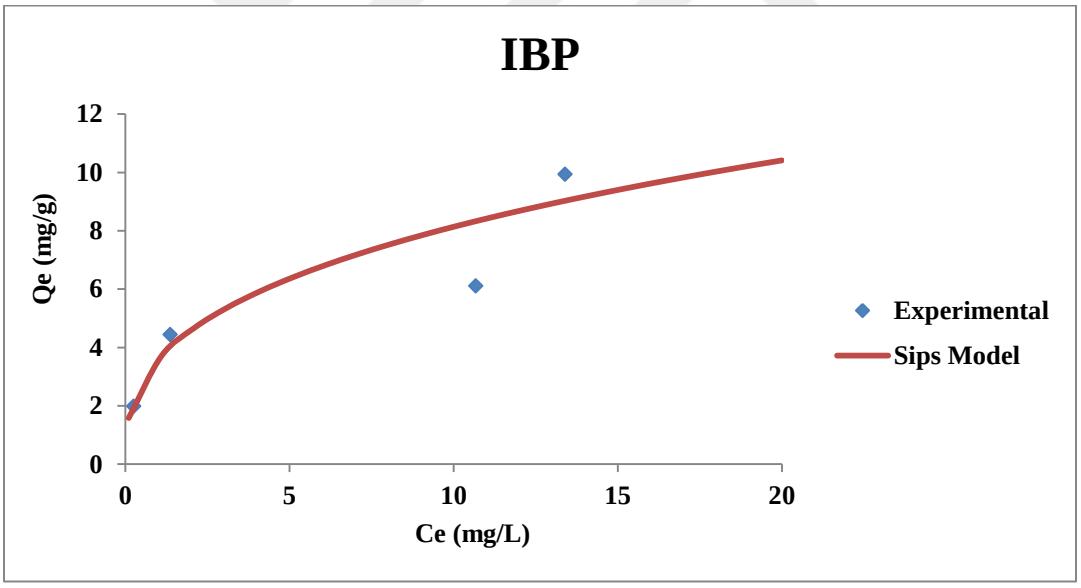

Figure 4.10. Sips Model

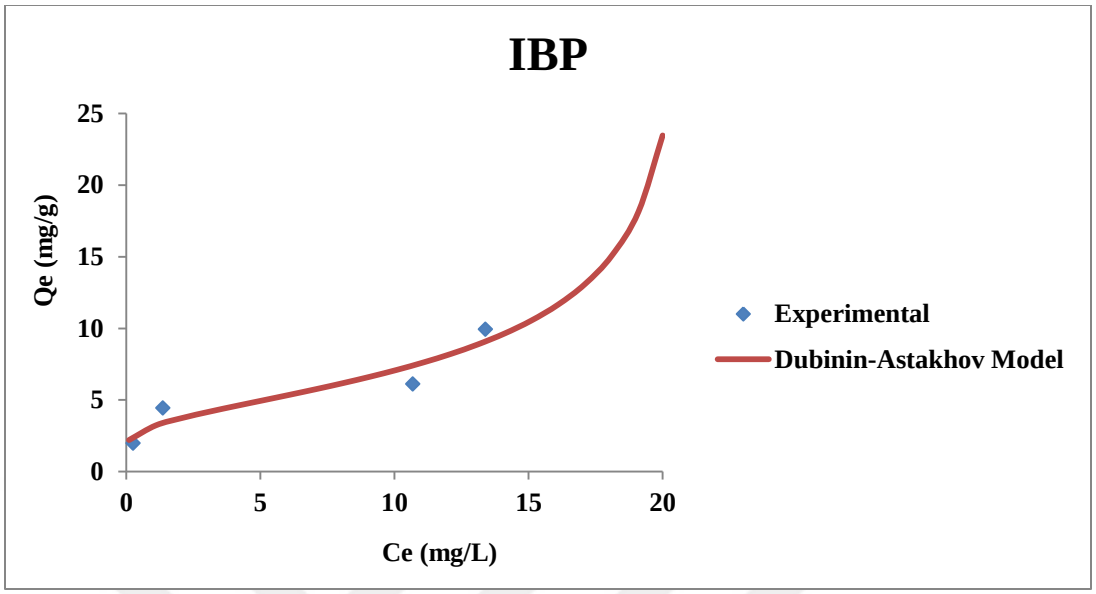

Figure 4.11. Dubinin-Astakhov Model

By comparing R2 values, it's concluded that Dubinin-Astakhov isotherm showed a slightly better fitting compared to the others as shown by Equation (4.2) which is what is going to be accepted as the formula resembling the behavior of IBP adsorption.

$$Qe = Q_{DA\ (max)}.\ \exp\{-K_{DA}\ [R.T\ .\ln(Cs/Ce)]^{nDA}\} \qquad (4.2)$$

The parameters obtained are as following: $Q_{DA\ (max)}$ = 469.706, K_{DA} = 2.9376, nDA = 0.124, R (L.atm/mol.K) = 0.0821, T (K) = 293, Cs (mg/L) = 21, R^2= 0.886, X^2= 0.749, NRMSE = 0.110.

4.2.3. Dubinin-Astakhov isotherm

The Dubinin-Astakhov isotherm supposes that the amount q (mg/g) of a given adsorbate on an adsorbent under equilibrium conditions is a function of the adsorption potential energy as expressed in equation (4.3).

$$q=f(\mathcal{E})=f\left[R.T.\ln\left(\frac{Ps}{P}\right)\right] \qquad (4.3)$$

The isotherm follows the Polanyi's potential theory that is centered on an adsorbent's thermodynamic energy. The latter is thought to be equal to the energy change value of an adsorbate negatively when this adsorbate migrates from bulk to adsorbent surface where

the adsorbate pressure is included in the equation of equilibrium side by side with the temperature and the ideal gas constant as seen in equation (4.4)[39].

$$q=qo\ .\exp\left[-\left(\varepsilon/_{E}\right)^{n}\right] \qquad (4.4)$$

This resultant applies only on adsorption of gases into porous solids and the identical representation mimicking adsorption in aqueous phases have replaced certain parameters from the equation finalizing it as demonstrated in equation (4.5)[45].

$$Qe = Q_{DA\,(max)}.\ \exp\{-K_{DA}\,[R.T\ .\ln(Cs/Ce)]^{nDA}\} \qquad (4.5)$$

It has been used widely for the adsorption of vapors and gases [39] and less often for organics adsorptive separation from aqueous media [40-42].

For the sake of laying a broader comprehension on the adsorption conditions of IBP presented by previous publications, Table 4.3 adds other potential adsorbents to consider in the future of which our MIL(101) Cr can be also assessed with respect to them. Similar adsorption capacity can be observed in study reference [55] that was carried out using MIL-53(Fe) that gave 10.67 mg/g maximum capacity.

Table 4.3. Adsorption capacity of Ibuprofen (literature overview)

Adsorbent	Max. Adsorption capacity (mg/g)	parameters	Reference
MIL-101(Cr)	9.9384 (Exp.) 469,706 (Dubinin-astakhov)	298 K; Dose = 1 g/L; Ci = 50 mg/L; pH = (was not adjusted); R2 = 0.886	This work
MIL-53(Fe)	10.67 (Langmuir)	Room temperature; Dose = 1 g/L; Ci = 10 mg/L; pH = 2.6 R^2 = 0.997	[55]
FeBTC	102.7	303 K; Dose = 0.06 g/L; Ci = 20 mg/L; pH = 5.6 R^2 = 0.996	[56]
Fe_3O_4–FeBTC	117.9	303 K; Dose = 0.06 g/L; Ci = 20 mg/L; pH = 5.6 R^2 = 0.994.	[56]
Aluminum-based	72.5	307 k; Dose = 100	[57]

A100 MOF	Second order	mg/L; 20 μM; ph = 7.5; R^2 = 0.9999.	
chitosan-modified waste tire crumb rubber	17.7 Freundlich isotherm model	Room temperature Dose = 3 g/L; Ci = 30 mg/l; pH = 6; R^2 = 0.9949.	[58]
Pre-treated cork	138.3 Second order	303 K; Dose : 0.6 g/L; Ci = 120; pH = 5; R^2 = 0.999.	[59]
Parthenium weed	1.025 Second order	298 K; Dose = 2 g/L; Ci = 20 mg/L; pH = 2; R^2 = 0.999.	[60]
AC cloth C0	491.9 Elovich model	298 K; Dose = 1 g/L; Ci = 100 mg L; pH = 3; R^2 = 0.99.	[61]

5. CONCLUSION

The synthesized MIL-101(Cr) has proven to be a functioning adsorbent for the uptake of Ibuprofen from aqueous solutions as demonstrated by both experimental (results from GC-MS) and analytical analysis (FTIR graphs) achieving a reduction of around 45%. It has been pointed out that IBP adsorption on the surface of MOF Cr follows Dubinin-Astakhov model with R2 of 0.886. This work is still insufficient and requires more data to dismiss the noise interfering in the process of establishing a firmer equation on the adsorption of IBP by the surface of MOF-Cr.

For BPS, we would love to clarify that we faced stubborn troubles trying to obtain reliable readings from the GCMS which have left us to deduce results analytically by FTIR spectrum only. There certainly has been reduction in the BPS concentration noticed from the visual evaluation of the FTIR graphs. Several sites on the MOF graph prior adsorption have gone through changes after adsorption some of which are enclosed with green ellipses. We believe that numerical measurements explaining the amount and tendency of BPS adsorption is still needed to back up the already stated allegations.

Despite that we started with 5 samples expecting to end up with 5-point graph, the device admitted to measure the concentration of residual IBP showed errors in manifesting a proper reading which could be due to the concentration of sample no.5 that went beyond the upper limit of detection. We suggest further study to be considered to fine the results and to lay down a more accurate model.

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