Adsorption of Mefenamic Acid From Water by Bentonite Poly urea formaldehyde Composite Adsorbent

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ABSTRACT

Poly urea formaldehyde –Bentonite (PUF-Bentonite) composite was tested as new adsorbent for removal of mefenamic acid (MA) from simulated wastewater in batch adsorption procedure. Developed a method for preparing poly urea formaldehyde gel in basic media by using condensation polymerization. Adsorption experiments were carried out as a function of water pH, temperature, contact time, adsorbent dose and initial MA concentration .Effect of sharing surface with other analgesic pharmaceuticals at different pH also studied. The adsorption of MA was found to be strongly dependent to pH. The Freundlich isotherm model showed a good fit to the equilibrium adsorption data. From Dubinin–Radushkevich model the mean free energy (E) was calculated and the value of 5 KJ/mole indicated that the main mechanism governing the adsorption of MA on PUF-Bentonite composite was physical in nature. The kinetics of adsorption tested for first order, pseudo second order models and Elovich's equation, results showed the adsorption followed the pseudo-second-order model.

Key Words: Mefenamic acid adsorption, Bentonite ,Analgesic ,Poly urea formaldehyde.

امتزاز حامض الميفيناميك من الماء بواسطة خليط البنتونيت البولى يوريا فورمالدهايد كمادة ممتزة

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الخلاصة

تم اختبار مزيج بولي يوريا فورمالدهايد (PUF) بنتونايت كمادة ممتزة جديدة لإزالة حمض الميفيناميك (MA) حيث اجريت تجارب الامتزاز بالدفعات لنموذج من الماء الملوث معد مختبريا. تم تطوير طريقة جديدة لتحضير بوليمر اليوريا فورمالدهايد في وسط قاعدي باستخدام البلمرة التكثيفية. اجريت تجارب الامتزاز من خلال دراسة متغيرات التاثير المختلفة مثل الدالة الحامضية (pH) ، الحرارة ، زمن التلامس ، كمية المادة الممتزة وتركيز الحامض الابتدائي. درس كذلك تأثير مشاركة السطح الممتز مع مواد مسكنة صيدلانية اخرى عند قيم مختلفة من pH . وجد ان امتزاز MA يعتمد بصورة اساسية على pH. اظهرت بيانات توازن ايزوثيرم الامتزاز تطابقها مع نموذج Freundlich. من نموذج

Dubinin Radushkevich تم حساب متوسط الطاقة الحرة (E)وكانت قيمتها 5 KJ/mole والتي تشير الى ان طبيعة امتزاز حامض الميفيناميك على خليط البولي يوريا فورمالديهايد بينتونايت هي ذات طبيعة فيزياوية . تم تطبيق نماذج دراسة حركيات الامتزاز الرتبة الاولى والرتبة الثانية ومعادلة Elovich’s واشارت النتائج الى ان الامتزاز يخضع الى نموذج حركية الرتبة الثانية.

الكلمات الرئيسية : امتزاز حامض المفناميك ، بنتونايت ، مثبط ، بولي يوريا فورمالدهايد.

1. INTRODUCTION

An increasing number of emerging contaminants have been detected in surface waters, sediment, soil and ground water in different locations in the world, which is a new environmental challenges need an actual concern for international scientific and legislative communities **Álvarez , et al. 2015** .Generally, these compounds, e.g., pharmaceuticals, personal care products surfactants, pesticides, and brominated flame retardants are not totally removed by conventional wastewater treatment plants (WWTP), due to its existing everywhere and stability against biodegradation. The effect of these pollutants in the environment does not only depend on its concentration level in the environment, but also on other factors, such as bioaccumulation , lipophilicity increases or persistence, exposition time and mechanisms of biotransformation and elimination ,**Esplugas ,et al. 2007**. From the other hand a wide range of these compounds are suspected to have endocrine-disrupting effects, possibly at long-term, in living organisms, including humans , **Nikolaou ,et al. 2007**.

Pharmaceuticals and their metabolisms are the most important emerging contaminants detected in environmental systems. Approximately 3,000 different compounds, with wide range of different chemical structures, are used in human and veterinary medicine ,**Halling-Sørensen ,et al. 1998.** Several researches focused on detection of pharmaceuticals at different therapeutic classes, analgesics, lipid-lowering agents, antipyretics, broncholitics, antidepres-sants, synthetic steroidal hormones, human and veterinary antibiotics, etc. in surface water, soil and ground water, with this purpose accurate and sensitive analytical method have to be developed capable to monitor these compounds in ng/L level **,Farré ,et al. 2001; Hernando, et al. 2007;Hao , et al. 2008;Silva, et al. 2008 ; Gracia-lor, et al. 2010;Du , et al. 2014 ; K’oreje ,et al. 2016** .

Among the pharmaceuticals reported in environment ,Analgesic and non-steroid anti-inflammatory drugs (NSAID) have been detected in the concentration ranges from ng/L to µg/L in surface and wastewater due to very high use of these pharmaceuticals also without prescription **Tauxe-Wuersch, et al. 2005; Fatta, et al. 2007; Durán-Alvarez, et al. 2009; Ziylan & Ince 2011; Carmona, et al. 2014; Lolić ,et al. 2015; Jung, et al. 2015**. Mefenamic acid [2-(2,3-dimethyl phenyl)amino] benzoic acid **Table 1** is a non-steroidal drug which has analgesic, anti-inflammatory and antipyretic actions and it is used specially in the treatment of rheumatoid arthritis and osteoarthritis and other muscular-skeletal diseases, **Reynolds, J.E.F., Prasad 1982**.

The present water and wastewater treatment plants have been designed for the treatment and removal of contaminants and eutrophicating pollution loads, which are specified in the existing regulations. However, the occurrence of the new unregulated contaminants requires advanced treatment ,**Bolong ,et al. 2009**.The removal technologies can be classified as three main classes' physiochemical treatments such as adsorption, biodegradation such as membrane bioreactor (MBR), and advance technologies such as advance oxidation by ozone. A Comparison for removal capacities between membrane bioreactor and conventional activated-sludge process showed a maximum removal of 74.8 % and 29.4% respectively ,**Radjenovic ,et al. 2007.**

Elimination of mefenamic acid MA by photolysis, ozonation, adsorption onto activated carbon (AC) was investigated **Gimeno ,et al. 2010** .The results showed that the addition of activated carbon don't enhanced removal process and get a removal efficiency of 60% in 120 min by combination of ozone and UV radiation .**Rodrigo, et al., 2014**, used adsorption of mefenamic acid with activated carbon and red mud then oxidation with chlorine ,they go to removal of 100% for activated carbon and 96 % for red mud . Different oxidative processes (H_2O_2, H_2O_2/UV, Fenton and Photo-Fenton) were investigated for mefenamic acid removal from water **Colombo, et al. 2016**.The results, shows that the photo-Fenton process is the best to get maximum removal efficiency of 95.5 at pH 6.1 and 60 min oxidation time .

Bentonite was used as adsorbent for different pollutants in aqueous media ,**Hefne ,et al. 2008; Hefne ,et al. 2010 ; Al-Khatib, et al. 2012; Chmielewská ,et al. 2013 ; Aljlil & Alsewailem 2014 ; Moradi ,et al. 2015**.From other side composite bentonite with other polymer or organic material were studied **,Ulusoy & Şimşek 2005 ; Anirudhan, et al. 2008;Anirudhan ,et al. 2010;Anirudhan & Suchithra 2010;Zhao, et al. 2010;Dalida ,et al. 2011;Anirudhan & Rijith 2012.**

Polymeric adhesive poly urea formaldehyde (PUF) gel is a condensation product of the chemical reaction of formaldehyde with urea, considered as one of the most important wood adhesives. Urea formaldehyde gel have been greatly used in wood based industries due to it low cost, low cure temperature, lack of color and ease of use under a wide variety of curing conditions , **Gürses, et al. 2014**.The composite mixture of poly urea formaldehyde and bentonite(PUF-Bentonite) will be studied as anew adsorbent .

There are very limited studies on the adsorption and removal of mefenamic acid from water and waste water. This study focused on the adsorption of mefenamic acid using new composite adsorbent poly urea formaldehyde and bentonite clay in a step to enhancement the surface with low cost adsorbent and minimize the waste treatment cost .The optimum bentonite dose in composite adsorbent , effect of contact time, temperature ,initial concentration , solution pH , adsorbent dose and sharing surface with other analgesic were investigated. Equilibrium and kinetic parameters were also determined to help provide a better understanding of the adsorption process and application it in a large and industrial scale.

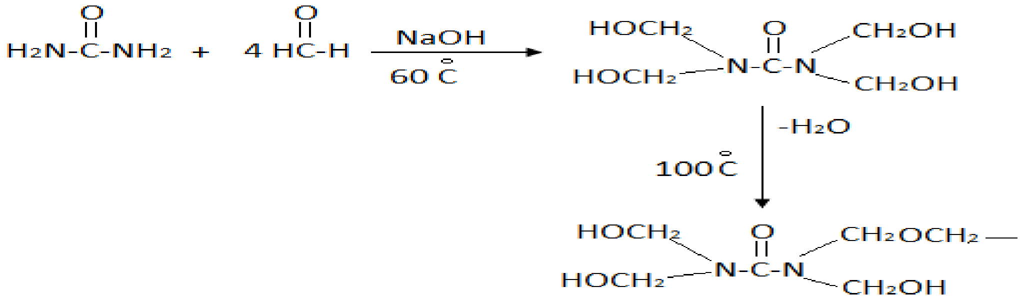
2. EXPERIMENTAL

2.1 Materials

The materials and chemicals used in this study, listed in **Table 2**, the solvents and reagent grade and used without further purifications.

2.2 Preparation of Poly Urea Formaldehyde Gel

Five grams of urea dissolve in 50 ml formaldehyde using 250 round flask with reflux, after completely dissolved adding a drops of 1M sodium hydroxide solution to adjust pH to 9 .The round put on a hot plate mixing stirrer, the temperature set to 60 ˚C. Left the condensation reaction for 3 hours and with pH control to 9.A viscous fluid formed after three hour of condensation reaction then left in oven at temperature 40 ˚C for 48 hour to remove excess water. Finally the urea formaldehyde gel store in glass container at room temperature for further use.The proposed equation for preparation polyureaformaldehyde clarified in **Eq.1**



………(1)

2.3 Preparation Urea Formaldehyde Bentonite Composite

Bentonite washed in deionized distill water for three times and then dried in an oven at 100 ˚C for two hours .Different masses ratios of bentonite to poly urea formaldehyde 0,1 ,2,3,4, and 5 took to prepare composite of PUF –Bentonite .The composite mixed vigorously at temperature 60˚C for 15 minutes , then put composite in an oven at 110 ˚C for 24 hour to solidification .The composite washed many times with deionized water finally dried in an oven to remove water . The sample was crushed and screened through a 200-mesh for further use.

2.4 Adsorbate

Mefenamic acid is poorly soluble in water and several solvents. In this study many solvent checked to test total solubility of MA such as methanol and ethanol.50 mg of MA dissolved in 250 ml of water solution 0.01 M NaOH at temperature 37˚ C for 12 hour to prepare 200 µg/ml MA solution .This stock solution used in next time to prepare different concentrations of MA by dilution in 0.01 M NaOH solution.

2.5 Calibration and Method Validation

UV spectrophotometer type Apel pd-303 UV were used to quantification of MA concentration , 30 µg/ml concentration solution of MA were used to tested maximum wave length from 200-400 nm **Fig.1** the results showed that the maximum wave length occurs at 285nm this results fit with , **Singh ,et al. 2011**,study . From the respective stock solution (200µg/ml) different concentration of 2.5, 5, 10, 20, 30, 40 and 50 µg/ml MA were prepared and scanned in UV at 285 nm region. Calibration curve were plotted as absorbance vs concentration and their linearity range was determined **Fig.2**.

2.6 Characterization

The mineralogical composition of bentonite samples and bentonite poly urea formaldehyde composite was determined using X-ray Diffraction (XRD) technique. X-ray analyses of the samples was performed on the (PAN ALYTICAL); a copper (Cu) anode was used in the X-ray tube and operated at current 20 Ma and power level of 4 kW. The surface morphology of each samples was determined by scanning electron microscopy (SEM) photography (INSPECT-550) was normally performed at 10 Kv . FTIR spectra were recorded in the region of 4000-400 cm^{-1} (SHIMADZU).

2.7 Adsorption Studies

The adsorption studies were conducted with 0.050 g of adsorbent and 20 mL of mefenamic acid solution at desired concentration, pH and temperature on a constant speed of 180 rpm. The solution was filter in 0.2 microns Millipore filter syringe and the concentration of MA in the supernatants was examined with a spectrophotometer at the wavelength of 285nm at which the maximum absorbency occurred. Then the amounts of MA adsorbed per unit mass of adsorbent were calculated from the differences between the initial and final MA concentrations in solution by the following equation Eq(1):

$$q = \frac{(C - C_e) \times V}{M} \quad .. \ \dots \ .. \qquad (2)$$

Where q is the adsorption capacity of mefenamic acid mg/g at any time t C and C_e is initial and equilibrium concentration respectively, V (L), the volume of MA solution used in adsorption experiment, M(g), the mass of the adsorbent used in the present study.

For the investigation of effect of composite mass ratio Bentonite/poly urea formaldehyde content on adsorption capacity, 50 mg of the adsorbent with 20 ml of 40µg/ml MA solution was put into the flask with fitted cub and stirred at 180 r.p.m for 240 min in water bath shaker (Polyscience) type .Temperature adjusted to 27 ˚C using chiller type DHC , pH set to 7 by using 0.01 M HCL or 0.01 M NaOH solution using pH meter type (HANNA pH 211) . To investigate the effect of contact time on adsorption, time changed between 15 to 120 minutes. Temperature effect studied with changing temperature from 15 to 64 ˚C at contact time 60 min. To investigate the effect of pH on adsorption, MA solution with an initial concentration of 40µg/ml with pH in the range of 1.5–12.5 for contact time 60 min and temperature 47˚ C. A series of MA solutions with different concentrations (20–200 µg/ml) at pH = 2 and temperature of 47˚C were prepared to investigate the adsorption isotherms. To investigate the effect adsorbent dose on adsorption, the concentration of MA 200 µg/ml used with the same previous conditions by changing the dose from 50 – 300 mg in 20 ml MA solution. The effect of sharing surface with other analgesic, used a complex wastewater containing other NSAIDs acetaminophen 40µg/ml , diclofenac sodium 40µg/ml, acetylsalicylic acid 40µg/ml, ibuprofen 40µg/ml and indomethacin 200 µg/ml this complex prepared at different pH values from 2-12, with contact time 60 min, temperature 47˚C and 50 mg adsorbent in 20 ml MA solution will be used .All experiment repeated double time and the average of absorbance took as a final reading.

3. RESULTS AND DISCUSSION

3.1 Characterization

Bentonite is considered one of the most abundant natural materials available in nature that can be used for adsorption pollutant from wastewater and other application **Al Khatib,et al. 2012**. The chemical composition of natural bentonite is different depending on the source of collection. The commercial bentonite XRD shown in **Fig.3** . Bentonite poly urea formaldehyde composite predominantly had a dark brown appearance. A typical XRD pattern of bentonite poly urea formaldehyde composite after mixing shown in **Fig.4** .FTIR spectra for bentonite , poly urea formaldehyde and bentonite polymer composite shown in **Fig.5 ,6,7** its seems shifting and missing groups as illustrated in **Table.3**.SEM image for raw material and composite shown in **Fig.8 a&b** it can be seen gathering of many microfine particles in bentonite -PUF composite compare with bentonite surface which lead to rough surface with presence of pore structures.

3.2 Effect of Composite Mass Ratio

The adsorption of MA by composite adsorbents with different mass ratios of bentonite and PUF shown in **Fig.9**. It could be observed that the adsorption capacity is 2.4, 5.7, 6, 9.6, 6.6 and 5.9 mg/g for composite with bentonite to PUF (bentonite only ,1:1,2:1,3:1,4:1 and 5:1) respectively. It observed that the adsorption capacity increase by increasing bentonite content until reaching the best ratio of 3:1(3g bentonite/1g PUF) then the increasing of bentonite reduce the adsorption capacity. This may attributed to increase organic /inorganic interaction between PUF and bentonite which responsible to convert the surface from hydrophilic to organophilic by urea groups. Increasing PUF in composite compare with bentonite weight caused also decrease in adsorption capacity because surface became more amorphous and reduce crystalline structure .This confirmed by previous investigator focused on mixing organic group with clay **Moazed & Viraraghavan 2005** & **Oleiwi 2014** . The best composite ratio bentonite to PUF will be used for further experiments is 3:1 for bentonite to PUF ratio.

3.3 Effect of Contact Time

Contact time is important parameter because it can determine the time required to achieve equilibrium of the adsorption system and predict the feasibility of an adsorbent for its use in wastewater treatment. Except for high adsorption capacity, fast adsorption rate is also indispensable for practical application. The effect of contact time on adsorption of MA onto PUF -Bentonite composite was studied over a contact time of 0–120 min.**Fig.10** shows that the amount of MA adsorbed per unit mass of adsorbent increased rapidly within 45 min . Further increase in contact time did not enhance the adsorption. Equilibrium was achieved around 45 min and increased slightly to 60 min .A contact time of 60 min was chosen as equilibrium time in further experiments . The initial rapid increased may be due to greater number of adsorbent active sites available for MA adsorption which caused higher driving force that made fast transfer. With increase in contact time, the availability of MA to the active sites on the PUF-Bentonite surface would be limited, which fixed the adsorption capacity. The contact equilibrium time achieved in this study is shorter than the contact time using different adsorbent in many researches focused on selected NSAIDs **Gimeno et al. 2010** ;**Khatem et al. 2015**&**Jodeh et al. 2016** .

3.4 Effect of Temperature

Fig. 11 illustrates the variation of MA adsorption capacity with temperature in the range from 15 to 67 ˚C. From the figure it is seen that temperature had a limited influence on adsorption capacity. The adsorption capacity of MA increased with increase in temperature in the range from 15- 49˚ C , then was observed at 50 ˚C it gradually decreases with again increase in temperature. The enhancement in adsorption with rise in temperature may be attributed to increases the rate of diffusion of the adsorbate molecules across the boundary layer and within the internal pores of the adsorbent particle, due to decrease in the viscosity of the solution from the other hand increasing temperature increase in the number of active surface sites available for adsorption, pore volume and the porosity of the adsorbent. The decrease in adsorption capacity with further increase in temperature is due to reduce the boundary layer thickness and increase the kinetic energy of MA molecules, this gave a tendency to escape from active site to fluid bulk .From the other hand MA is hydrophobic and water structuring existing around hydrophobic part of MA molecules ,at high temperature water structuring decreasing and make the molecule more free to diffusion and increased diffusion rate **Steinby et al. 1993** & **Nam et al. 2014** . Previous literatures working with temperature range from 30 to 40 ˚C for same group of NSAIDs have similar behavior **Cabrita et al. 2010** ;**Álvarez, R.S. Ribeiro, et al. 2015** & **Mohd et al. 2015** .

3.5 Effect of pH

Generally pH is considered to be an important parameter that controls the adsorption at water-adsorbent interfaces. Results of the influence of pH on adsorption are illustrated in **Fig.12**, pH seems had significant influence on adsorption capacity of MA. Experiments were conducted varying the solution pH from 1.5 -13 while rest of the factors were kept constant. The maximum capacity was observed at pH range 1.5-3.5. Result indicated a pH less than the pK_a of MA (pK_a = 4.20), is efficient for MA removal. The solubility of MA with carboxylic acid groups decrease when pH decrease then 'van der Waal' interaction between MA and the adsorbent surface increased. At pH more than 6 MA are quantitatively dissociated, increasing their water solubility and decreasing their interaction by hydrogen bonds **Bui & Choi 2009** ; **Guedidi et al. 2014** & **Jodeh et al. 2016** .

3.6 Effect of Initial Concentration

The initial concentration provides an important driving force to overcome all mass transfer resistances of all molecules between the aqueous and solid phases **Malkoc & Nuhoglu 2007**. From the other hand pharmaceutical pollutant are variable concentrations in water then the understanding the variation in concentration is important to control the adsorption process. MA acid concentration changed from 20 to 200 µg/ml with adjusted pH value to 2 .It seems from **Fig.13** that the adsorption capacity increase with increasing initial MA concentration This is a result of the increasing driving force resulting from increment in concentration gradient to reduce the mass transfer resistance between solid and liquid phases and raised the number of available molecules per adsorption site. It's important to show in this situation that the percent removal of MA from aqueous phase decrease with increasing initial concentration due to saturated the adsorbent active sites **Khalaf et al. 2013** .

3.7 Effect of Adsorbent Dose

The effect of adsorbent dose on the adsorption capacity of MA is shown in **Fig.14** the adsorbent mass changed from 50 to 350 mg with 40µg/ml initial concentration. It was observed that as the mass of PUF- Bentonite composite increased the adsorption capacity decrease and increasing percent removal. This is mainly due to an increase in the adsorption surface area and the availability of more active sites on the surface .The reverse trend of adsorption capacity would be attribute to the gathered and unsaturated adsorption sites **Nam et al. 2014** & **Mupa M et al. 2015**.

3.8 Effect of Surface Sharing

In previous parameter checked the effect of different parameters regarding MA adsorption on PUF-Bentonite surface, if water contain only MA as pollutant .In this part investigate the effect of present of other pollutants in water to adsorption of MA at different pH values. Adsorption experiment were carried out for water containing MA (40µg/ml) and other analgesic acetaminophen 40µg/ml , diclofenac sodium 40µg/ml , acetylsalicylic acid

40µg/ml, ibuprofen 40µg/ml and indomethacin 200 µg/ml at different pH value of 2,5,7 and 12. The results illustrated in **Fig.15** ,and its seems that the adsorption capacity decrease with existing of other pollutant in water ,this due to sharing the free sites in the adsorbent surface with other pollutant and solute-surface interactions and competition of pollutant with each other to attack surface and overcoming mass transfer resistance **Bui & Choi 2009**.

3.9 Adsorption Isotherm and Kinetic Study

Adsorption isotherm is important to sketch how adsorbate interact with adsorbent, and it is critical in optimizing an adsorption process to suggest how the adsorbed molecules distribute between the liquid phase and solid phase until the adsorption process achieve an equilibrium at a constant temperature **Buckley1992**.Adsorption isotherms are basic requirements for the design of adsorption systems. In order to understanding the adsorption isotherm of MA on bentonite PUF adsorbent the experimental data were applied to the Langmuir, Freundlich, Tempkin and Dubinin–Radushkevich equations. The constant parameters of the isotherm equations for adsorption process were calculated by regression using linear form of the isotherm equations ($\boldsymbol{R}^2$). The constant parameters and correlation illustrated in **Table. 4**.

3.10 Error analysis

The use R^2 is limited to describe the fitting to linear behavior ,and doesn't describe the nonlinear behavior . In this study used chi-square test (χ^2) obtained by judging the sum squares differences between the experimental and the calculated data, with each squared difference is divided by its corresponding value (calculated from the models). Small χ^2 value indicates its similarities while a larger number represents the variation of the experimental data **Boulinguiez ,et al. 2008**.The value of (χ^2) for different isotherms listed in **Table .5**. It's clear from **Fig.16** and **Table 5** that the Freundlich isotherm was the fit to the experimental behavior, describing the non-ideal and reversible adsorption, not restricted to the formation of monolayer. This empirical model can be applied to multilayer adsorption, with non-uniform distribution of adsorption heat and affinities over the heterogeneous surface. A favorable adsorption is when Freundlich constant (n) is between 1 and 10. When n is higher than that range it implies stronger interaction between the adsorbent and the adsorbate. From **Table. 5**, it can be seen that the (n) value was between 1 and 10 showing favorable adsorption of MA. The constant k_{ad} in Dubinin –Radushkevich model gives an idea about the mean adsorption energy, E, which is defined as the free energy transfer of 1 mole of solute from infinity of the surface of the adsorbent and can be calculated using the relationship :

$$E = \frac{1}{\sqrt{2k_{ad}}} \quad \ldots\ldots\ldots\ldots(3)$$

The parameter gives information about the type of adsorption mechanism as chemical ion-exchange or physical adsorption. If the magnitude of E is between 8 and 16 kJ /mole, the sorption process is supposed to proceed via chemisorption, while for values of E< 8 kJ /mole, the sorption process is of physical nature . The magnitude of E in this study is 5 kJ/mole indicates the adsorption of MA in PUF-Bentonite adsorbent is physical adsorption via physical binding forces **Kundu & Gupta 2006** ;**Das et al. 2013** .

Adsorption kinetic models were applied to the experimental data, in order to analyze the rate of adsorption and possible adsorption mechanism of MA on PUF-Bentonite composite. Adsorption process is normally controlled by three diffusion steps for adsorbate transport first from the bulk of water to the solid liquid film, the next step from the film to the surface of adsorbent then from the surface to vacant site in the adsorbent then binding of MA molecules with active site. The kinetic models applied in this study are the Lagergren first order, pseudo-second order and Elovich's equation listed in **Table. 5**. The results of kinetics plots showed in **Fig.17, 18 and 19** for three models and results listed in **Table. 5**, its seems the pseudo second order model is nearly to describe adsorption of MA on PUF-Bentonite adsorbent.

4. CONCLUSION

PUF-Bentonite composite prepared from mixing commercial bentonite with poly urea prepared in basic media in mixing ration of bentonite to polymer of 3 is efficient for removal of MA acid from water .pH is the significant parameter affecting the adsorption capacity gives maximum capacity at pH 2 .Also the adsorbent concentration is a significant effect on adsorption capacity. Other parameters temperature, adsorbent dose and contact time studied at different values .Maximum adsorption capacity of 16 mg/g achieved at 47 ˚C and pH 1.5 .Adsorption isotherms model applied and kinetics model and adsorption of MA fit to Freundlich model and pseudo second order model .

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Table 1. Physical, chemical and pharmacological properties of MA.

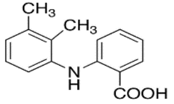
Structure	
Formula	$C_{15}H_{15}NO_2$
Usage	For the treatment of rheumatoid arthritis, osteoarthritis, dysmenorrhea, and mild to moderate pain, inflammation, and fever.
Molecular weight	241.285 g/mol
Water solubility	20 mg/L (at 30 °C)
Pk_a	4.2
Elimination half-life	2 hour
Excretion	52% by urine ,20% in faeces from the dose
Metabolites in urine	hydroxymethyl mefenamic acid, 3-carboxymefenamic acid ,

Table 2. Chemical used in Experiment.

Material	**Manufacture**
Formaldehyde solution 37%	Merck
Urea powder (MW=60.06)	Romil
Hydrochloric acid 37%	Scharlau
sodium hydroxide pellets	Analytical Rasayan
Deionized water with conductivity less than 0.07µS/cm	Al-Najebia gas station from EDI effluent /Basra
Pure Mefenamic acid	SIGMA life science
Acetylsalicylic acid >99% crystalline	SIGMA life science
Acetaminophen 98-101 %(USP XXIV),Powder	SIGMA life science
Diclofenac Sodium	SIGMA life science
Indomethacin 99%(TLC)	SIGMA life science
Ibuprofen 98%(GC)	SIGMA life science

Table 3. FTIR spectra for Bentonite, Poly urea formaldehyde and Bentonite polyuria formaldehyde composite.

Functional groups	(cm^{-1})		
Resin	Bentonite	PUF	B-PUF Composite
O-H	3300-3600w	3200-3500s	3400-3500w
CH_2 ,CH_3asym	-------------	2960-3000w	2960-3000w
CH_2 ,CH_3sym	-------------	2800-2950s	2800-2950w
C=O	1650w	1650-1660s	---------------
N-H bending	--------------	1350-1540s	----------------
O-H bending	1176-1180	1000-1150	1000-1100
Si-O	1083-1100	--------------	1083-1100

Table 4. Definition of adsorption isotherm models and kinetics models used in this study.

Isotherm model	Linear form	Parameters	Reference
Langmuir	$\frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{Q_0\, b\, C_e}$	Q_0: maximum monolayer coverage capacities (mg/g)	**Foo & Hameed 2010**
Freundlich	$\ln q_e e = \ln K_f + \frac{1}{n} \ln C_e$	K_f : Freundlich isotherm constant (mg/g) (L/g) related to adsorption	**Dada ,et al. 2012**
Tempkin	$q_e = \frac{RT}{b_T} \ln A_T + \frac{RT}{b_T} \ln C_e$	A_T : Tempkin isotherm equilibrium binding constant	**Tempkin and Pyzhev,194**
Dubinin–Radushkevich	$\ln q_e = \ln q_s - K_{ad}\, \varepsilon^2$	Q_s : theoretical isotherm saturation capacity (mg/g)	**Dubinin and Radushkevi**
Kinetics' models	Linear form	Parameters	Reference
pseudo-first order		q:capacity at time t mg/g q_e : capacity at equilibrium	**Álvarez, et al. 2015**
pseudo-second order	$\frac{t}{\ } = \frac{1}{\ } + \frac{t}{\ }$	q:capacity at time t mg/g q_e : capacity at equilibrium	**Álvarez, et al. 2015**

Elovich's equation	$q = \frac{1}{b}\ln(ab) + \frac{1}{b}\ \ln(t)$	q:capacity at time t mg/g a: is the initial adsorption	**Fierro ,et al. 2008**

Table 5. Parameters results for application of adsorption isotherm models and kinetics models used in this study.

Model	Parameters	value
Langmuir	q_0	28.01mg/g
	b	12.3 L/mg
	R^2	0.9189
	χ^2	7
Freundlich	K_f	29.17(mg/g)(L/g)
	n	2.5
	R^2	0.97
	χ^2	0.63
Tempkin	A_T	63.8 L/g
	b_T	360
	R^2	0.8929
	χ^2	3.87
Dubinin–Radushkevich	Q_s	29.9 mg/g
	K_{ad}	2.00E-08
	R^2	0.83
	χ^2	6.28
	E	5 KJ/mole
Pseudo-first order	q_e experimental	10.51 mg/g
	q_e calculated	6.42 mg/g
	K_1	0.0422min^{-1}
	R^2	0.78
	χ^2	12.6
Pseudo-second order	q_e experimental	10.51 mg/g
	q_e calculated	12.2 mg/g
	K_2	0.0069 g/mg. min
	R^2	0.9381
	χ^2	0.67
Elovich's equation	a	0.6 mg/g.min
	1/b	1.3 mg/g
	R^2	0.7129
	χ^2	17.2

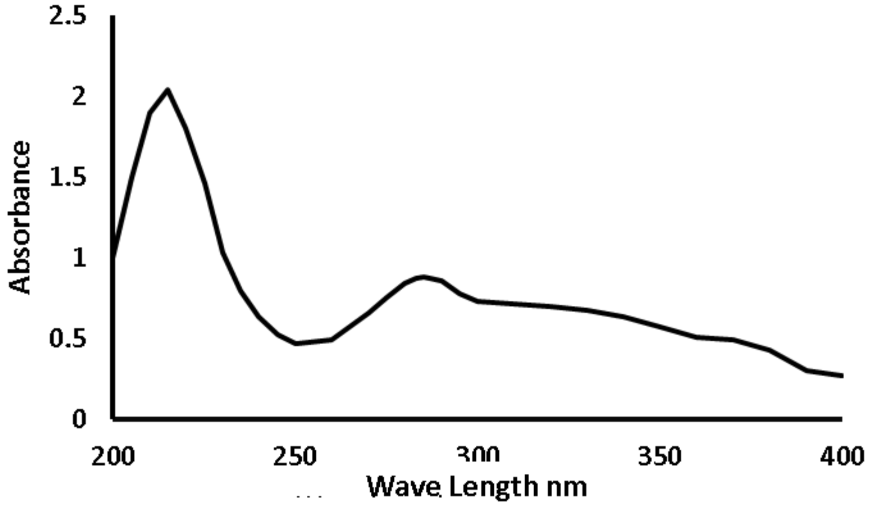


Figure 1. UV spectra of MA.

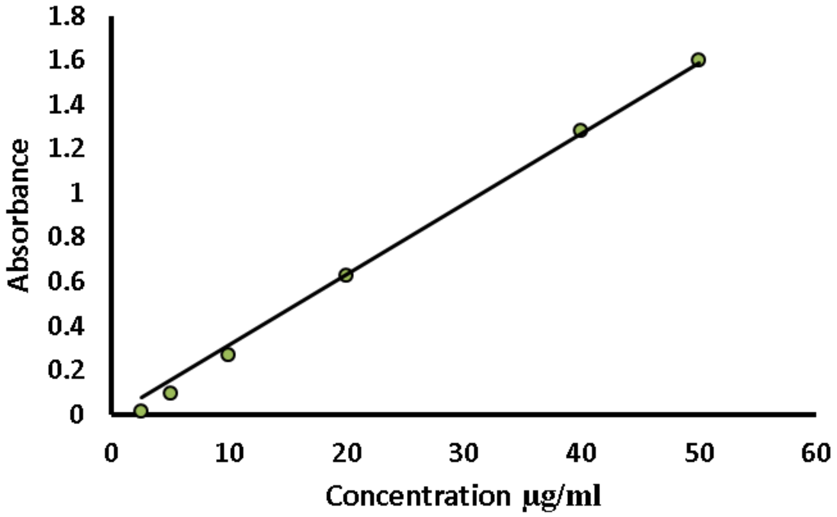


Figure 2. Standard Calibration curve of MA.

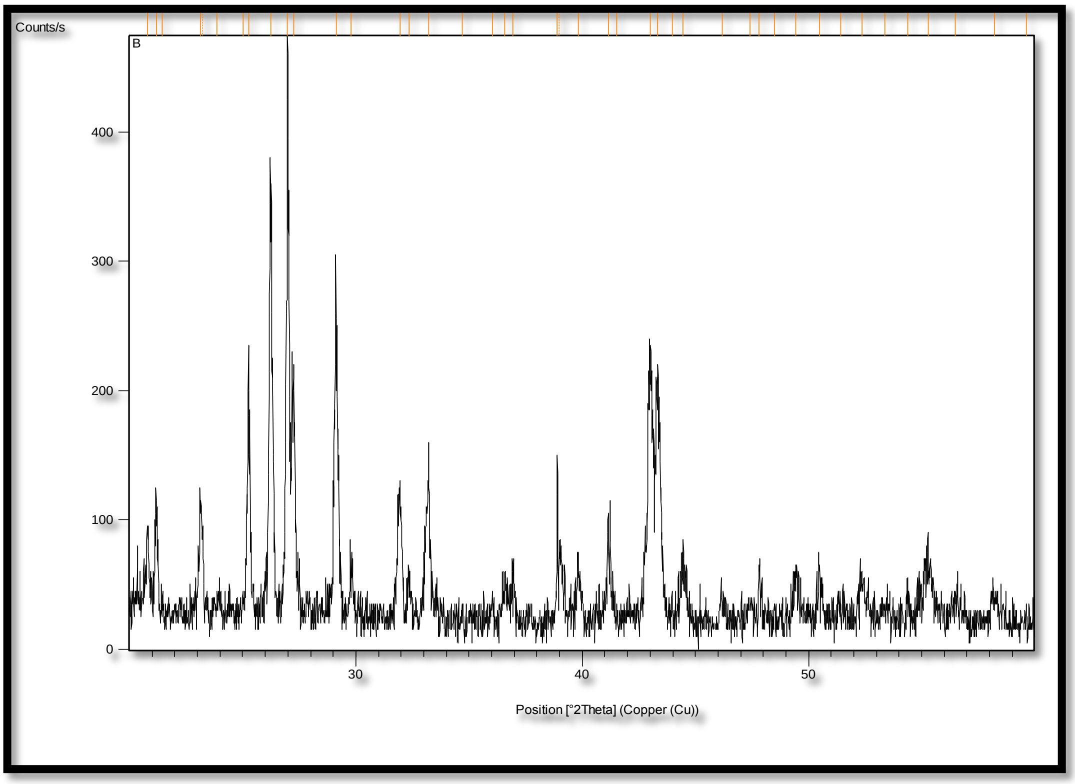


Figure 3. XRD of Bentonite**.**

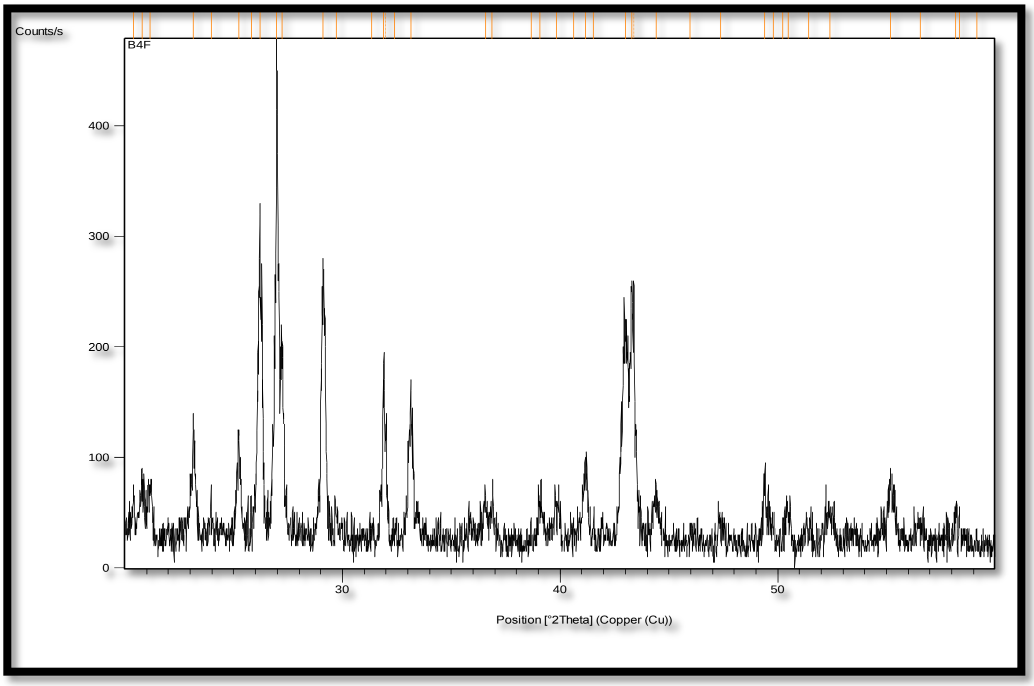


Figure 4. XRD for Bentonite poly urea formaldehyde composite.

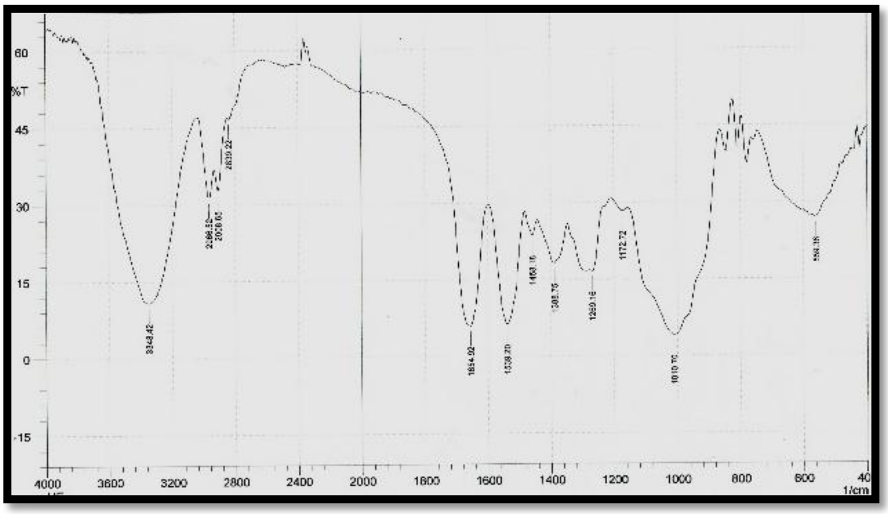


Figure 5. FTIR spectra for ureaformaldehyde resin.

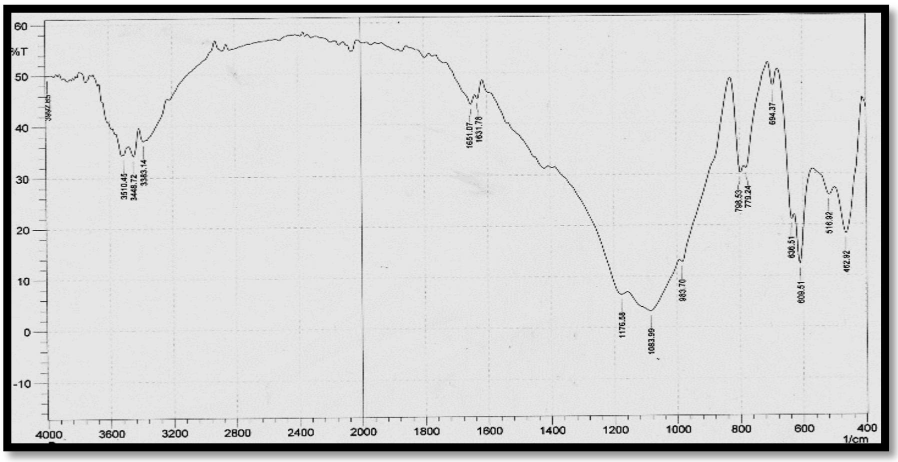


Figure 6. FTIR spectra for bentonite.

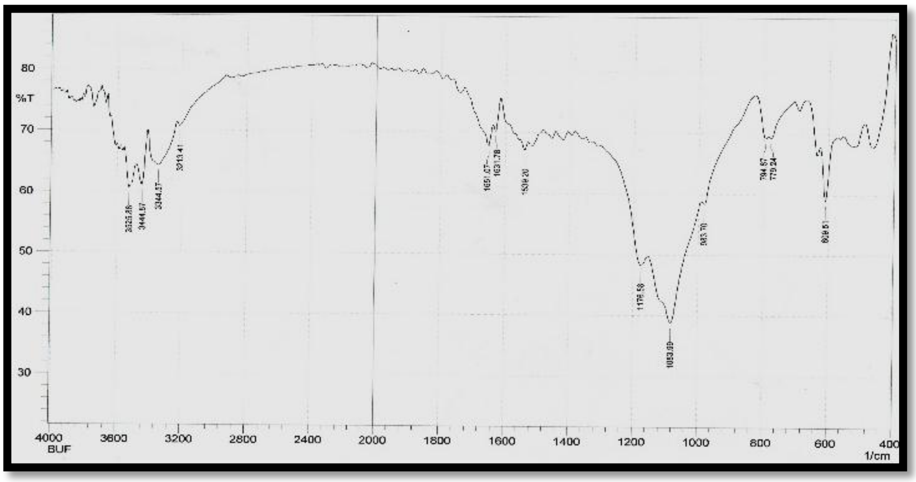


Figure 7. FTIR spectra for bentonite -PUF composite.

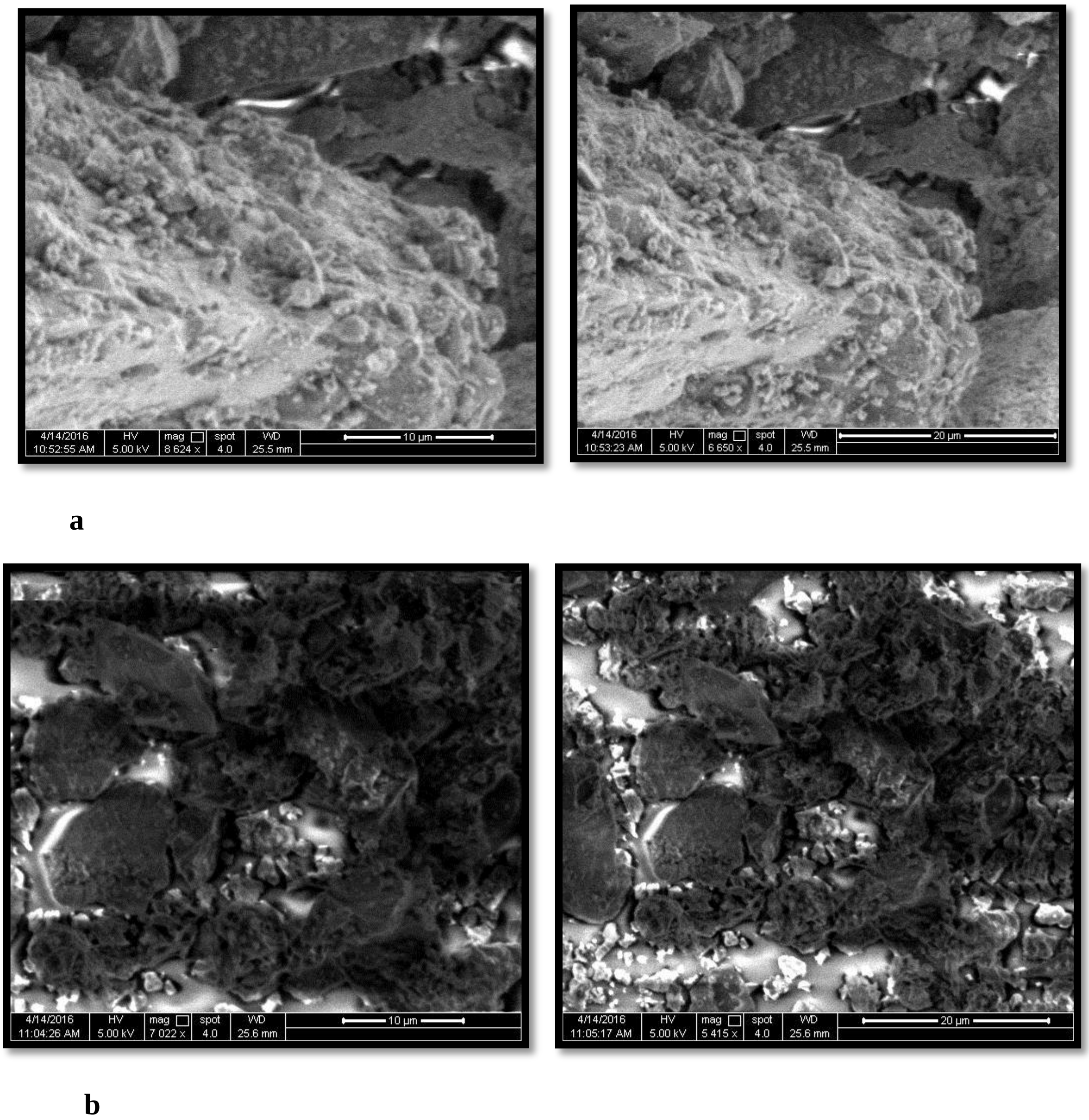


Figure 8. SEM image for (a) bentonite (b) bentonite-PUF composite.

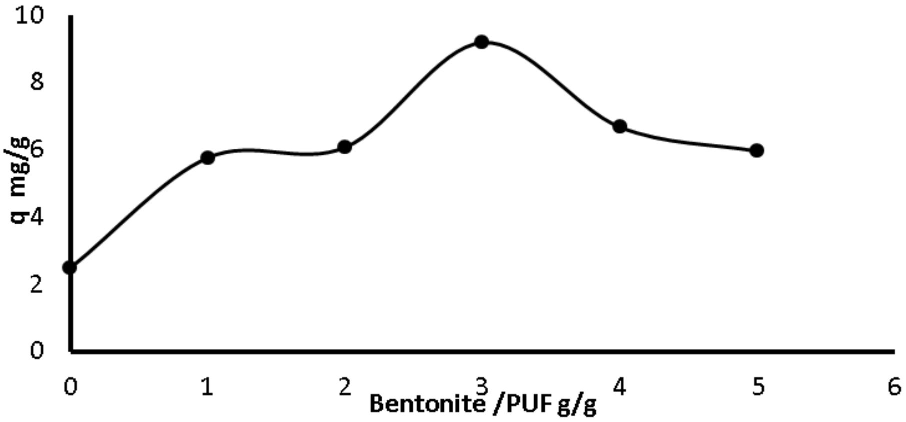


Figure 9. Effect of bentonite mass on adsorption capacity pH=7,R.P.M =180,T=27˚C ,adsorbent mass =0.05 g, contact time 240 min and initial concentration 40µg/ml.

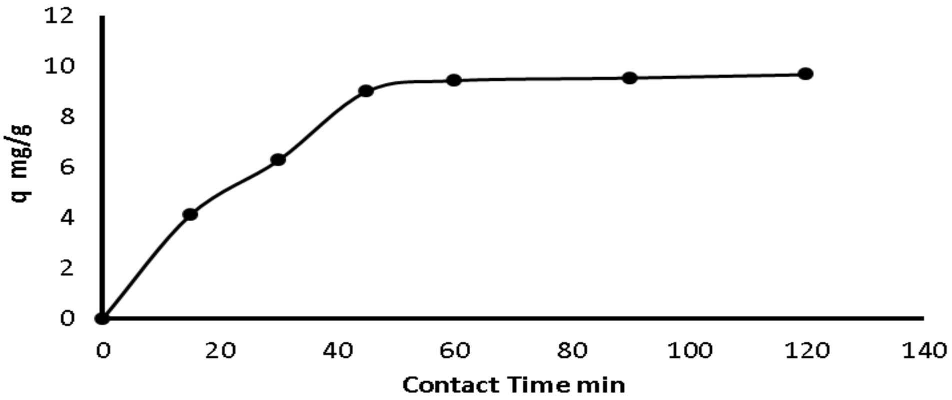


Figure 10. Effect of contact time on adsorption capacity pH=7,R.P.M =180,T=27˚C ,adsorbent mass =0.05 g and initial concentration 40µg/ml.

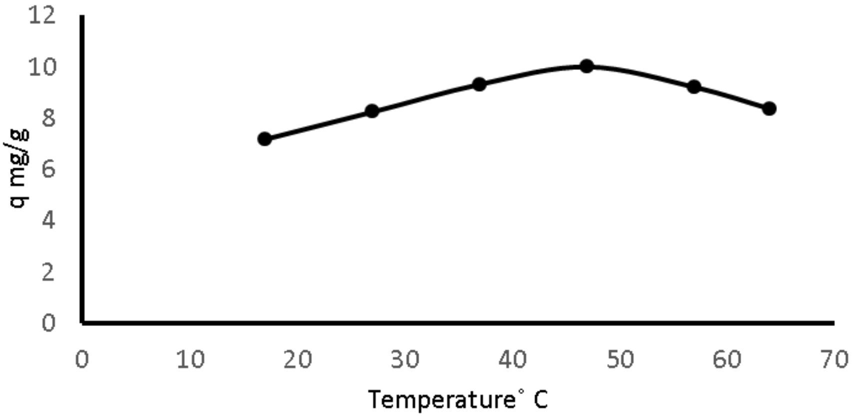


Figure 11. Effect of Temperature on adsorption capacity pH=7, R.P.M =180, contact time = 60 min, adsorbent mass =0.05 g and initial concentration 40µg/ml.

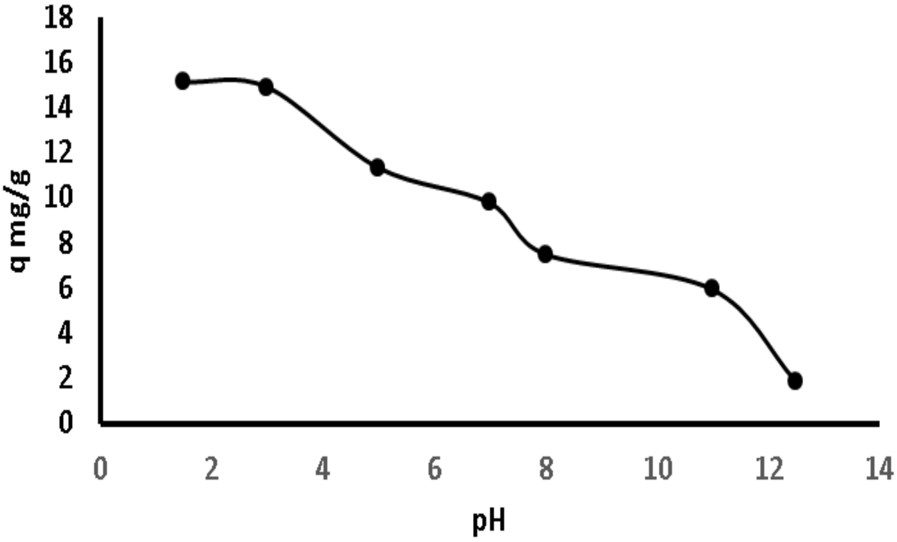


Figure 12. Effect of pH on adsorption capacity ,Temp.=47˚C, R.P.M =180, contact time = 60 min, adsorbent mass =0.05 g and initial concentration 40µg/ml.

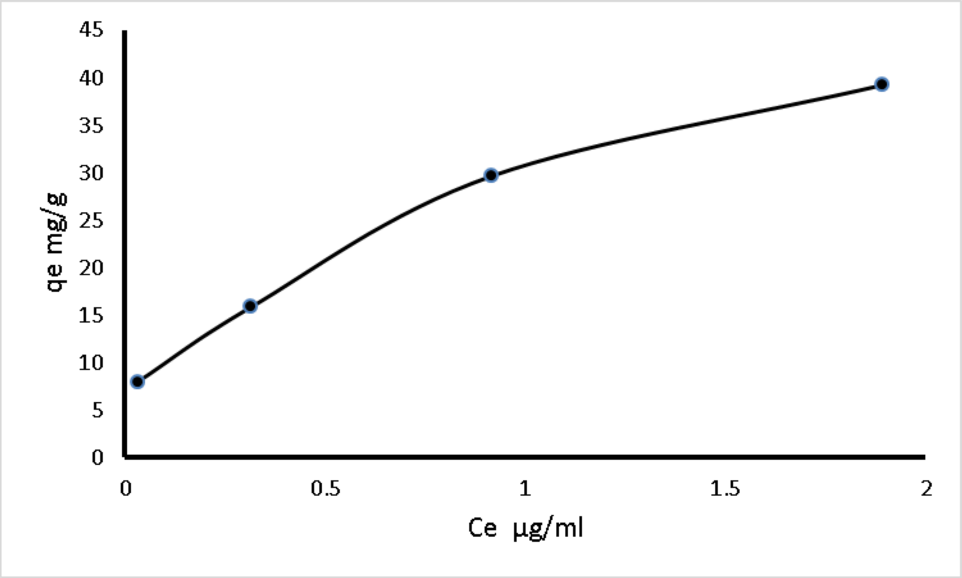


Figure 13. Effect of initial concentration on adsorption capacity, Temp.=47˚C, R.P.M =180, contact time = 60 min, Adsorbent mass =0.05 g and pH = 2.

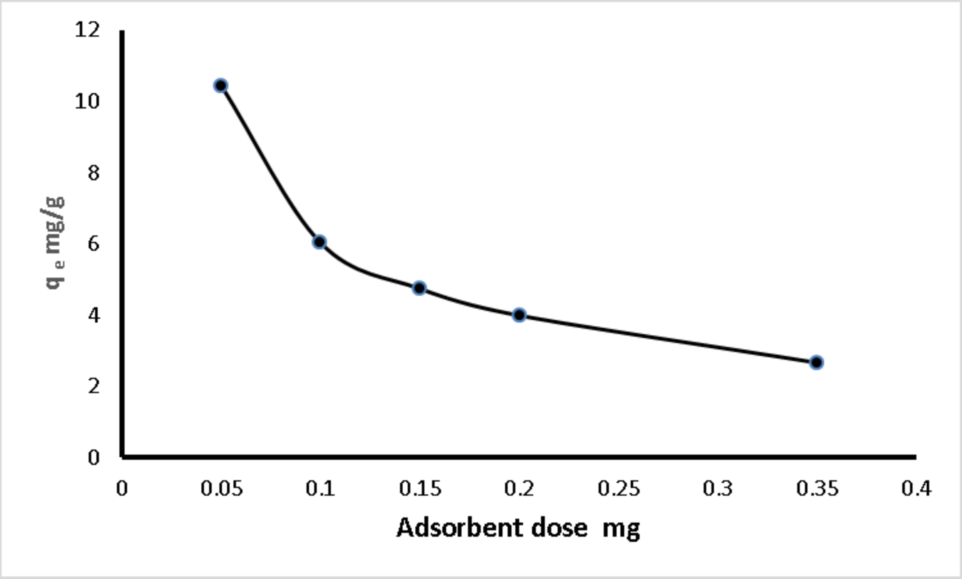


Figure 14. Effect of Adsorbent dose on adsorption capacity, Temp.=47˚C, R.P.M =180, contact time = 60 min, Adsorbate initial concentration =40µg/ml and pH = 7.

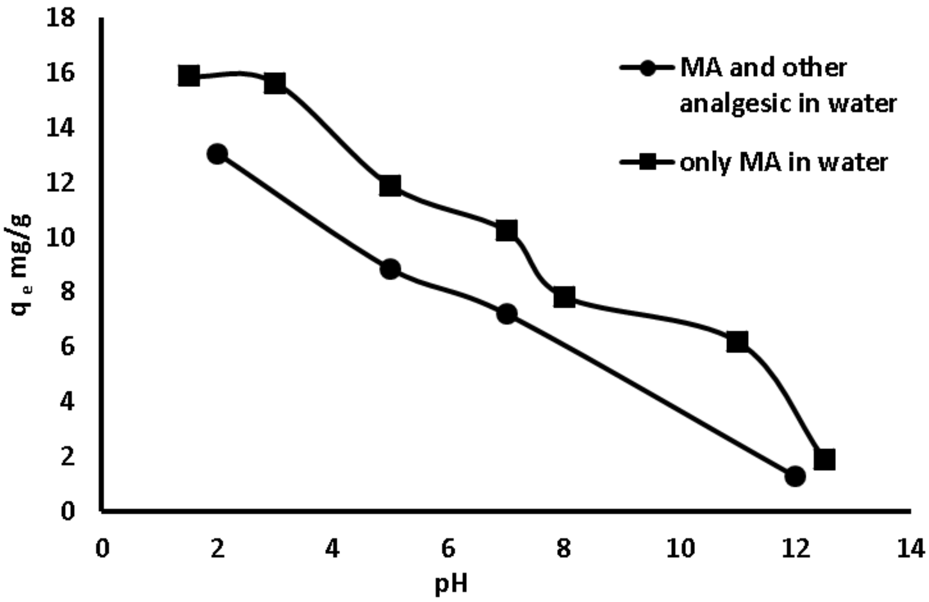


Figure 15. Effect of sharing adsorbent surface on adsorption capacity, Temp.=47˚C, R.P.M =180, contact time = 60 min, Adsorbate initial MA concentrations =40 µg/ml and adsorbent mass =0.05 g**.**

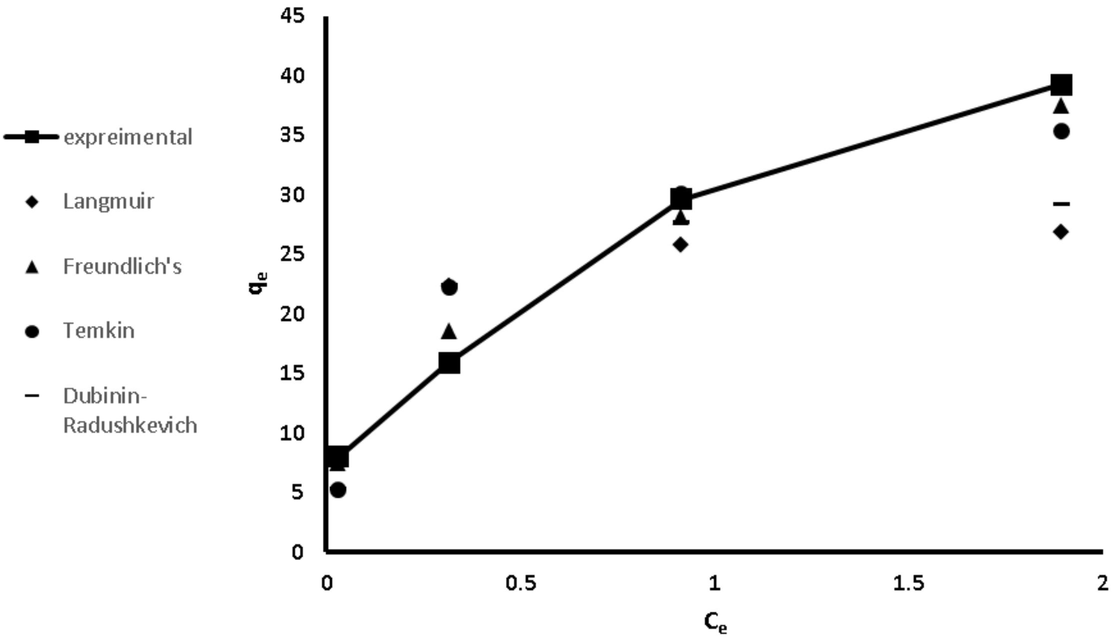


Figure 16. Experimental and isotherm models data for MA adsorption on PUF - Bentonite composite.

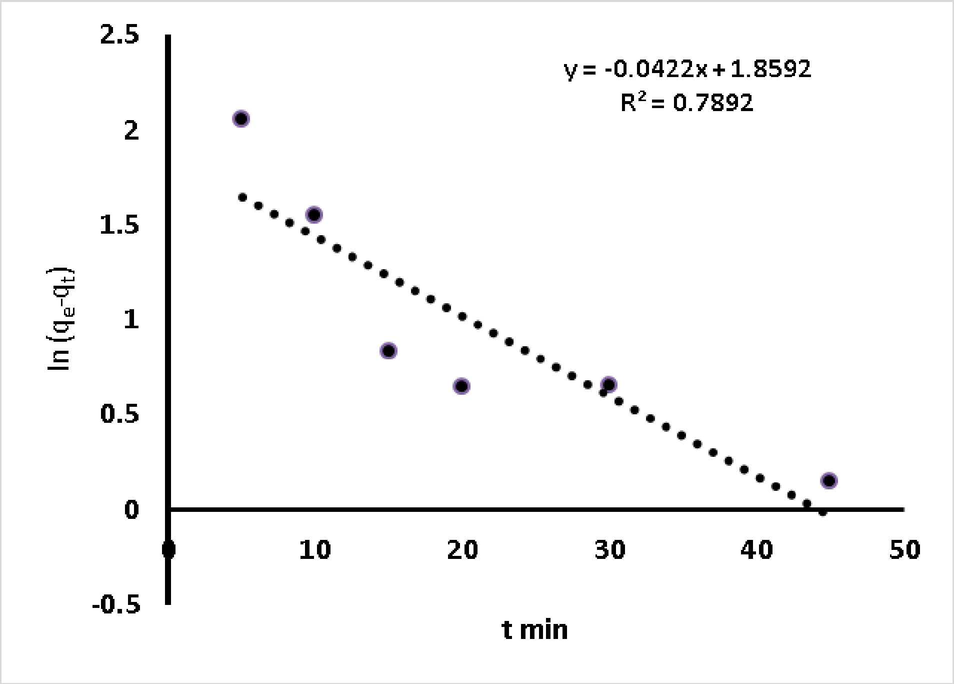


Figure. 17. linear form of first order kinetics.

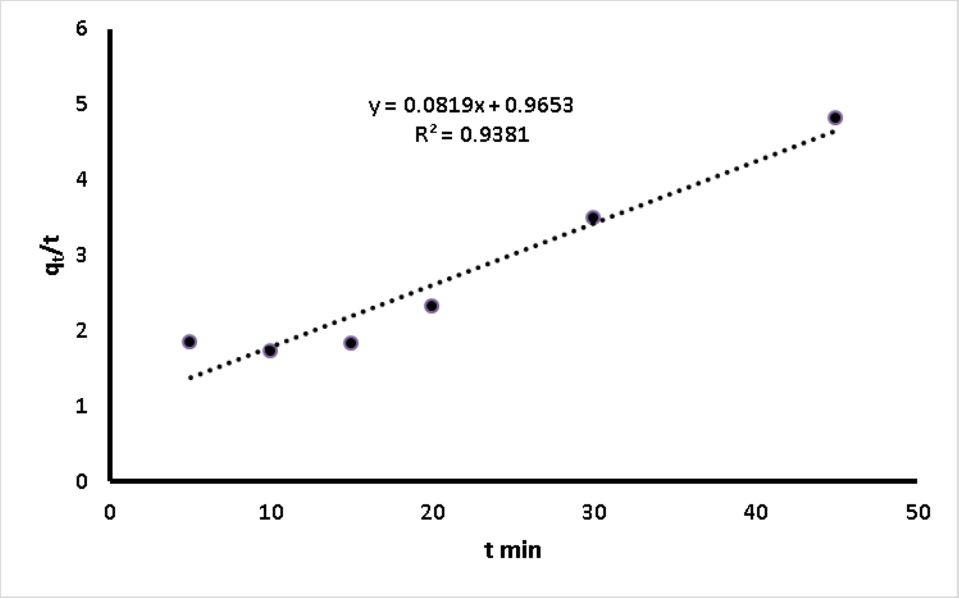


Figure. 18. linear form of second order kinetics.

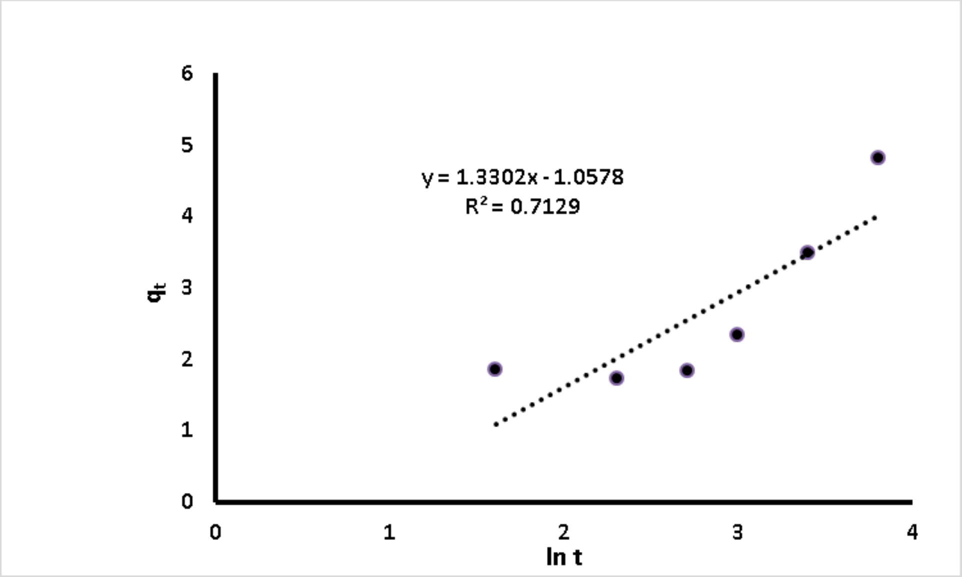


Figure. 19. linear form of Elovich's equation.