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Research Article

STUDIES ON TREATMENT OF PHARMACEUTICAL WASTE EFFLUENTS BY POLYMER MATERIALS MIXED WITH INORGANIC ADSORBENTS

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Abstract

In the present study, sorption technique was used to achieve the optimum recovery of the pharmaceutical waste from effluents. The modified urea formaldehyde resin was prepared and mixed with inorganic adsorbent at various proportions. The removal capabilities of pharmaceutical waste by the prepared composite materials were investigated. Different factors affecting the uptake such as contact time, pH value and aqueous volume to resin 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: Sorption technique, Pharmaceutical waste, Different factors.

Introduction

Pharmaceutical compounds (around 3000) approved as constituents for medicinal products throughout the world [1], are inherently biologically active and can have unforeseen adverse effects on non target ecological species when released into environment [2, 3]. Wastewater treatment studies have shown that pharmaceuticals are released directly into environment [4-8]. 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. Some of drugs are used worldwide, with a production volume estimated to be many hundreds of tons annually, and are present in environment all over the world [9-17]. An effective treatment technology for removal of pharmaceuticals is by adsorption onto activated carbons [18-20]. Pharmaceutical compounds reach the aquatic environment mainly through effluent discharge in wastewater treatment plants.

Polymer resins are becoming more common in wastewater treatment due to low costs, easy regeneration and selective removal of pollutants [21-23]. Lewait VP OC 1163, a micro porous, hypercrosslinked absorber resin with good chemical and mechanical stability, has been characterized as having very high adsorption capacity [24].

Many adsorptions have been used for remaining water pollutant. The area of systematic study of pharmaceutical wastewater of our Indian zone not been well studied. Hence it was through to study such aspect.

Experimental

A. Chemicals and reagents

a. All the chemicals used were of analytical grade.

b. An Effluent sample from Pharma industry zone at Ahmedabad, Gujarat was collected.

c. It's TDS was determined by filtration and then evaporated to dryness in vacuum.

B. Preparation of modified Urea Formaldehyde resin

Urea Formaldehyde resin was prepared by conventional method. Its adduct with H_2O_2 was prepared by method reported [25]. The resultant resin is designated as Modified Urea Formaldehyde (MUF).

C. 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].

D. Preparation OF ZrO_2 – Al_2O_3 / MUF Composite resin

Four various composite materials were prepared with various metal oxide/ MUF ratios. 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:

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

Sample	MUF	Saw Dust	Oxide
A-1	75	20	10
A-2	60	30	10
A-3	50	40	10
A-4	50	30	20

E. Effluent characteristics:

The physio-chemical characterization of effluent 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 literature data in the present case was found to be 0.58, which indicate that most of the organic compounds in the wastewater from pharmaceutical based drug industry should that are easily biodegradable. Suspended solids in wastewater was found to be 712 mg/L. Suspended solids in wastewater from pharmaceutical based drug industry originates from coagulated effluent of chemicals from drug processing units.

Table-2 Characterization of effluent

Sr No.	Parameters	Data
1	pH	6.7
2	BOD at 20°C (mg/L)	675
3	TCOD (mg O_2/L)	1163
4	TS (mg of TS/L)	1780
5	TSS (mg of TSS/L)	712
6	TDS (mg of TDS/L)	1156
7	Chloride (mg of Cl/L)	115
8	Alkalinity (mg of $CaCO_3$/L)	482
9	Oil and Grease (mg/L)	18

F. Sorption studies:

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 effluent was determined by evaporation method. So according to TDS in effluents the solutions of effluent 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.

G. Adsorption investigation:

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:

$$U\% = (C_0 - C)/C_0 \, x 100 \qquad (1)$$

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 effluent pollutant. This technique depends on mixing of a particular weight of the composite powder with the aqueous solution of effluent pollutant. The influence of critical variable such as solution pH, shaking time and resin weight were tested. After attainment of equilibrium, the samples were centrifuged and supernatant liquid was analyzed for effluent pollutant using UV-VIS spectrophotometrically Shimadzu-160 (UV-visible).

Effect of pH:

The effect of hydrogen ion concentration on uptake of effluent pollutant from aqueous solution on ZrO2 – Al_2O_3 / polymer composite resin (A-4) in **Fig.1**, while the data for all composite were displayed in **Table-3**. The plot exhibit different behaviours related to the degree of ionization of adsorbent. The equilibrium adsorption of effluent pollutant 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 effluent pollutant 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 effluent pollutant (pKa = 9.98). At higher values (pH > pKa), the degree of effluent pollutant 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 effluent pollutant at values greater than its pKa value.

Table-3 Effect of pH on adsorption of effluent pollutant, by different ZrO_2 – Al_2O_3 / MUF composite resins

pH	q_α (mg/g)			
	Composite A-1	**Composite A-2**	**Composite A-3**	**Composite A-4**
2	118	120	121	123
3	116.8	119.1	120	122.5
4.5	115.2	117.6	118.5	121
5.5	113.9	115	116.8	120.7
8	113.1	114.2	116	120
10	103	105.4	106.3	108
12.5	47	48.5	49.1	50

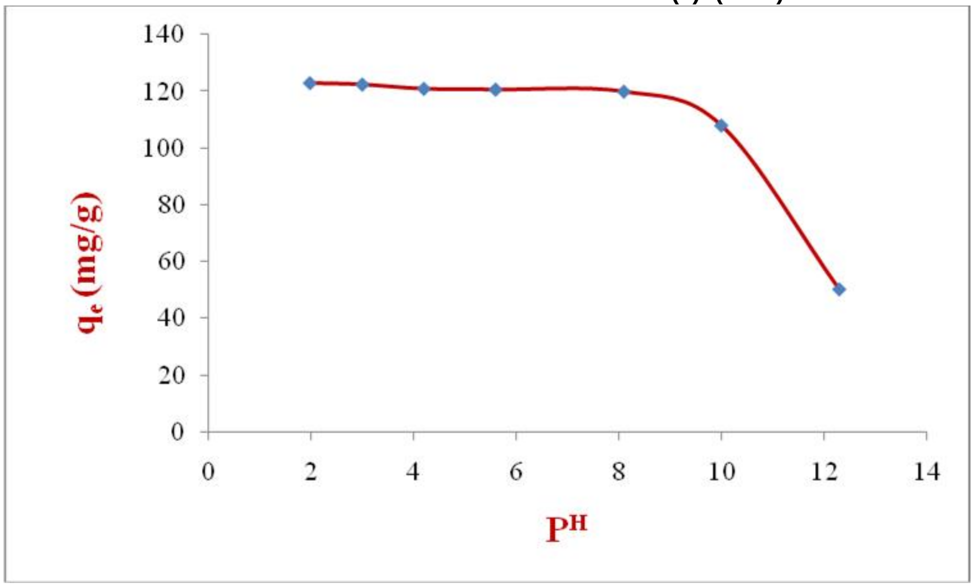

Fig.1: Effect of pH on adsorption of effluent pollutant, by ZrO_2 – Al_2O_3 / MUF composite resin (A-4), Co=100 mg/L, Mass = 5 mg, Volume = 10 ml and Time = 24hr

Effect of adsorption weight

The effect of adsorbent weight variation on the removal efficiency of effluent pollutant studied was using different adsorbent weights ranged from 1 to 40 mg. The results show that for removal of effluent pollutant 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 effluent pollutantby ZrO_2 – Al_2O_3 / MUF composite resins

Mass (mg)	Concentration. (mg/L)			
	Composite A-1	Composite A-2	Composite A-3	Composite A-4
2	85	87	92	94
5	74	75	78	79
8	58	60	63	66
12	39	42	44	46
16	22	25	27	29
22	04	05	07	08
32	00	00	00	00
40	00	00	00	00

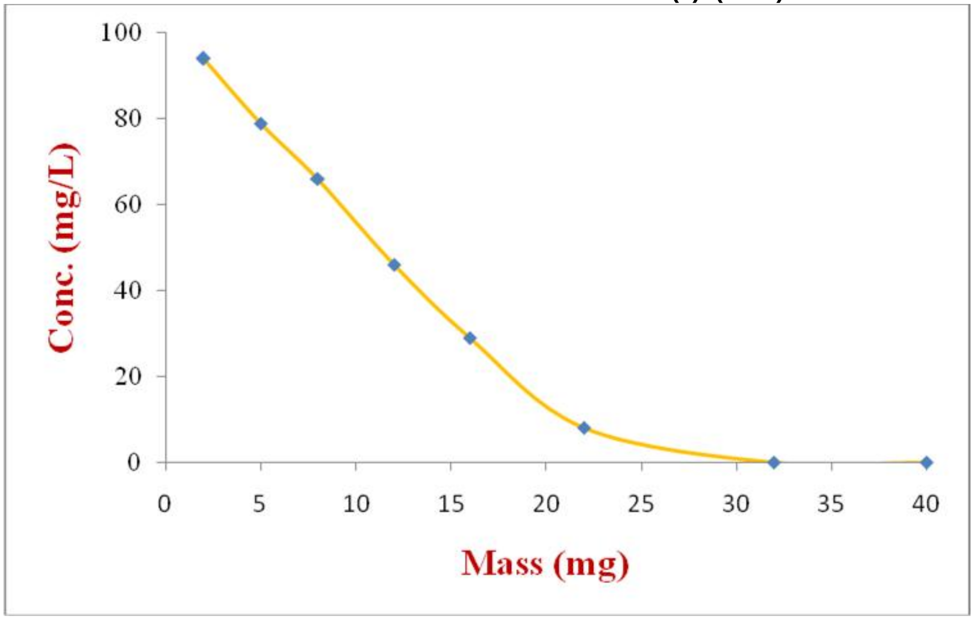

Fig.2: Effect of composite material on the residual concentration of effluent pollutant by $ZrO_2 – Al_2O_3$ / MUF composite resin (A-4)
C_0= 100 mg/L, Volume= 10 ml and Time = 24hr.

Effect of contact time

The adsorption data for the uptake of effluent pollutant versus contact time at 100 mg/L initial concentration on 20 mg of $ZrO_2 – Al_2O_3$ / polymer composite resin were carried out. The results show that the equilibrium time required for the adsorption of effluent pollutant on $ZrO_2 – Al_2O_3$ / polymer 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 effluent pollutant on the composite material attains the saturation level after 24 hours.

Table-5 Effect of contact time on the residual concentration of effluent pollutant by $ZrO_2 – Al_2O_3$ / MUF composite resins

Time (h.)	Concentration. (mg/L)			
	Composite A-1	Composite A-2	Composite A-3	Composite A-4
0.5	95	101	103	110
1.5	102	107	110	117
2.5	106	112	114	121
4	110	116	119	134
8.5	122	127	129	143
12	131	135	137	149
24	138	142	144	157
46.5	139	144	145	159

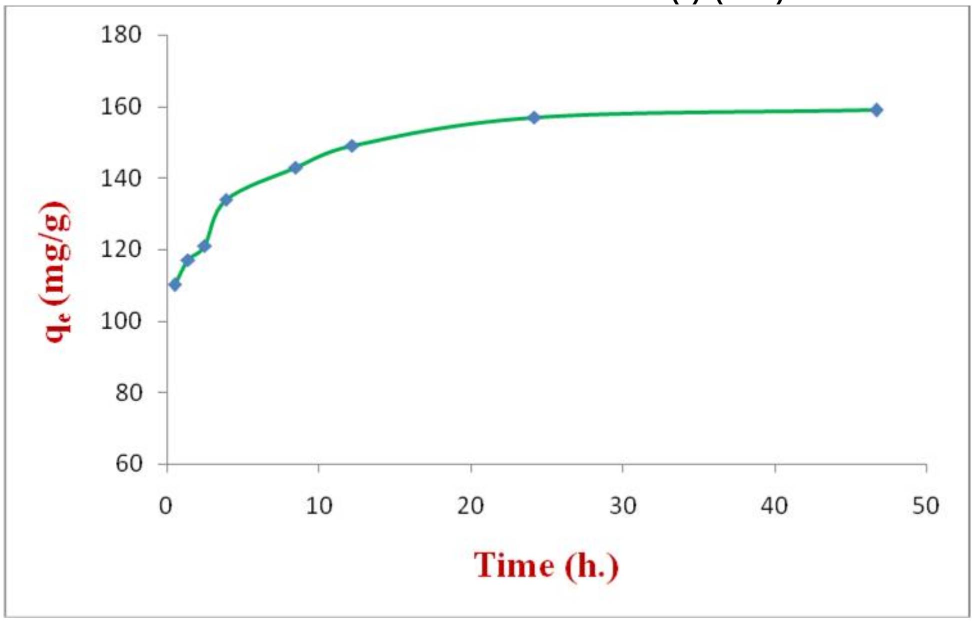

Fig.3: Effect of contact time on the residual concentration of effluent pollutant by $ZrO_2 – Al_2O_3$ / MUF composite resin (A-4)
C_0= 100 mg/L, Volume = 10 ml and Time = 24hr.

Initial solute concentration

The initial solute concentration of an effluent is important issue since a given mass of adsorbent can only adsorb a certain amount of organic solute. Therefore, the more concentrated a waste effluent, the smaller is the volume of effluent that a fixed mass of adsorbent can purify. The effluence of the initial concentration of effluent pollutant on their amount adsorbed onto $ZrO_2 – Al_2O_3$ / polymer composite (A-4) resin at temperature range (298 - 333 ^oK) 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 (effluent pollutant). This indicated that the rapid surface interactions between the solute molecule and the active sites of the composite resin.

Table-6 Adsorption isotherms of effluent pollutant by different $ZrO_2 – Al_2O_3$ / MUF composite resins.

Co (mg/L)	q_α (mg/g)			
	Composite A-1	**Composite A-2**	**Composite A-3**	**Composite A-4**
0.2	22	25	26	30
0.5	44	49	53	60
2.2	87	93	96	102
3.8	116	124	127	135
6.4	143	150	152	159
13.5	165	166	169	175

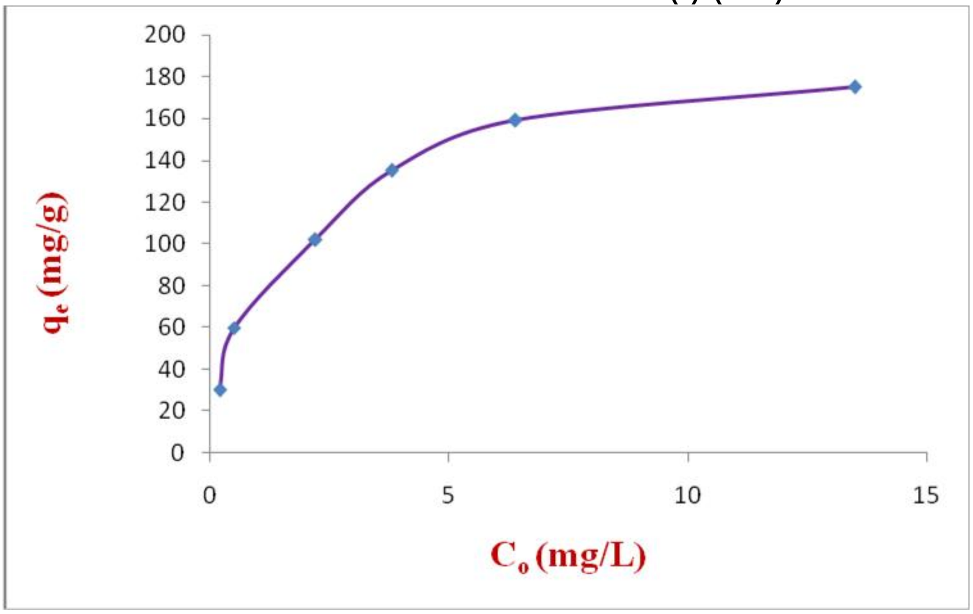

Fig.4 Adsorption isotherms of effluent pollutant by ZrO_2 – Al_2O_3 / MUF composite resin (A-4).

Temperature:

The adsorption studied for effluent pollutant compound onto composite resin at different temperatures is represented in **Fig.5** & **Table-7** for A-4 composite depicts the equilibrium adsorption of effluent pollutant 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 effluent pollutant by MFU composite material (A-4) at various temperatures

Temp.	Composite A-4						
298 °K	Ce (mg/L)	0.5	1.3	1.7	2.2	4.7	15.5
	q_α (mg/g)	22	34	75	118	152	165
313 °K	Ce (mg/L)	0.5	1.5	2.7	4.6	6.9	18.3
	q_α (mg/g)	22	34	75	116	148	162
323 °K	Ce (mg/L)	0.5	1.8	3.2	6.1	11.5	28.3
	q_α (mg/g)	22	35	74	106	132	138
338 °K	Ce (mg/L)	0.5	2.1	4.9	10.6	15.8	32.6
	q_α (mg/g)	22	34	68	102	124	130

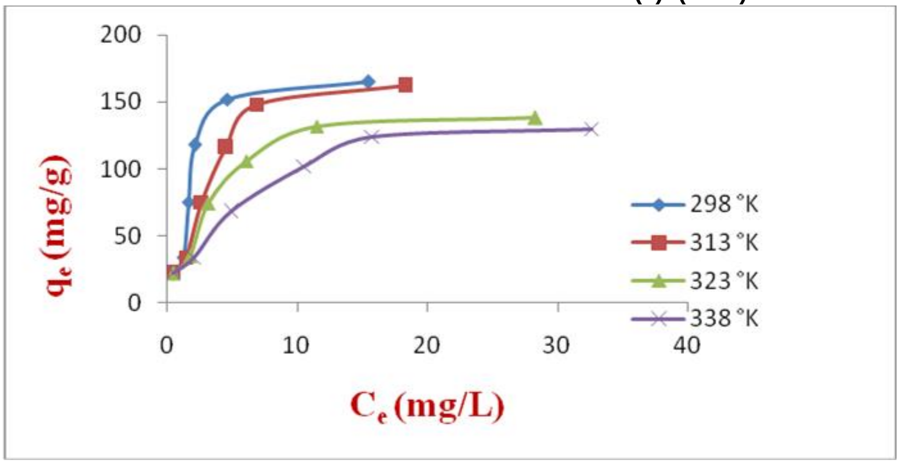

Fig.5 Absorption isotherm of effluent pollutant by MFU composite material (A-4) at various temperatures (V/m = 200 ml g^{-1}) at different temperatures

Conclusion

Successfully, composite materials formed by the combination of 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 A-1 to A-4 would be utilized for the removal of pharma waste.

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