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Adsorption of Diclofenac Sodium and Ibuprofen by Bentonite Polyureaformaldehyde Thermodynamics and Kinetics Study

Basma Abbas Abdel Majeed[a], Raheem Jameel Muhseen[b] and Nawras Jameel Jassim [c]

[a] *College of Engineering -University of Baghdad*
[b] *College of Pharmacy-University of Basra*
[c] *Basra Technical Institute -Southern Technical University*

Abstract

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.

The nonprescription and huge used pharmaceuticals ibuprofen and diclofenac sodium will be focused in this study. New adsorbent developed using cheap inorganic clay material (bentonite) and organic polymer polyureaformaldehyde (PUF), the combination of these two materials gave the surface more roughness with wide active site distribution. Batch adsorption experiment performed to each pharmaceutical individually to determine the optimum separation parameters and understanding the adsorption process pathway. Both pharmaceuticals adsorbed on bentonite –PUF adsorbent in short time ranges from 15 min for ibuprofen to 30 min for diclofenac sodium .Thermodynamic analysis indicates the adsorption process is endothermic in nature and fall in the region of physical adsorption for tested pharmaceuticals (ΔH°=23.33 and 14.69 KJ/Mol for both ibuprofen and diclofenac sodium respectively).Elovichs equation for describing kinetics of adsorption seemed a good fit with adsorption of both pharmaceuticals .The effect of pH had a significant effect for both pharmaceuticals with high removal (99.8% for diclofenac and 99.2 % for ibuprofen) at acidic pH=2 below Pka value. Isotherm studied at different initial concentration, the results showed that the Dubinin-Radushkevich model suitable for describing ibuprofen adsorption, and Freundlich's isotherm for diclofenac sodium.

Keywords: emerging contaminants, (bentonite), polyureaformaldehyde (PUF)

1- Introduction

A global interest on development active separation technology for emerging contaminants ECs removal from water, filtration with coagulation, precipitation, ozonation,photolysis, membrane bioreactor (MBR) , advance oxidation, ion exchange and reverse osmosis.

These methods are restricted and consume high operation and capital costs. Or in some cases don't rid of contaminants permanently [1].

The most efficient separation process used in wastewater treatment is adsorption ,due to low cost , low investment and simple design and operation. Ibuprofen is nonsteroidal anti-inflammatory drugs NSAIDs act by inhabit hormones that cause pain in the body cylooxygenase-2 (COX-2).Ibuprofen is the dominated non-prescription pharmaceutical used worldwide**.**

Diclofenac is NSAID , this medicine works by reducing substances in the body that cause pain and inflammation used to treat mild to moderate pain, or signs table (1) clarified some physiochemical properties of interested pharmaceuticals.

Several researches focused on removal of diclofenac sodium and ibuprofen, adsorption of ibuprofen and diclofenac sodium using mesoporous silica confirmed at pH range from 3-5 and 15 minutes contact time [2].

Interaction of indomethacin and diclofenac solutions, on multi-walled carbon nanotube MWCNT adsorbent reported high adsorption capacity value for diclofenac sodium than indomethacin in MWCNT surface [3].

Adsorption of diclofenac on functionalized silica-based material [4], clay and activated carbon [5].

Ibuprofen adsorption on bentonite surface in the presence of surfactant, authors concluded that the presence of surfactant enhance adsorption capacity and don't affect the equilibrium time [6].

Different adsorbent materials activated carbon cloths [7],activated carbon [8],activated biochar [9] and cyclamer persicum tubers activated carbon [10] used in literature for adsorption of ibuprofen or diclofenac.

2- Experimental Work

2.1. Materials & Method

Oren hydrocarbons Middle East LTD commercial bentonite were used in this study, the chemicals used in this research clarified in table (2).

Corresponding Authors: Basma Abbas Abdel Majeed, Email: basma1957@yahoo.com, Raheem Jameel Muhseen, Email: raheemjamail@yahoo.com, Nawras Jameel Jassim, Email: nawras.jassim@gmail.com

All reagents and solvent used during this work were reagent grade and used without further purification.

2.2. Preparation Urea Formaldehyde –Bentonite Composite

Bentonite washed in ultrapure deionized water for three times and then drying in oven at 100 ˚C for two hours **.**Different masses ratios of bentonite to poly urea formaldehyde 1:1,2:1,3:1,4:1 and 5:1 g/g and 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 for solidification .The composite washed many times with ultrapure deionized water finally dried in an oven to remove moisture at 100 ˚C. The sample was crushed and screened through a 200-mesh for further use in batch experiments.

2.3. Adsorption Experiments Protocols

The adsorption studies were conducted with 0.050 g of 200 Mesh adsorbent and 20 mL of single pharmaceutical solution at desired concentration, pH and temperature on a constant speed of 180rpm.

The solution was filter in 0.1 microns filter syringe and the concentration of pharmaceuticals in the supernatants was examined with a spectrophotometer at the wavelength of each pharmaceutical at which the maximum absorbency occurred.

Then the amounts of pharmaceuticals adsorbed per unit mass of adsorbent and removal efficiency of adsorbent were calculated from the following equations:

$$q = \frac{(C_i - C_e)V}{M} \quad (1)$$

$$\%Removal = \frac{C_i - C_e}{C_i} * 100 \quad (2)$$

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

Different experiment will be conducted in batch form using adsorbent (bentonite-PUF) and fixed 180 r.p.m, such as checking different mass ratio of bentonite to PUF(bentonite only to 5:1 g/g), effect of pH(from 1.5 to 13), and interaction between temperature and contact time(temperature range from 10 ˚C to 77˚C).Thermodynamic parameters will be determine using a conventional thermodynamic equations.

Adsorption Kinetic will be tested using four three type of kinetic equations .Adsorption isotherm tested using four isotherm models.

2.4. Calibration and Method Validation

UV spectrophotometer were used to quantification of pharmaceuticals concentration , maximum wave length tested from 200-400 nm .The maximum wave length tested ,for ibuprofen is 222nm and agreed with Joshi [11] and diclofenac sodium at 276 nm and agreed with Khaskheli and Khan [12]**&**[13].

Stock solution of each pharmaceuticals prepared in concentration range from 0 to 100 µg/ml to draw the concentration against absorbance to further use in concentration quantification experiment. The calibration curves illustrated in Fig. 1&2

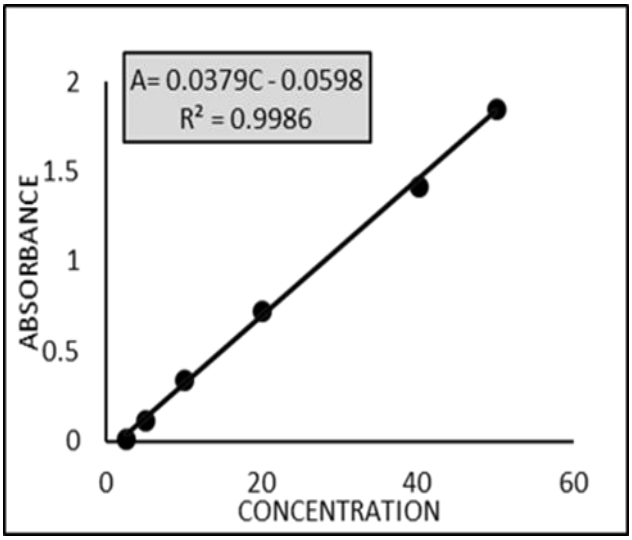


Fig. 1, Standard Curve for ibuprofen in .01M NaCl solution in .01M NaCl solution

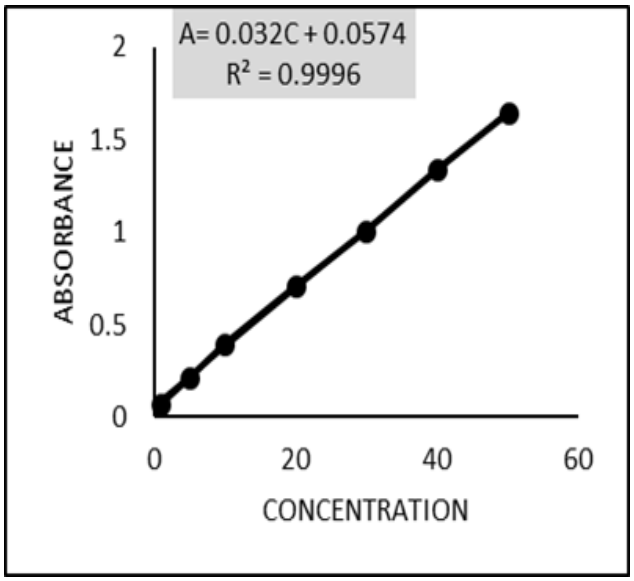


Fig. 2, Standard Curve for diclofenac Sodium in .01M NaCl solution in 0.01M NaCl solution

Table 1. Physical, chemical and properties of Ibuprofen & Diclofenac Sodium

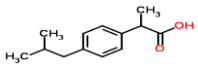
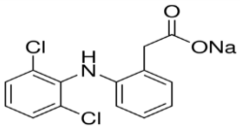
Item	Description /value Ibuprofen	Description /value Diclofenac Sodium
Structure		
Formula	$C_{13}H_{18}O_2$	$C_{14}H_{10}C_{l2}NNaO_2$
IUPAC Name	2-[4-(2-methylpropyl)phenyl]propanoic acid	sodium;2-[2-(2,6-dichloroanilino)phenyl]acetate
Molecular weight	206.28 g/mol	318.14 (g/mol)
Pk_a	5.2	4
Log K_{ow}	3.97	4.51
Melting Point	75-77.5	283-285 °C

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
Diclofenac Sodium	SIGMA life science

3- Characterization and Testing

3.1. FTIR Spectroscopy

FTIR spectra of the bentonite-PUF samples after and before adsorption of single and all pharmaceuticals and bentonite only using SHIMADZU spectrophotometer.

The FTIR spectrum of the sample obtained by method including KBr pellet .Mixture of sample to KBr ratio of 1:50 will be used .FTIR spectra were recorded in the region of 4000-400 cm^{-1}

3.2. Scanning Electron Microscopy

Scanning electron micrograph and surface morphology of the sample was obtained by using (INSPECT 550) microscope was normally performed at 10 Kv**.**

3.3. XRD Analysis

Powder XRD analysis of both bentonite and bentonite-PUF was obtained using samples was performed on the (PAN ALYTICAL); a copper (Cu) anode was used in the X-ray tube and operated at current 20mA and 40 kV.

4- 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) ,root mean square error (RMSE) and average relative error (ARE) .Below the formulas to calculate each error function[14]**;**[15]**;**[16]**&**[17] **:**

$$\chi^2 = \sum_{i=1}^{n} \frac{(q_{exp.} - q_{mod.})^2}{q_{exp.}} \quad (3)$$

$$\text{RMSE} = \frac{1}{n}\sqrt{\sum_1^n (q_{mod.} - q_{exp.})^2} \quad (4)$$

$$\text{ARE} = \frac{100}{n}\sum_1^n \left|\frac{q_{mod} - q_{exp.}}{q_{exp}}\right| \quad (5)$$

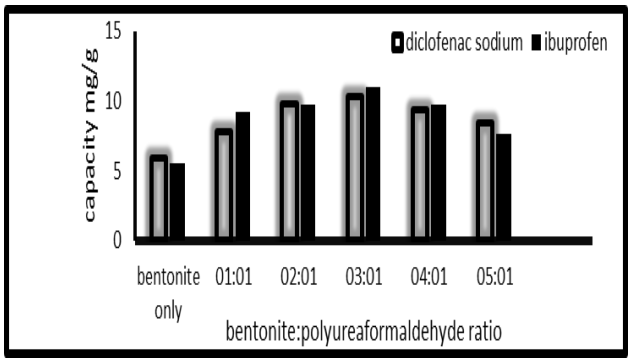


Fig. 3, Effect of composite mass ratios on ibuprofen and diclofenac sodium adsorption, parameters conditions ,pH=7,contact time 3h ,adsorbent mass 0.05g ,sample volume 20 ml, mixing speed 180 r.p.m and initial concentration 40 µg/ml

5- Results and Discussion

5.1. Effect Of Bentonite To PUF Mass Ratio

The adsorption of diclofenac sodium and ibuprofen by composite adsorbents with different mass ratios of bentonite and PUF shown in Fig.3. 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[18]&[19]. The best composite ratio bentonite to PUF will be used for further experiments is 3:1 for bentonite to PUF ratio.

5.2. Interaction Between Equilibrium Time & Temperature

Except for high adsorption capacity, fast adsorption rate is also indispensable for practical application. From the other hand heat stress had a significant effect on adsorption behavior.

Regarding the temperature effect variable temperatures will help in evaluating the basic thermodynamical functions (ΔH°, ΔG°, ΔS°) of the adsorption process. Sometimes temperature gave indicator about whether the adsorption is chemical or physical in nature .Adsorption of selected pharmaceuticals at different contact times were studied as a function of temperature difference in single compound phase .Keeping all other parameters constant using neutral pH and 40 µ/ml initial concentration for each pharmaceuticals except ,mixing speed of 180 r.p.m and bentonite –PUF composite mass about 0.05g in 20 ml of individual pharmaceutical solution. Batch adsorption experiments were conducted with bentonite –PUF composite by varying string times from 0 to 60 min and temperature changing from 10 to 77˚C.The results for both adsorption removal and capacity are presented in Fig.(4 &5).Ibuprofen attained equilibrium at very short time 15 min with maximum removal of 81.5% at temperature 47˚C and 13.3mg maximum capacity. Percentage removal of 78.4%, and 12.6 mg/g capacity for diclofenac in equilibrium time of 30 min and 47˚C. The contact equilibrium time achieved in this study is shorter than the contact time using different adsorbent in many researches focused on selected NSAIDs [20];[21] ;[22] &[10].

As emerging contaminants (ECs), the time graphs for all pharmaceuticals indicates a quick initial adsorption rate at the first 15 min and then slowly increased until reach equilibrium, the adsorption rate became practically constant. The adsorption capacity alteration at the early minutes was Observed, this may be attributed to high driving force and large number of empty active site available on bentonite–PUF surface.

Further increase in contact time did not show significant change in adsorption capacity; that is, the adsorption phase reached equilibrium and limited active sites and reduction the concentration gradient (driving force) .The remaining active site still vacant even with achieving equilibrium then trying with other parameters to shift the driving force to enhanced capacity are required .

The overlap between temperature and contact equilibrium time showed increasing adsorption removal and capacity with increasing temperature until reach temperature of 47˚ C ,then any further increasing in temperature lead to decrease adsorption capacity.

The enhancement in adsorption capacity with rising in temperature may be attributed to increases the rate of diffusion of the adsorbate pharmaceuticals molecules across the boundary layer and within the internal pores of the adsorbent particle, due to decrease in the viscosity of the solution. At high temperature water structuring around hydrophobic part of pharmaceuticals decreased the adsorbate molecule become more free to diffusion and increased diffusion rate,[23] & [24].

Álvarez concluded increasing adsorption capacity with increasing temperature for diclofenac adsorption on carbon xerogels [25].

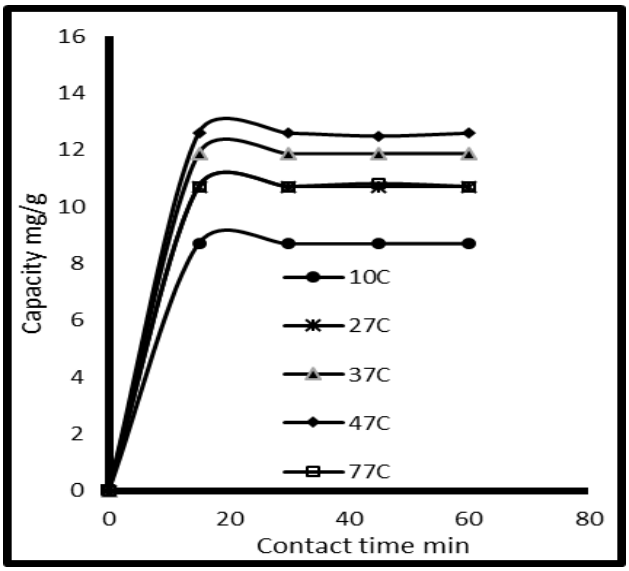


Fig. 4, Interaction between temperature and contact time on adsorption capacity of Ibuprofen initial concentration of 40 µg/ml ,pH=7and 0.05 g adsorbent weight

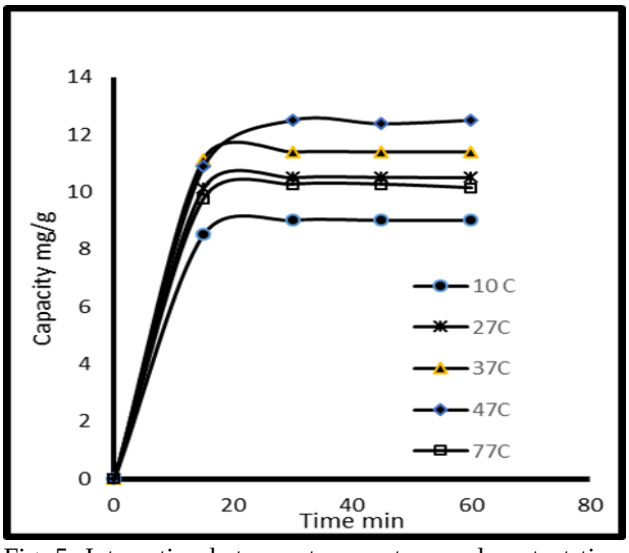


Fig. 5, Interaction between temperature and contact time on adsorption capacity of diclofenac sodium initial concentration of 40 µg/ml ,pH=7and 0.05 g adsorbent weight

5.3. Thermodynamic Aspects

The thermodynamics parameters, which characterize the equilibrium of the pharmaceuticals adsorption system such as Gibbs free energy change ΔG˚,the entropy change ΔS˚ and the enthalpy change ΔH˚ will be determined in this section .The temperature range took in this section from 10˚C to 47˚C for each ibuprofen ,indomethacin ,acetylsalicylic acid , acetaminophen ,diclofenac sodium and mefenamic acid. These parameters can be determine using the following relations [26]

$$LnK_d = Ln\frac{C_a}{C_e} = \frac{-\Delta G^\circ}{RT} \quad (6)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (7)$$

$$LnK_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (8)$$

Where:
K_d : Equilibrium constant
C_e : Equilibrium concentration of adsorbate in aqueous solution
C_a : Concentration of adsorbate in solid adsorbent (C_i – C_e)
ΔS˚ : Entropy Change J/mol.˚K
ΔG˚ : Gibb's free energy change
ΔH˚: Enthalpy Change J/mol
T: Absolute Temperature ˚K
R: Universal Gas Constant 8.314 J/mol.˚K

By drawing the linear relationship between Ln Kd and 1/T of Eq. (6) can obtain the values of ΔH˚ and ΔS˚, ΔG˚ values were computed for each temperature by the Helmholtz relation Eq.'s (7) or (8).Fig. (6) Explain the linear plot between Ln Kd and 1/T , with R2 value of 0.9983 other thermodynamic parameter listed in table (3) for ibuprofen the results show a negative value of -ΔG˚ for all temperature ranges and positive value for both ΔS˚&ΔH˚, same results for ibuprofen adsorption investigated in previous literatures[26]; [27]&[28],opposite behavior observed [29].

Fig.(7) explain the linear plot between Ln Kd and /T , for diclofenac sodium with R2 value of 0.9773 ,other thermodynamic parameter listed in table (4). Results for diclofenac sodium agreed with Carvalho &Suriyanon[30] &[4], negative ΔH˚ and ΔS˚ obtained by Jodeh[10],exothermic adsorption observed Antunes[31]. It's evident from the figures and tables for selected pharmaceuticals that the ΔG˚ values in all temperatures ranges were negative and increase its absolute value with temperature increased.

This negative values indicates the feasibility and spontaneity of ongoing adsorption process so the adsorption process of both pharmaceuticals is spontaneous in nature and were more favorable at high temperature in other words the adsorption driving force increase with temperature increased.

General aspects that the ΔG˚ value in the range of 0 to -20KJ/mol and -80 to 400KJ/ mol for physical and chemical adsorptions, respectively[32]. The ΔG˚ values for this study pharmaceuticals ranging from (-0.002 to -3.4 KJ/mol) this findings refers to the physical nature of adsorption of ibuprofen and diclofenac sodium on bentonite –PUF composite.

The positive value of ΔH˚ (23.33 and 14.69) KJ/mol for ibuprofen and diclofenac sodium affirm that the adsorption of adsorbate pharmaceuticals on the bentonite –PUF composite are an endothermic in nature .The high value of ΔH˚ for ibuprofen confirm the strong temperature depending to perform physical adsorption.

The concerned process achieved equilibrium by consuming energy from the considered adsorption system [28].

The positive value of ΔS˚ shows an increase in the disorder and randomness at the surface /solution interface, accompanying with some structural changes in both adsorbate and adsorbent as a results of interaction of pharmaceuticals molecules with active sites in the bentonite–PUF composite surface. The ΔS˚value for ibuprofen greater than diclofenac sodium. Generally the obtained ΔS˚ results are close to the previous researchers [26] & [28].

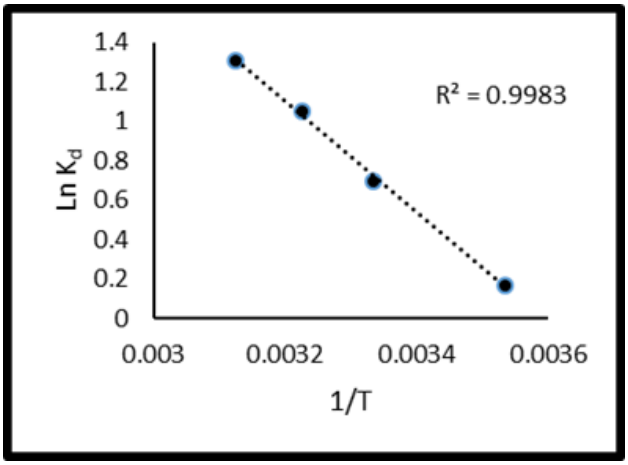


Fig. 6, Determination of thermodynamic parameters (ΔG˚, ΔS˚&ΔH˚) for the adsorption, of ibuprofen

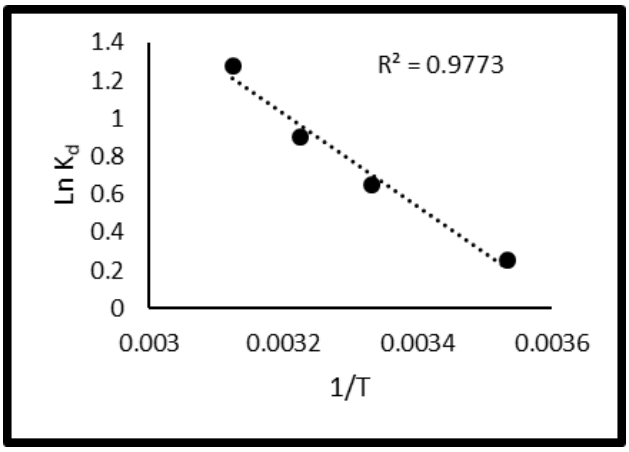


Fig. 7, Determination of thermodynamic parameters (ΔG˚, ΔS˚&ΔH˚) for the adsorption, of diclofenac sodium

Table 3. Thermodynamics parameters for Ibuprofen

Temperature ˚C	K_d	ΔG˚ KJ/Mol	ΔH˚ KJ/Mol	ΔS˚ KJ/Mol.˚K
10	1.188	-0.405	23.33	0.08
27	2.015	-1.74		
37	2.859	-2.70		
47	3.696	-3.47		

Table 4. Thermodynamics parameters for diclofenac sodium

Temperature ˚C	K_d	ΔG˚ KJ/Mol	ΔH˚ KJ/Mol	ΔS˚ KJ/Mol.˚K
10	1.	-0.002	14.6925	0.051859
27	1.382	-0.807		
37	1.677	-1.33		
47	2.099	-1.973		

5.4. Determination of Rate Parameters

Determination the efficiency of adsorption processes requires a brief an understanding of kinetics of pharmaceuticals uptakes by bentonite –PUF composite, and the time influence on concentration distribution of adsorbate in both solid adsorbent surface and liquid solution.

Also determination the rate controlling step during the adsorption process important to know.The adsorption kinetic of ibuprofen and diclofenac sodium were modeled using pseudo first order, pseudo second order, Elovich's equation and intraparticle modules. Pseudo first order rate equation is expressed as follows [33]:

$$\frac{dq_t}{dt} = K_1\,(q_e - q_t) \tag{9}$$

Where

q_t : adsorption capacity at time t (mg/g)

q_e : adsorption capacity at equilibrium(mg/g)

K_1: pseudo first order rate constant (min.$^{-1}$)

After integration and applying boundary conditions t=0 and q_t=0 to t = t and q_t=q_e at equilibrium, the above equation becomes:

$$\ln(q_e - q_t) = \ln q_e - K_1 \,.\, t \tag{10}$$

The pseudo second order mode is given by the following [33]:

$$\frac{dq_t}{dt} = K_2\,(q_e - q_t)2 \tag{11}$$

Where:
K_2: pseudo second order rate constant.

For the same boundary conditions, the integrated form of equation (11) becomes:

$$\frac{t}{q_t} = \frac{1}{K_2\, q_e^2} + \frac{t}{q_e} \tag{12}$$

The Elovich's equation is generally expressed as follows [26] **:**

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln(t) \tag{13}$$

Where: α is the initial adsorption rate (mg/g) and β is adsorption constant (mg/g.min).

The intraparticle diffusion model is formulated by [26]:

$$qt = Kp\ t0.5 + C \tag{14}$$

Where: K_p intraparticle diffusion rate constant (mg/g.min$^{0.5}$)

The kinetic experiments conducted at different temperature ranges and all results applied to the linear kinetics models in above equations to calculate rate constant parameters. Different statistical functions used R^2,χ^2,ARE and RMSE to describe the best fit model . The kinetic experiment of ibuprofen conducted with time intervals from 5 to 30 min with initial solution concentration of 40 µg/ml and pH adjusted to 7.The linear plot of applying different models at different temperatures constants values and error function listed in table (5).

It's clear from the table that the best fit model for ibuprofen is Elovichs equation and second order kinetics due to minimum error function value observed at 10 ˚C.

This comparison cleared in Fig.(8) between (q_t) calculated from the kinetic models and the experimental values.The adsorption initial rate of ibuprofen on to bentonite-PUF composite (α) increased with temperature increased. The value of 1/β, indicative of the number of sites available for adsorption, was found higher value of 5 g.min./mg at temperature 47˚C and decreased as temperature decreased to value of 3.4 g.min./mg at temperature10˚C .From the other hand the values of second order rate constant increase with temperature increased as in table (5).

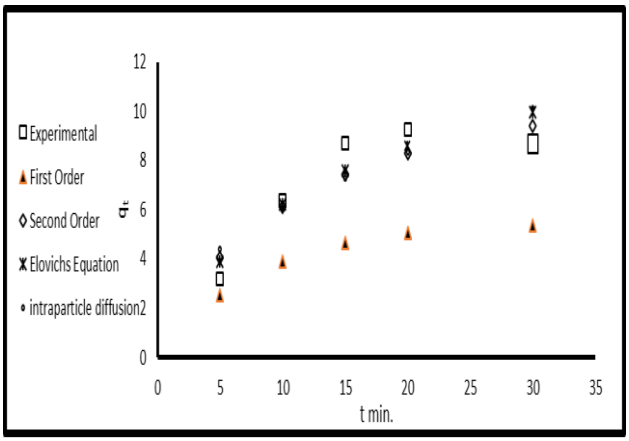


Fig. 8, comparison between experimental and different kinetics models for ibuprofen at temperature 10˚C

Any way the first order kinetics model and intraparticle diffusion model were not in good agreement to describe the experimental kinetics of ibuprofen. These results are agreed with previous work [26] ; [29] ; [34]&[28] .

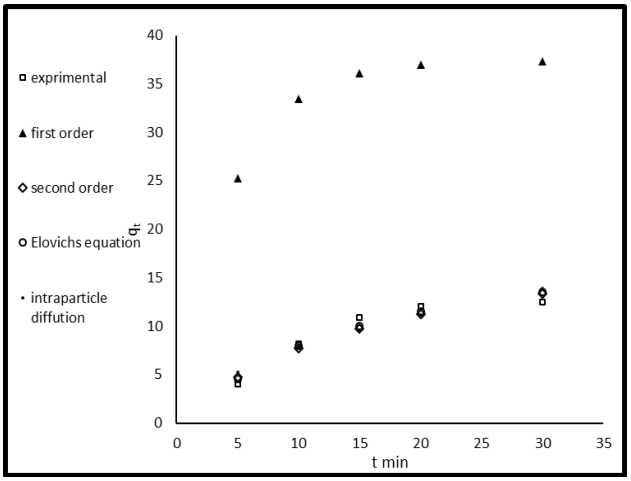


Fig. 9, comparison between experimental and different kinetics models of diclofenac sodium at temperature 47˚C

The calculated parameters for bentonite-PUF adsorbent , four kinetics models, and the respective error functions for the data and model, are summarized in table (6) for diclofenac sodium .From the review the value of error correlations coefficients, the adsorption of diclofenac sodium on to bentonite-PUF adsorbent is closely performed by Elovichs equation kinetics although agreeable, but not perfect fit with pseudo-second rate model Fig.(9).Intraparticle diffusion coefficient appear with high values and limited error and increase with temperature increased this indicates the adsorption of diclofenac sodium at low temperature required a higher amount of bentonite –PUF than at high temperature to reach the same adsorption efficiency. The number of site available 1/β increased with temperature from the value 3.5 to 5 g.min./mg.

The adsorption initial rate of diclofenac sodium α increase with temperature increased. For all studied NSAIDs , the adsorption plots of intraparticle diffusion model did not pass through the origin and the external mass transfer played an important role in the NSAIDs adsorption [4].

It was observed that intra-particle rate constant values increased with temperature for both pharmaceuticals . This may attribute promoting large number of pharmaceutical molecules to diffuse to pore before being adsorbed.

Table 5. Values of kinetic constants and error functions for ibuprofen

FIRST ORDER							
T (C˚)	R^2	χ^2	RMSE	ARE	q_e exp.	q_e Model.	K_1
47.00	0.28	8.88	4.67	0.37	13.40	7.65	0.15
37.00	0.32	8.38	4.40	0.37	12.60	7.30	0.14
27.00	0.29	7.50	3.96	0.37	11.38	6.52	0.14
10.00	0.39	6.12	3.20	0.38	9.27	5.50	0.12
SECOND ORDER							
T (C˚)	R^2	χ^2	RMSE	ARE	q_e exp	q_e Model.	K_2
47.00	0.87	38.33	7.13	0.88	13.40	18.80	0.05
37.00	0.87	0.80	1.19	0.13	12.60	17.70	0.005
27.00	0.87	0.70	1.07	0.13	11.38	15.97	0.006
10.00	0.87	0.56	0.86	0.13	9.27	12.89	0.007
ELOVICH							
T (C˚)	R^2	χ^2	RMSE	ARE	q_e	β	α
47	0.8534	0.757126	1.254	0.1174	13.4	0.202	3.057685
37	0.8525	0.726908	1.183	0.12	12.6	0.21	2.885768
27	0.8535	0.641559	1.064	0.1171	11.38	0.23	2.596596
10	0.8536	0.513099	0.859	0.1159	9.27	0.295622	2.128285
INTRAPARTICLE							
T (C˚)	R^2	χ^2	RMSE	ARE	qe	K_P	C
47	0.7474	1.511686	1.646	0.1731	13.4	2.56	0.6421
37	0.7452	1.452947	1.555	0.1759	12.6	2.4047	0.6298
27	0.7476	1.280814	1.397	0.1728	11.38	2.1737	0.5453
10	0.7478	1.023028	1.127	0.171	9.27	1.7557	0.4901

Table 6. Values of kinetic constants and error functions of diclofenac sodium

FIRST ORDER							
T(C°)	R^2	χ^2	RMSE	ARE	q_e	q_{mode}	k_1
47.00	0.98	350.26	24.35	0.40	12.55	37.39	0.23
37.00	0.47	2.41	2.24	0.04	11.70	9.01	0.17
27.00	0.43	2.23	2.09	0.04	10.90	8.32	0.16
10.00	0.62	0.99	0.93	0.01	9.25	8.59	0.16
SECOND ORDER							
T(C°)	R^2	χ^2	RMSE	ARE	q_e	q_{mode}	k_2
47.00	0.89	0.37	0.80	0.01	12.55	20.83	0.00
37.00	0.87	0.65	1.05	0.02	11.70	17.45	0.00
27.00	0.87	0.57	0.94	0.02	10.90	16.16	0.00
10.00	0.88	0.42	0.75	0.02	9.25	13.93	0.01
ELOVICH EQUATION							
T(C°)	R^2	χ^2	RMSE	ARE	q_e	β	α
47.00	0.95	0.25	0.68	0.02	12.55	0.20	2.49
37.00	0.88	0.57	1.02	0.03	11.70	0.22	2.62
27.00	0.89	0.49	0.91	0.03	10.90	0.24	2.40
10.00	0.90	0.36	0.72	0.02	9.25	0.28	2.02
INTRAPARTICLE							
T(C°)	R^2	χ^2	RMSE	ARE	qe	K_P	C
47.00	0.88	0.77	1.09	0.02	12.55	2.66	-0.71
37.00	0.78	1.21	1.38	0.03	11.70	2.34	0.27
27.00	0.79	1.07	1.25	0.03	10.90	2.17	0.19
10.00	0.81	0.82	1.00	0.03	9.25	1.86	0.09

5.5. Effect of Solution pH

The effect of pH studied in the range 1.5 to 13 for ibuprofen, and diclofenac sodium. The results of pH effect on both adsorption capacity and removal efficiency are explained in Fig.(10& 11) for ibuprofen and diclofenac sodium . It observed from Fig.(10) that ibuprofen removal efficiency about 96% at pH value of 1.5 and dropped at pH of 13 to 51%. the adsorption removal efficiency of diclofenac sodium equal to (99.8%).

The maximum capacity was observed at pH range 1.5-3.5 for (diclofenac sodium, and ibuprofen adsorption. the pKa value of these pharmaceuticals (ibuprofen=5.2 and , diclofenac sodium = 4) which vary according to their molecular structure .At pH value below pKa ionization of pharmaceutical compound will be occur ,then additional to electrostatic interaction increased in nonelectrostatic interactions occur ,including hydrogen bonding between pharmaceuticals and bentonite –PUF surface by increasing the positive charges .From the other hand 'van der Waal' interaction between pharmaceuticals and the adsorbent surface increased due to decrease the solubility with increasing pH.

For the same group of pharmaceuticals diclofenac sodium and ibuprofen, the removal capacity decrease with increase pH to basic media. This behavior due to the successive deprotonation of positive charged groups at pH above pKa. Therefore, more molecules exist in anion forms this caused electrostatic increase pH to basic media.

This behavior due to the successive deprotonation of positive charged groups at pH above pKa. Therefore, more molecules exist in anion forms this caused electrostatic repulsion between negatively charged sites on the adsorbent and pharmaceuticals .Also competition between -OH and pharmaceuticals to fill the positively charged adsorption active sites will be dominate [35].

Similar path observed in literature [21];[36] & [10]. Generally pH variation control the hydrophilic part in pharmaceutical
molecules ,in the other words responsible for increase or decrease the interaction between active pharmaceutical molecule groups and surface groups rather than hydrophobic molecules adsorption

5.6. Adsorption Isotherm

The successful adsorption separation process to remove pharmaceutical contaminants depends on a good description of equilibrium distribution between two phases. By plotting residual liquid phase concentration against equilibrium capacity at specified time, it can possible to describe the equilibrium adsorption isotherm.

Requirement of design concentration of adsorption system to eliminate pharmaceutical pollutants from contaminant water, it's important to establish the most fit correlation to describe an equilibrium curves.

There are many theories relating to adsorption equilibrium and among the used models are Langmuir, Freundlich, Dubinin-Radushkevich and Temkin [37].In order to optimize the design the mathematical equations of these models are illustrated in literatures [38];[39];[40] will be used to describe the best fit data to experimental results. The selection of the best fitting model is determine by calculating three error deviation functions χ^2,ARE and RMSE between experimental and predicted equilibrium data after applying linear and nonlinear form of adsorption isotherm [37].

Important parameter denoted the essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor, R_L, can be defined as follows [41] :

$$RL = 1/1 + kLC \quad (15)$$

Where $C_\circ$ initial pharmaceutical concentration µg/ml,K_L Langmuir adsorption constant (ml/µg).The adsorption process consider as favorable when $0< R_L<1$ and linear when $R_L=1$, $R_L = 0$ indicates irreversible adsorption, while an R_L value greater than 1 signifies an unfavorable adsorption process [42] & [41].In addition, the Freundlich adsorption intensity parameter 1/n had an indication about the adsorption difficulty .The adsorption is considered easy when 1/n<0.5 and difficult when 1/n>2 [41]. The characteristic adsorption energy E_o (kJ/mole) used to distinguish the physical and chemical adsorption. Value of E is between 8 and 16 kJ /mole indicates the adsorption is chemisorption, while for values of $E_0< 8$ kJ /mole, the sorption process is physical [43] &[44].

Adsorption isotherm of ibuprofen tested using concentration range from 20 to 100 µg/ml , pH of solution fixed on 2 to 2.5 ,the contact time was 15 min., temperature used was 47˚C finally used 0.05 g of bentonite-PUF adsorbent.

The results of application linear form of adsorption isotherms and isotherm constants and error functions listed in table (11).The comparison between experimental results and models results clearly showed in Fig.(12) for ibuprofen. By comparing the isotherms applied for ibuprofen ,its seems from error functions values table (7) that the best fit isotherms sorts as Dubinin-Radushkevich > Temkin> Langmuir> Freundlich's.The best fit isotherm with Dubinin-Radushkevich isotherm which assumed that the characteristic of the adsorption curve is related to the porosity of the bentonite –PUF adsorbent .The Dubinin-Radushkevich model is more general than Freundlich and Langmuir isotherms ,because it was studied the difference between physical and chemical adsorption [27].

The maximum sorption capacity calculated from this model q_{DR}=27.6 mol/g. The magnitude of K_f calculated from Freundlich isotherm showed that bentonite-PUF adsorbent had a high capacity for ibuprofen adsorption from the aqueous solutions studied.

The Freundlich adsorption intensity parameter 1/n had a value of 0.13 indicate the adsorption process of ibuprofen on bentonite –PUF surface is easy.

The separation factor, R_L calculated from Langmuir isotherm showed the values <1 and greater than zero in all adsorption concentrations which suggest that the adsorption process of ibuprofen on bentonite –PUF surface is favorable. The characteristic adsorption energy E_o calculated from Dubinin-Radushkevich isotherm for ibuprofen equal to 0.845 KJ/mol this another confirmation that the adsorption process physical in nature of ibuprofen on bentonite –PUF surface rather than thermodynamic parameters calculated previously. Approximated issues in previous studies for ibuprofen adsorption using different adsorbent [45];[36] & [27].

Adsorption isotherm of diclofenac sodium conducted using concentration range from 20 to 100 µg/ml, pH of solution fixed on 2 to 2.5, the contact time was 30 min., and temperature used was 47˚C finally used 0.05 g of bentonite-PUF adsorbent. The results of application linear form of adsorption isotherms and the isotherm constants and error functions listed in table (8).

The comparison between experimental results and models results clearly showed in Fig.(13). By comparing the isotherms applied for diclofenac sodium ,its seems from error functions values table (8) that the best fit isotherms sorts as Freundlich's> > Langmuir> Temkin> Dubinin-Radushkevich.The best fit isotherm with Freundlich's isotherm shows that capacity will increase with diclofenac sodium concentration increased .The main assumption regarding Freundlich model that the adsorption of diclofenac sodium occurred in a multilayered system rather one layered on the bentonite –PUF surface [2].

The magnitude of K_F calculated from Freundlich isotherm showed that bentonite-PUF adsorbent had a high capacity for diclofenac sodium adsorption from the aqueous solutions and its value above value calculated for ibuprofen, acetylsalicylic acid, acetaminophen and indomethacin. the Freundlich adsorption intensity parameter 1/n had a value of 0.33 indicate the adsorption process of diclofenac sodium on bentonite –PUF surface is in the favorable and easy region .The separation factor, RL calculated from Langmuir isotherm showed the values <1 and greater than zero in all adsorption concentrations which suggest that the adsorption process of diclofenac sodium on bentonite –PUF surface is favorable. The characteristic adsorption energy Eo calculated from Dubinin-Radushkevich isotherm for diclofenac sodium equal to 5 KJ/mol indicates that the adsorption process physical in nature of diclofenac sodium on bentonite –PUF surface .This results approached to results finding by [2]&[10].

5.7. 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 [46].

The chemical composition of natural bentonite is different depending on the source of collection. The commercial bentonite XRD shown in Fig.(14).

Bentonite polyureaformaldehyde composite predominantly had a dark brown appearance. A typical XRD pattern of bentonite polyureaformaldehyde composite after mixing shown in Fig.(15) .FTIR spectra for bentonite , polyureaformaldehyde and bentonite polymer composite shown in Fig.(16,17,18) its seems shifting and missing groups.

SEM image for raw material and composite shown in Fig.(19,a and 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.

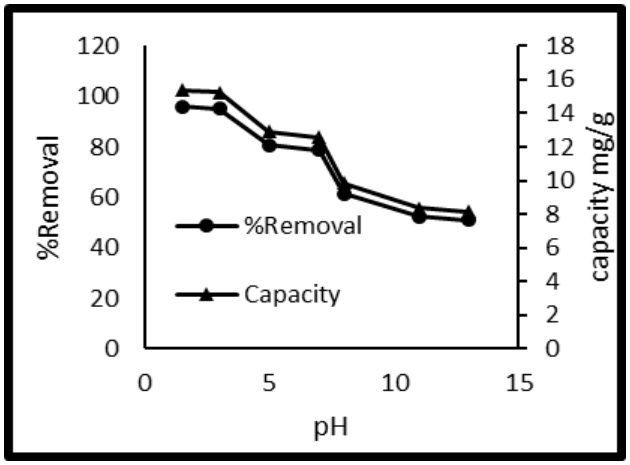


Fig.10, Effect of pH on both adsorption capacity and removal efficiency of ibuprofen, experiment conditions (adsorbent mass =0.05g,r.p.m=180,intial concentration =40µg/ml, temperature =47˚C and contact time 15 min).

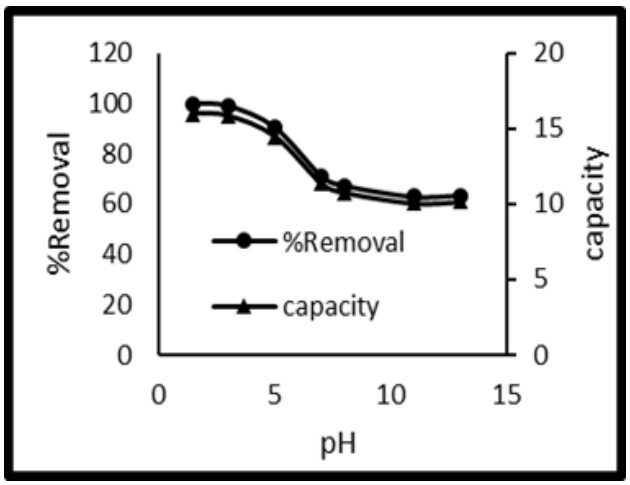


Fig. 11, Effect of pH on both adsorption capacity and removal efficiency of diclofenac sodium, experiment conditions (adsorbent mass =0.05g,r.p.m=180,intial concentration =40µg/ml, temperature =47˚C and contact time 15 min).

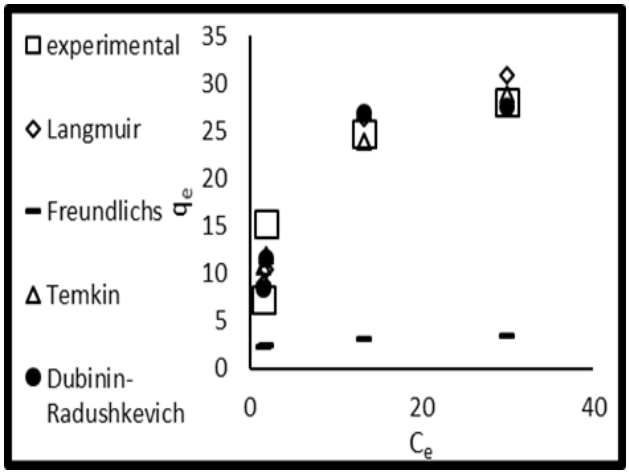


Fig. 12, Comparison between experimental and model isotherms for ibuprofen

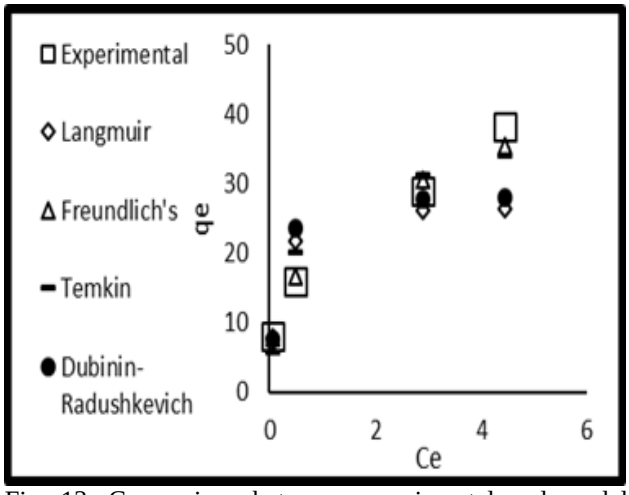


Fig. 13, Comparison between experimental and model isotherms for diclofenac sodium

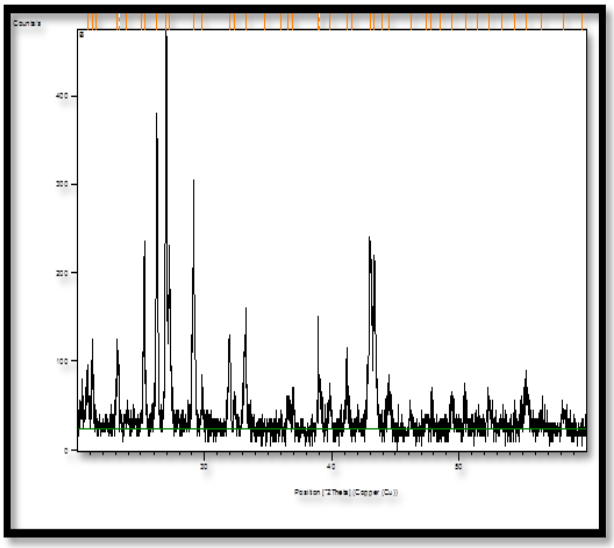


Fig. 14, XRD of Bentonite

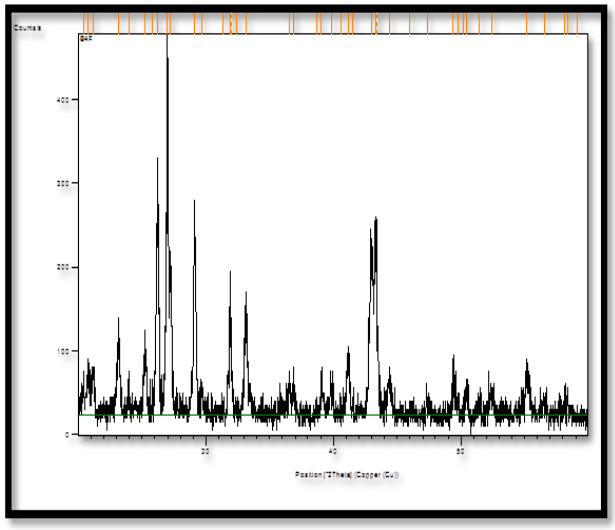


Fig. 15, XRD for Bentonite poly urea formaldehyde composite

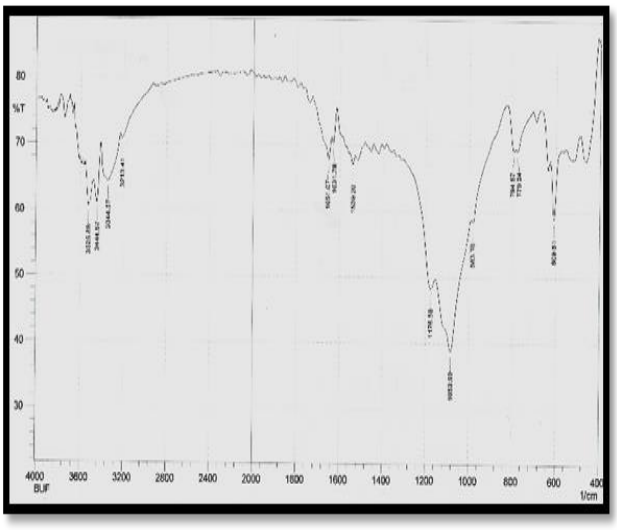


Fig. 18, FTIR spectra for bentonite -PUF composite

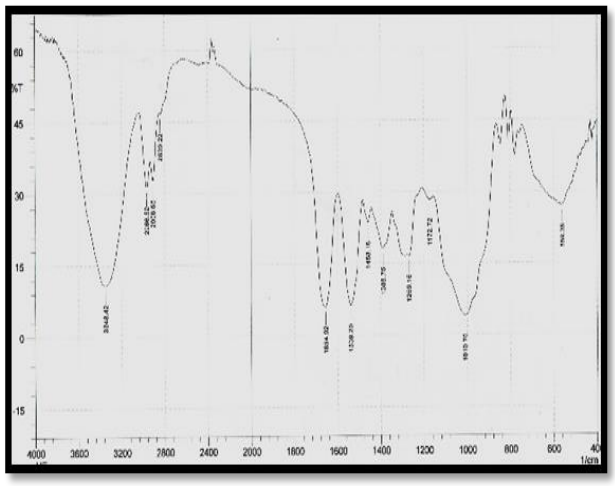


Fig. 16, FTIR spectra for ureaformaldehyde resin

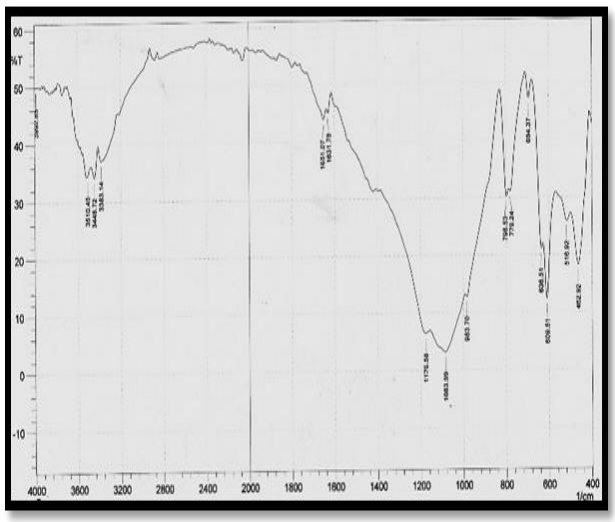
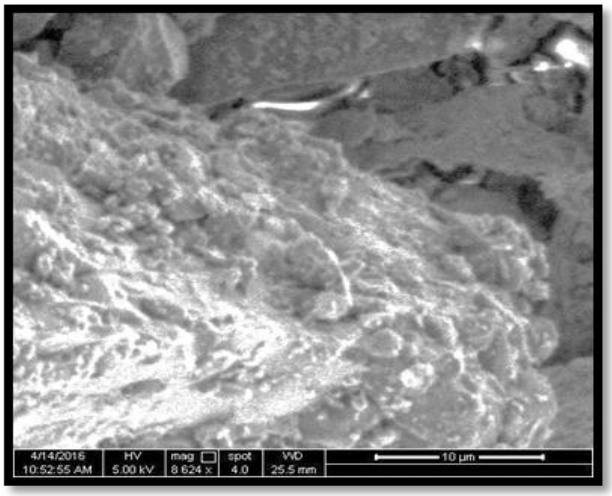
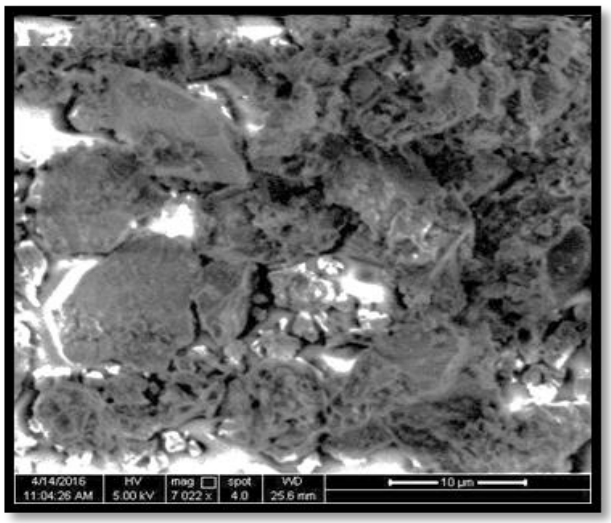


Fig.(17):FTIR spectra for bentonite



(a)



(b)

Fig. 19, SEM image for (a) bentonite (b)bentonite-PUF composite

Table 7. Adsorption isotherm constants parameters and error values for ibuprofen

Isotherm model	Constants	Value	Accuracy	
Langmuir	q_{max}	35.71429mg/g	χ^2	2.305038
	K_L	0.213577 l/mg	R^2	0.7557
	r_{20}	0.189698	RMSE	3.043193
	r_{40}	0.104788	ARE	0.17738
	r_{75}	0.05876		
	r_{100}	0.0447		
Freundlich's	K_f	2.208((mg/g) (L/mg)$^{1/n}$)	χ^2	54.6839
	1/n	0.1311	R^2	0.7922
			RMSE	17.7558
			ARE	0.81887
Temkin	A	3.578971 l/g	χ^2	2.2796
	b	430.5402	R^2	0.9109
			RMSE	2.42305
			ARE	0.18328
Dubinin-Radushkevich	q_{DR}	27.629 mol/g	χ^2	1.22724
	β	7E-07 mol^2 /KJ^2	R^2	0.9124
	E_o	0.8451 KJ/mol	RMSE	2.21678
			ARE	0.12162

Table 8. Comparison between experimental and model isotherms for diclofenac sodium

ISOTHERM	CONSTANTS		ACCURCY	
Langmuir	q_{max}	11.94743	χ^2	6.130058
	K_L	8.2	R^2	0.9257
	r_{20}	0.006061	RMSE	6.75862
	r_{40}	0.00304	ARE	0.198062
	r_{75}	0.001623		
	r_{100}	0.001218		
Freundlich's model	K_f	21.29559	χ^2	0.375814
	1/n	0.3385	R^2	0.9907
			RMSE	1.737598
			ARE	0.055589
Temkin	A	49.3063	χ^2	2.458081
	b	422.7413	R^2	0.9135
			RMSE	3.426319
			ARE	0.187223
Dubinin-Radushkevich	q_{DR}	28.14304	χ^2	6.642404
	β	2E-08	R^2	0.8191
	E_o	5	RMSE	6.457195
			ARE	0.21193

6- Conclusions

1- PUF-Bentonite composite prepared from mixing commercial bentonite with poly urea prepared in basic media in mixing ration of bentonite to polymer of 3g:1g is efficient for removal of diclofenac sodium and ibuprofen from wastewater
2- pH is the significant parameter affecting the adsorption capacity gives maximum removal of 99.8 for diclofenac and 99.2 for ibuprofen at pH 2 due to ionization of pharmaceutical compound .
3- Thermodynamic and kinetics parameters had been calculated and appears spontaneity of ongoing adsorption process for both pharmaceuticals studied and indicates the physical nature of adsorption of ibuprofen and diclofenac sodium.
4- Elovich's equation appear fit with both pharmaceuticals to describe kinetic model ,intraparticle diffusion model plot did not pass through the origin this indicates the external mass transfer played an important role in the diclofenac sodium and ibuprofen adsorption.

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