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ADSORPTION STUDIES ON TREATMENT OF PHARMACEUTICAL WASTE BY POLYMER MATERIALS MIXED WITH INORGANIC ADSORBENTS-II

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Abstract

In the present study, the optimum recovery of the pharmaceutical waste from effluents has been done. Polymer-inorganic blends were used for such study. The removal capabilities of pharmaceutical waste by such adsorbent blends were investigated. Different factors affecting the uptake such as contact time, pH value and aqueous volume to adsorbent weight ratio have been investigated. The reaction mechanisms and the optimum conditions for the treatment were deduced in the light of the obtained results.

Keywords: Inorganic adsorbant, Pharmaceutical waste, Urea-formaldehyde resin, Adsorbant studies, Coconut Flour.

Introduction

Pharmaceutical compounds approved as constituents for medicinal products throughout the world [1], are inherently biologically active and can have unforeseen adverse effects on environmental segments [2-8]. They have generated rising awareness owing to their huge variety and consumption, recognized toxicity, as well as their unpredictable environment impact, even at low concentration levels. Many of drugs are used worldwide, with a huge production and are present in environment all over the world [9-17]. An efficient technology for removal of pharmaceuticals by adsorption onto activated carbons is well established [18-20].

Many adsorptions have been used for removing water pollutants [21-24]. The area of systematic study of pharmaceutical wastewater of our Indian zone not been well studied. Hence the present author reported initial work is in this regard [25]. In continuation of this work the present paper describe the studies on pharmaceutical waste of two zones of Vadodara area.

Experimental

Materials and Methods:

All the chemicals used were of analytical grade. Pharmaceutical waste samples were collected from different zone (**E-1** and **E-2**) of pharma industries situated near Vadodara, Gujarat. TDS of these pharmaceutical waste samples was determined by filtration technique. Urea Formaldehyde resin was prepared by conventional method. Its adduct with H_2O_2 was prepared by method reported [26]. The resultant resin is designated and reported as Modified Urea Formaldehyde (MUF) [27].

Preparation of $ZrO_2 – Al_2O_3$ System (Oxide):

Aluminum trisec-butalate and zirconium n-propoxide were used as precursors for ZrO_2 and Al_2O_3 respectively in the production of Aluminum-Zirconia composite by sol gel process [26].

Preparation of ZrO_2 – Al_2O_3 / MUF Composite Resin:

Four various composite materials were prepared with different ratios of metal oxide, MUF resin and coconut flour. These materials are designated as A-1, A-2, A-3 and A-4 respectively **(Table-1)**, throughout this work. The composition of each composite is demonstrated as follow:

Characterization of pharmaceutical waste samples:

The physio-chemical characterization of pharmaceutical waste samples collected from different pharma industry is given in **Table-2**. The key pollutants in the waste water from pharmaceutical based drug industry are organic compound, suspended solids and biogeneous elements. Biodegradability may be estimated on the basis of ratio between BOD and COD, BOD: COD ratio obtained from the different pharmaceutical waste samples were found to be 0.50 for **E-1** and 0.53 for **E-2**, which indicate that most of the organic compounds in the wastewater from pharmaceutical based drug industry are easily biodegradable. Suspended solids in wastewater was found to be 625 **(E-1)** and 714 **(E-2)** mg/L. Suspended solids in wastewater from pharmaceutical based drug industry originates from coagulated pharmaceutical waste samples of chemicals from drug processing units.

Table-1: The concentration of MUF and oxides in the composite powders

Sample	MUF	Coconut Flour	Oxide
A-1	80	10	10
A-2	70	20	10
A-3	60	20	20
A-4	50	30	20

Table-2 Characterization of pharmaceutical waste samples collected from different pharma industry

Sr No.	Parameters	E-1	E-2
1	pH	6.9	6.3
2	BOD at 20°C (mg/L)	640	714
3	TCOD (mg O_2/L)	1265	1358
4	TS (mg of TS/L)	1510	1220
5	TSS (mg of TSS/L)	625	740
6	TDS (mg of TDS/L)	950	1220
7	Chloride (mg of Cl/L)	225	200
8	Alkalinity (mg of $CaCO_3$/L)	510	435
9	Oil and Grease (mg/L)	12	7

Adsorption Experiments:

The solid-liquid phase interactions play a significant role in the removal of pollutants from aqueous solutions. Batch equilibrium is the most commonly used technique to study such heterogeneous phase interaction. The total dissolved solid of pharmaceutical waste samples were determined by evaporation method. So according to TDS in pharmaceutical waste samples were prepared by further dilution with distilled

water to give the desired test samples.

Sorption studies were conducted at different size fractions (50, 75, 100, 125 and 150µm). pH values (2, 3, 4, 5, 6, 7, 8 and 10) at room temperature were studied. The pH of the solution was adjusted with HCl or NaOH solution by using pH meter. Batch adsorption investigation were carried out by contacting different weights of each of the prepared composite material with 10 ml of pollutants of a known initial concentration, in tightly sealed glass bottles. The percentage uptake (%U) was calculated from:

$$U\% = (C_0 - C)/C_0 \, x100 \qquad (1)$$

Where Co and *C* are the concentration of pollutant before and after equilibrium (mg L^{-1}).

Also the adsorbed amount per unit mass of adsorbent *q* (mg g^{-1}) was calculated using the formula:

$$q = (C_0 - C)/W \, xV \qquad (2)$$

Where *W* is the dry weight of the resin (g) and V is the solution volume (L).

Results and Discussion

Adsorption studies:

Batch method was employed in the present work to study the adsorption behaviour of the prepared composites towards pharmaceutical waste samples from different zones of pharma industry. This technique depends on mixing of a particular weight of the composite powder with the aqueous solution of pharmaceutical wastes. The influence of critical variable such as solution pH, shaking time and resin weight were tested and compared. After attainment of equilibrium, the samples were centrifuged and supernatant liquid was analyzed for pharmaceutical waste samples using UV-VIS spectrophotometrically Shimadzu-160 (UV-visible).

Effect of pH:

The effect of hydrogen ion concentration on uptake of pharmaceutical waste samples from aqueous solution on composite material (A-4) given in **Fig. 1**, while the data were displayed in **Table-3**. The plot exhibit different behaviours related to the degree of ionization of adsorbent. The equilibrium adsorption of pharmaceutical waste samples at different pH values exhibits a constant value of uptake percentage with increasing pH value upto ~ 10 clarifying a negligible effect over this range. At higher values, the adsorbability falls sharply with pH increase. The revealed behaviour can be explained on the basis of solute ionization [27]. At the initial stage, the degree of pharmaceutical waste samples ionization, which acts as weak acid in aqueous solutions, as a function of pH value seems to be independent and attains an equilibrium state with increasing the pH values from 3 to 10. Hence, the adsorptionis slightly affected over pH range amounts to the dissociation constant value of pharmaceutical waste samples (pKa = 9.98). At higher values (pH > pKa), the degree of pharmaceutical waste samples ionization increase and the adsorbent surface becomes negatively charged. Owing to the repulsive forces prevailing between adsorbent surface and solute molecules, the adsorption extent decreases. This avouches that the solution pH value has adverse effect on the adsorb ability of pharmaceutical waste samples at values greater than its pKa value.

Table-3 Effect of pH on adsorption of pharmaceutical wastes, by different composite resins

pH	q_α (mg/g)							
	Composite A-1		Composite A-2		Composite A-3		Composite A-4	
	E-1	E-2	E-1	E-2	E-1	E-2	E-1	E-2
2	125	100	140	109	152	118	160	125
3	123	99	138	108	150	117	159	123
4.5	119	97	135	106	146	116	157	120
5.5	112	92	130	100	140	114	152	117
8	99	75	119	91	129	97	146	101
10	78	52	89	68	105	70	137	83
12.5	54	28	67	36	77	48	95	60

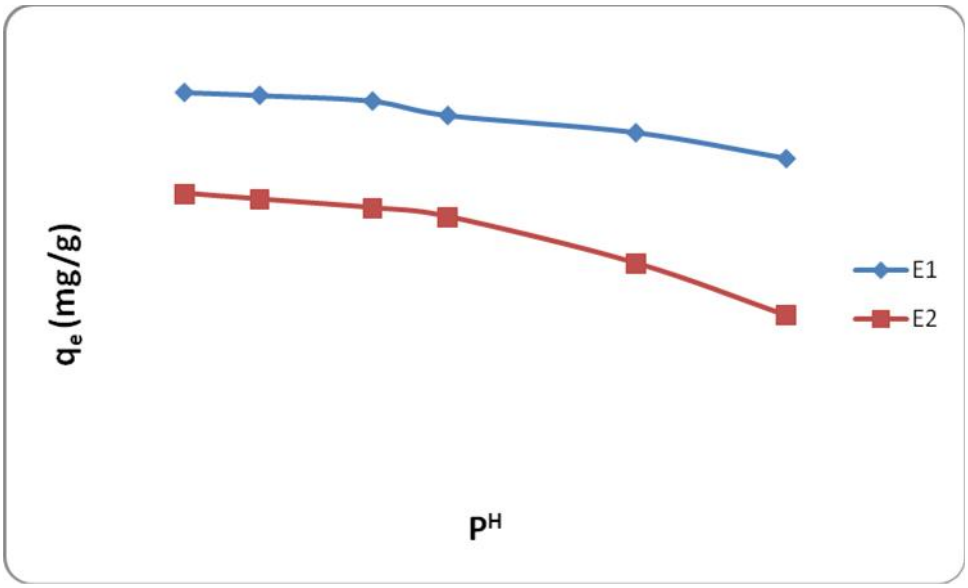

Fig.1: Effect of pH on adsorption of pharmaceutical wastes, by composite (A-4), Co=100 mg/L, Mass = 5 mg, Volume = 10 ml and Time = 24hr

Effect of adsorption weight:

The effect of adsorbent weight variation on the removal efficiency of pharmaceutical waste samples studied was using different adsorbent weights ranged from 1 to 40 mg. The results show that for removal of pharmaceutical waste samples in 10 ml with initial concentration 100 mg/L of stock solution. The data obtained are given in **Table-4** from which **Fig.2** for A-4 composite shows that, the removal efficiency increases with increases with increasing the adsorbent weight up to a certain dose, where the removal curve becomes steady. The further additions of adsorbent were found to have appreciated effect on the removal efficiency whereas the amount of organic solute adsorbed per unites weight of adsorbent decreases with increasing the adsorbent weight [28].

Table-4 Effect of composite material on the residual concentration of pharmaceutical waste samples by composite resins

Mass (mg)	Concentration. (mg/L)							
	Composite A-1		Composite A-2		Composite A-3		Composite A-4	
	E-1	E-2	E-1	E-2	E-1	E-2	E-1	E-2
2	80	72	83	75	88	79	92	84
5	68	60	69	61	72	65	75	70
10	50	42	54	44	57	50	60	54
15	32	23	29	25	32	28	38	30
20	17	05	14	08	18	12	22	15
25	06	01	05	02	09	03	10	05
30	00	00	00	00	00	00	00	00
40	00	00	00	00	00	00	00	00

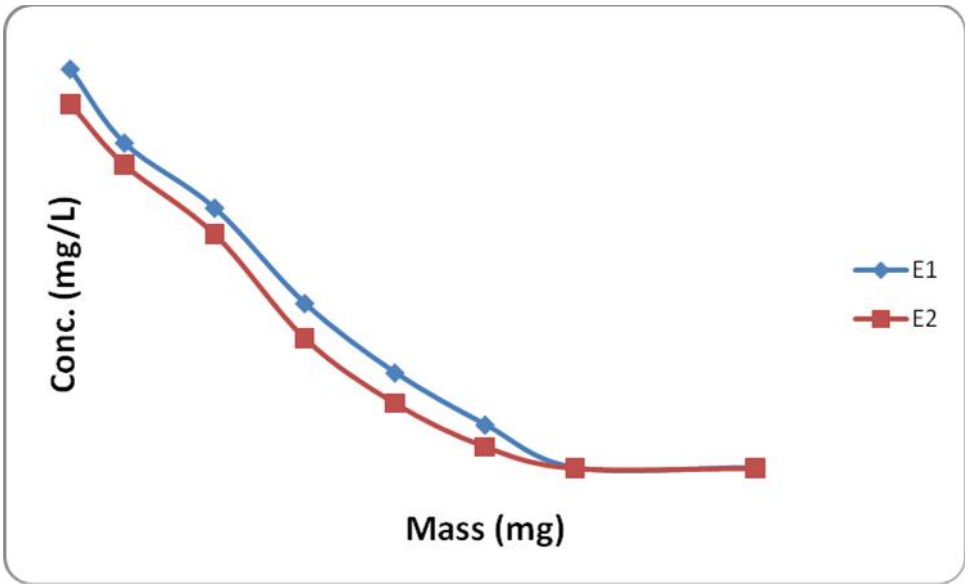

Fig.2: Effect of composite material on the residual concentration of pharmaceutical waste samples by composite resin (A-4)
C_0= 100 mg/L, Volume= 10 ml and Time = 24hr.

Effect of contact time:

The adsorption data for the uptake of pharmaceutical waste samples versus contact time at 100 mg/L initial concentration on 20 mg of composite resins (A-1 to 4) were carried out. The results show that the equilibrium time required for the adsorption of pharmaceutical waste samples on composite (A-4) is illustrated in **Fig.3**. The data **(Table-5)** imply that the adsorption extent increases with elapsed time till reached saturation level where the uptake percentage attains a constant value. The data in **Fig.3** clarify that the adsorption of pharmaceutical waste samples on the composite material attains the saturation level after 24 hours.

Table-5 Effect of contact time on the residual concentration of pharmaceutical waste samples by composite resins

Time (h.)	Concentration. (mg/L)							
	Composite A-1		Composite A-2		Composite A-3		Composite A-4	
	E-1	E-2	E-1	E-2	E-1	E-2	E-1	E-2
0.5	99	60	110	87	118	97	125	102
2	108	71	125	98	132	112	138	115
3	119	85	136	106	144	120	150	126
4	135	100	152	118	160	135	164	140
10	148	115	164	137	174	152	180	158
15	156	121	167	144	180	160	187	171
24	159	125	172	148	183	164	196	179
48	160	126	172	150	185	164	198	180

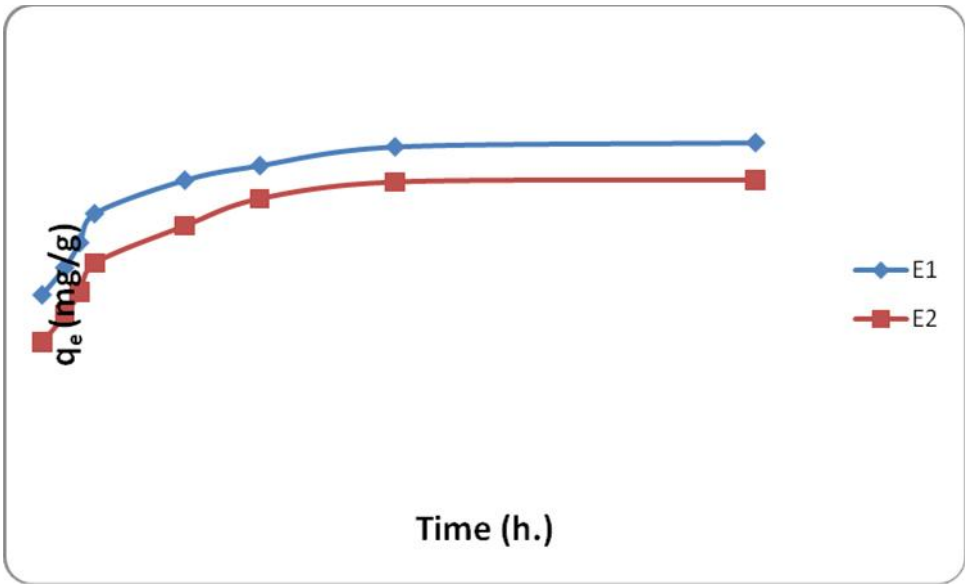

Fig.3: Effect of contact time on the residual concentration of pharmaceutical waste samples by composite (A-4)
C_0= 100 mg/L, Volume = 10 ml and Time = 24hr.

Initial solute concentration:

The initial solute concentration of pharmaceutical waste samples are important issue since a given mass of adsorbent can only adsorb a certain amount of organic solute. Therefore, the more concentrated pharmaceutical wastes, the smaller is the volume of pharmaceutical waste samples that a fixed mass of adsorbent can purify. The effluence of the initial concentration of pharmaceutical waste samples on their amount adsorbed onto composite (A-4) resin at temperature range (298 - 333 ^{o}K) with different concentration ranges and the results are shown in **Fig.4**, while data of all composite are given in **Table-6**. The plot illustrate that the adsorbed amount (q, mg g^{-1}), increases with increasing the initial concentration of the solute This indicated that the rapid surface interactions between the solute molecule and the active sites of the composite resin.

Table-6 Adsorption isotherms of pharmaceutical waste samples by different composite resins.

Co (mg/L)	q_α (mg/g)							
	Composite A-1		Composite A-2		Composite A-3		Composite A-4	
	E-1	E-2	E-1	E-2	E-1	E-2	E-1	E-2
0.5	45	25	51	43	59	48	70	58
1.5	61	42	67	57	79	67	90	75
2.5	77	62	86	73	97	81	115	93
4	102	86	114	98	129	108	141	120
10	153	140	168	151	181	165	195	178
15	178	164	192	175	204	188	220	198

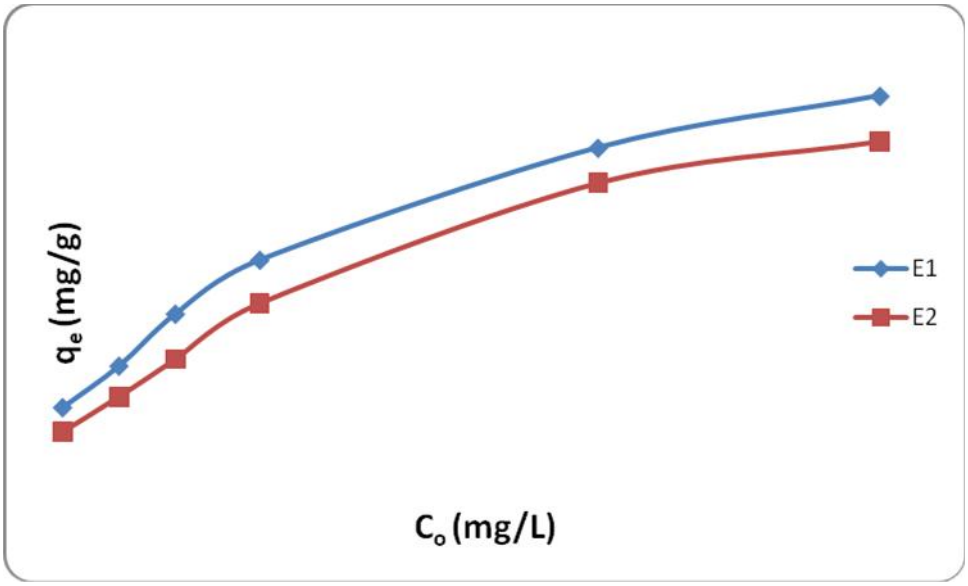

Fig.4 Adsorption isotherms of pharmaceutical waste samples by composite (A-4).

Temperature:

The adsorption studied for pharmaceutical waste samples onto composite resin at different temperatures is represented in **Table-7 & 8** for A-4 composite depicts the equilibrium adsorption of pharmaceutical waste samples onto a composite resin at different temperatures. It was found that the adsorbed amount of the pollutant decreased with increasing temperature indicates that the adsorption process is an exothermic process. Generally, the adsorption of organic contaminants from aqueous solutions is related with the system temperature, where both the adsorption rates as well as the sorption capacity are affected [29]. The rise in temperature affects both solubility and chemical potential of the organic adsorbate. It has earlier reported that, if the solubility of an organic adsorbate increases with temperature, the chemical potential will decreases [30]. On the other hand, if the temperature has the revere effect on the solubility, then both the mentioned effects will act in the opposite direction.

Table-7 Absorption isotherm of pharmaceutical waste (E-1) by MFU composite material (A-4) at various temperatures

Temp.	Composite A-4 (E-1)						
298 °K	Ce (mg/L)	0.5	1.0	1.5	2.0	4.5	15.0
	q_α (mg/g)	54	67	92	141	194	210
323 °K	Ce (mg/L)	0.5	1.2	2.3	4.1	6.4	18.0
	q_α (mg/g)	52	65	88	139	190	205
328 °K	Ce (mg/L)	0.5	1.6	2.9	5.7	11.1	27.6
	q_α (mg/g)	50	62	85	132	182	202
343 °K	Ce (mg/L)	0.5	2.0	4.5	10.1	15.4	31.2
	q_α (mg/g)	52	59	81	125	177	195

Table-8 Absorption isotherm of pharmaceutical waste (E-2) by MFU composite material (A-4) at various temperatures

Temp.	Composite A-4 (E-2)						
298 °K	Ce (mg/L)	0.5	1.2	1.6	2.2	4.6	15.3
	q_α (mg/g)	42	58	84	120	164	182
323 °K	Ce (mg/L)	0.5	1.4	2.5	4.3	6.9	18.4
	q_α (mg/g)	40	54	77	112	159	175
328 °K	Ce (mg/L)	0.5	1.8	3.2	5.9	11.6	28.1
	q_α (mg/g)	39	53	74	107	157	170
343 °K	Ce (mg/L)	0.5	2.5	4.8	10.3	15.6	31.9
	q_α (mg/g)	35	48	68	102	144	162

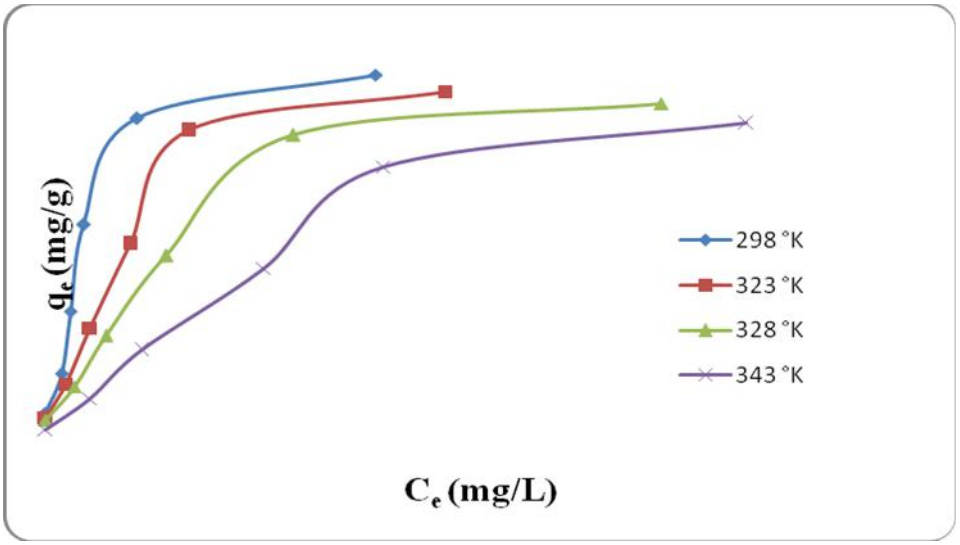

Fig.5 Absorption isotherm of pharmaceutical waste (E-1) by composite (A-4) at various temperatures (V/m = 200 ml g^{-1}) at different temperatures

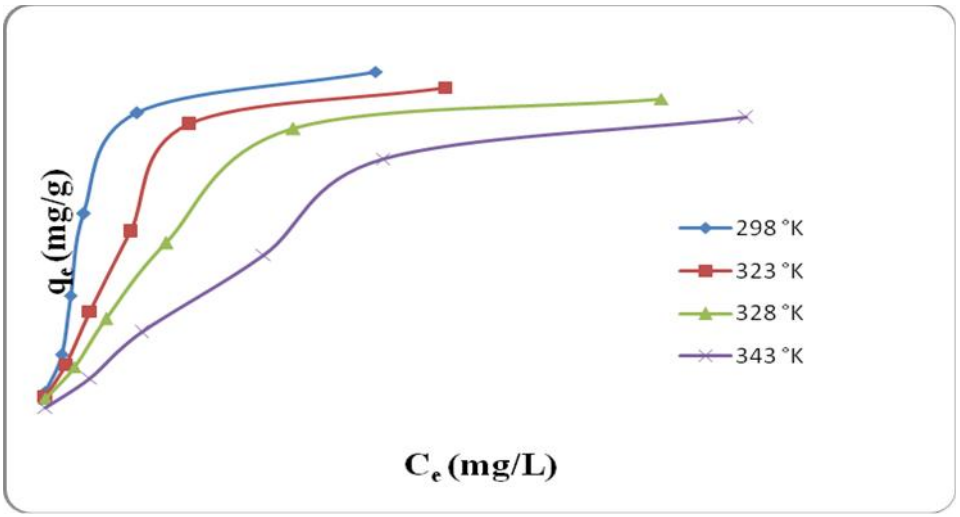

Fig.6 Absorption isotherm of pharmaceutical waste (E-2) by composite (A-4) at various temperatures (V/m = 200 ml g^{-1}) at different temperatures

Composite materials formed by the combination of coconut flour and oxide as inorganic ion-exchanger and modified urea formaldehyde (MUF) as resin. The incorporation of ZrO_2 /Al_2O_3 at micro scale size improves the thermal stability polymer, which facilitates the applications of the resulting composites in many fields. Reaction mechanisms are highly dependent on the surface characteristics at a specific pH–value and the relative molar concentration ratio of the composite/inorganic polymer. Thus, it could be concluded that prepared composites containing inorganic adsorbents would be utilized for the removal of pharma waste.

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