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Removal of Cetirizine Hydrochloride and Cyclopentolate Hydrochloride from Water by Poly Urethane Foam

Samah Ali [1, 2,*]

[1]Chemistry Department, College of Science,
Taibah University, Al-Madinah Al-Munawarah 41477, SAUDI ARABIA.
[2]The National Organization for Drug Control and Research,
Al-Agouzah, Giza, EGYPT.
*Corresponding author; email: samali@taibahu.edu.sa.

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ABSTRACT

Simple and low cost method for extraction of Cetirizine hydrochloride and Cyclopentolate Hydrochloride by polyurethane foam from aqueous systems. PUF was characterized using FT-IR and scanning electron microscopy. The batch technique was performing to evaluate the effects of initial pH, contact time, volume of sample and initial concentration of both drugs. The isotherm for absorption process was studied. It is found that the Cetirizine Hydrochloride in undergo Freundlich isotherm (R^2=0.9743) but in Cyclopentolate Hydrochloride undergo Langmuir isotherm (R^2 =0.9809).

Keywords: polyurethane foam (PUF); Cetirizine hydrochloride; Cyclopentolate Hydrochloride; separation; adsorption isotherms.

I. INTRODUCTION

Cetirizine hydrochloride (CTZ) the chemical structure of drug is shown in Figure 1(a). It is consider weak acid and it is freely soluble in water, practically insoluble in acetone and in methylene chloride[1]. Cetirizine is a an anti-histaminic drug used to treat seasonal allergic rhinitis, perennial allergic rhinitis and chronic idiopathic urticarial[2].

A number of chromatography methods developed for quality control of racemic cetir izinein biological samples and pharmaceutical formulations have been reported. Some researchers reported that cetirizine enantiomers have been separated by HPLC-UV, LC–mass spectrometry and supercritical fluid chromatography with α1-acid glycoprotein or

ovomucoid protein based chiral stationary phase[3-5]. There are many methods for determination of CTZ such as high performance liquid chromatography (HPLC)[1,6,7], spectrophotometry[8-10], gas chromatography[11].

Cyclopentolate Hydrochloride (Cp-Cl) C17H25NO3•HCl shown in Figure 1(b), molecular weight is 327.85. It is usually used as eye drops in pediatric eye examinations to dilate the eyes (mydriatic) and avoid the focus/accommodation of the eye (cycloplegic)[12]. Among the methods for determining Cp-Cl HPLC[13,14], flourimetric method[15], titration method[16] and spectrophotometric determination[17].

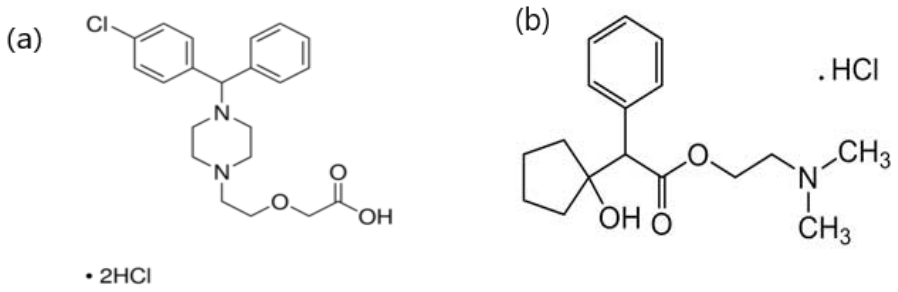

Figure 1. Chemical structure of (a) Cetirizine Hydrochloride CTZ. (b) Cyclopentolate Hydrochloride (Cp-Cl)

Polyurethane foam (PUF) is a good absorbent material and has been the subject of many articles[18-21]. PUF has advantages over other adsorbents including low cost, ease of removal, and good resistance to pH changes[22].

The study aims to study capability of PUF for removal of CTZ and Cp-Cl from aqueous solutions by examining the pH, adsorbent dosage, and contact time. Furthermore, the sorption isotherm was also evaluated to describe the experimental data.

II. EXPERIMENTAL SECTION

II.1. Apparatus

UV–Vis spectrophotometer Model G10S UV-VIS (Thermo Fisher Scientific) was used to measure the absorbance of the drugs using a plastic cell. Hanna digital pH-meter (HANNA Instruments) was used to measure the pH of the aqueous solutions. Ultrasonic, model 2510 (BRANSON), and the morphology of PUF was studied using scanning electron microscope model (JEOL1400, Japan).

II.2. Materials and Reagents

All chemicals were used without further purification. All reagents used were of analytical grade, Hydrochloric acid 37% from Panreac Applichem Company, sodium

phosphate monobasic, sodium phosphate dibasic and sodium acetate from Fisher Biotech Company. Cetirizine hydrochloride (CTZ) and Cyclopentolate Hydrochloride (Cp-Cl) were supplied by the National Organization for Drug Control and Research (NODCAR), Open cell polyether-type PUF (31.6 kg m−3) was supplied by the Egyptian company for foam production, Cairo, Egypt). All solutions were prepared in deionized water. The pH of the samples was adjusted using acetate and phosphate buffer. A stock solution of drugs (100 ppm) was prepared dissolving exact mass of drugs in distilled water. The working standard solutions of drugs were prepared by appropriate dilution. The laboratory glassware was soaked in chromic acid solution overnight.

II.3. General Procedures

PUF was cut into small cubic pieces, then washed by HCl (2M), followed by washing with distilled water then left to dry at room temperature. For the construction of calibration curves, 100 ppm from CTZ and Cp-Cl was prepared by dissolve 0.025 g from each drug and complete the volume to 250 mL by deionized water. Different concentration (2- 80 ppm) from stock concentration (100 ppm) for both CTZ and Cp-Cl were prepared. The absorbance measurement was detected by using spectrophotometer instrument. The λmax of CTZ and Cp-Cl was determined at 255and220nm respectively. For pH adjustment25 mL of CTZ and Cp-Cl solutions (100 ppm), was shaken with 0.1 g of PUF for 30 min, and 2.5 ml of acetate and phosphate buffer to adjust the pH of the solutions in the range of 0-8 the remained drugs were determined spectrophotometrically. To study the contact time on the removal capacity of CTZ and Cp-Cl,2.5 ml of each drugs (5 ppm) with 0.1g PUF were mixed at the optimum pH value and shaking at different time (0 to 120 min), the absorption of all samples determined spectrophotometry at their λmax. Effect of sorbent amount measured by adding2.5 ml of buffer at optimum pH with 2.5 ml of CTZ (5 ppm) mixed different mass of PUF (0.02 to 1.5 g). Then, the remaining drugs in the solution were determined.

II.4. Sorption Capacity

For the determination of the sorbent capacity experiments were carried out by the sorption of CTZ and Cp-Cl from separate aqueous solution. Typically, 0.1 g of foam was equilibrated with 5 ppm to 100 ppm for CTZ and Cp-Cl. The pH of the solution adjusted at the optimum value, and then the solution was shaken for 30 min at room temperature. After equilibration, the remaining drugs were determined. The sorption capacity per gram foam (Q, mg g−1) was calculated from equation (1).

$$[Q = \frac{(C_0 - C)xV}{m}] \quad (1)$$

Where (V) is the volume in liter and (m) is the weight of the foam in gram. The adsorption capacity of the adsorbent for their continuous use in further removal was studied at experimental optimum conditions, by using Optimum absorption was at 0.6 and 0.3 g of foam are used with 100 ppm of CTZ and Cp-Cl respectively. The samples were equilibrated by shaking for 30 min, the leftover of drugs was determined spectrophotometrically. This procedure was repeated five times to test the foam capacity.

III. RESULTS AND DISCUSSION

III.1. Characterization

PUF morphology was examined by scanning electron microscopy (SEM). The PUF is obtained to have an open cell structure, in which the drugs can flow freely between the cells since they are interconnected with each other as shown on Figure 2(a). After adsorbing 80 ppm of CTZ and Cp-Cl, drug molecules were observed on the surface and in the voids of the polyurethane foam absorbents covering part of the surface of the polyurethane foam as shown in Figure 2(b) and (c). This is evident for the adsorption of drugs on the surface of adsorbent material.

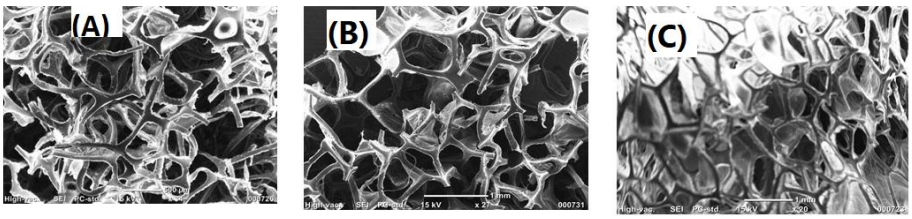

Figure 2. SEM images for (a) PUF. (b) PUF-CTZ. (c) PUF-Cp-Cl

III.1.1. Fourier Transfer Infra-Red (FTIR)

In Figure 3 the IR spectra of the PUF shows bands for νNCO, νOH, νCO and νNH2 groups at 2100, 3509, 1655, 3111 and 3299 cm-1, respectively[23]. Evidently, showed disappearance of νOH absorption bands at 3509 cm-1which indicate the incorporation of these groups during complex formation.

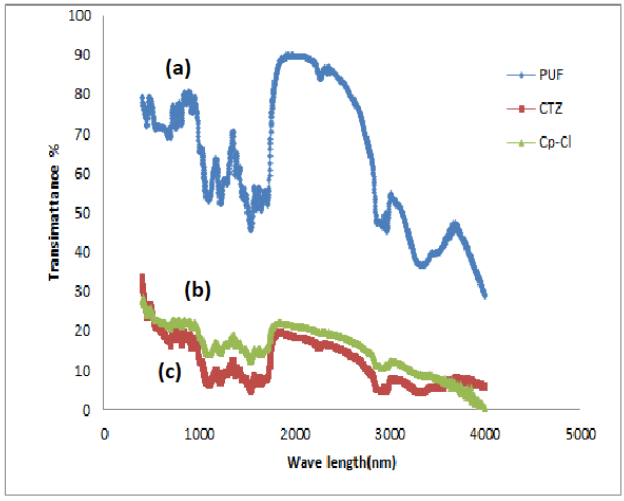

Figure 3. IR spectra of (a) PUF. (b) CTZ -PUF. (c) Cp-Cl -PUF

III.2. Effect of pH

The initial solution pH the most important parameter in the adsorption process, this is because the pH value can influence the surface charge of foams[24]. The pH was studied from pH 0 to 8. The effect of absorption of Cp-Cl increases with increases in the pH from 0 to 8. While absorption of CTZ increases with increase of pH from 0 to 4.8, then decrease of value until pH 8. The concentration of H+ ions is high at a low pH, so protonation neutralizes the OH groups on the surface of the adsorbent. The presence of H+ ions raises the number of positively charged adsorbent sites at a lower pH, thereby facilitating the adsorption of negatively charged CTZ and Cp-Cl molecules[25]. The optimum pH of CTZ and Cp-Cl was found at pH=4.8 and 7.3, respectively as shown in Figure 4.

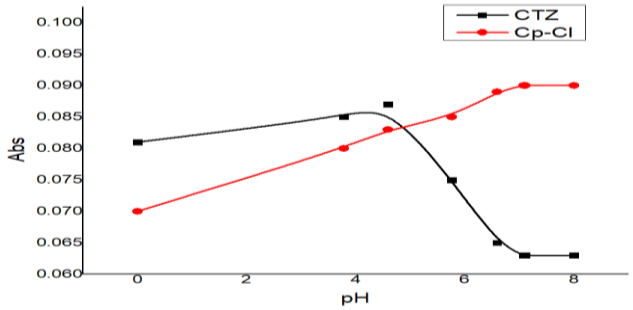

Figure 4. Effect of pH on CTZ and Cp-Cl Drugs onto PUF.

III.3. Effect of Shaking Time

In this effect the absorption of CTZ increases with time of shaking increase from 0 to 60 min, then decrease of value until 120 min. The maximum absorption of CTZ was 60 min as shown in Figure 5. In case of Cp-Cl this effect the absorption increases with increase time of shaking from 0 to 40 min, then decreasing of value until 120 min. As a result of reduced surface area and saturation of the active sites[26]. The maximum of absorption of Cp-Cl was 40 min as shown in Figure 5.

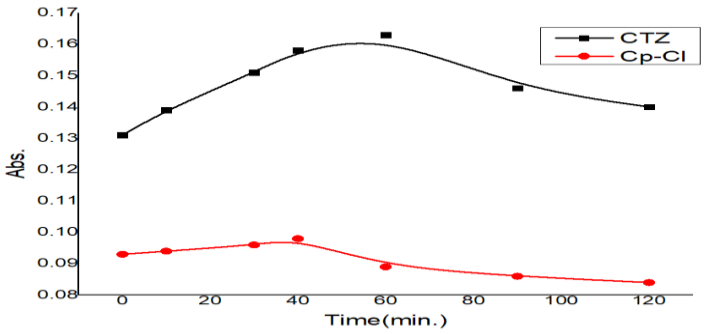

Figure 5. Effect of Shaking Time on CTZ and Cp-Cl Drugs onto PUF.

III.4. Effect of Mass of PUF

The effect of mass on the absorption was studied from 0.02 to 1.5 g. The absorption of CTZ and Cp-Cl was increasing with increase the mass of PUF from 0.02 to 0.6 and 0.3 g respectively, then decrease of value until 1.5 g. When the absorbent material is overloaded, the PUF efficiency decreases, resulting in a decrease in the binding between drugs and PUF[27]. Optimum absorption was at 0.6 and 0.3 g for CTZ and Cp-Cl respectively as shown in Figure 6.

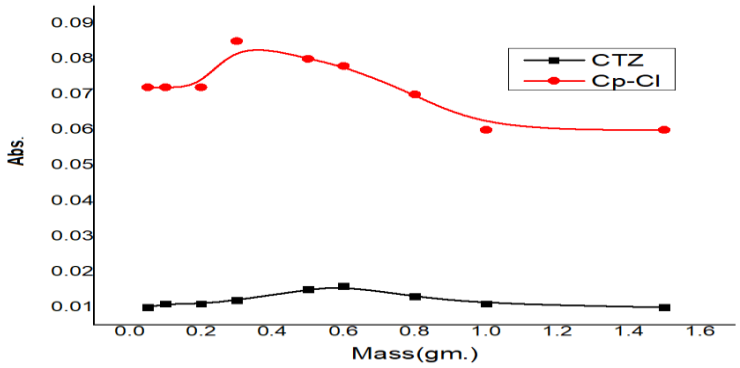

Figure 6. Effect of Mass PUF on CTZ and Cp-Cl Drugs.

III.5. Effect of Drug Capacity

Effect of CTZ and Cp-Cl on absorption capacity from 2 to 100 ppm was studied. The absorption increase with increasing the concentration from 2 to 30 and 20 for CTZ and Cp-Cl respectively, then decrease of value until 100 ppm. These results can be interpreted to mean that if the concentration of the drug increases to a certain value, the available active adsorption sites may be exhausted, resulting in saturation[24]. The optimum absorption was at 30 and 20 ppm for CTZ and Cp-Cl respectively, as shown in Figure 7.

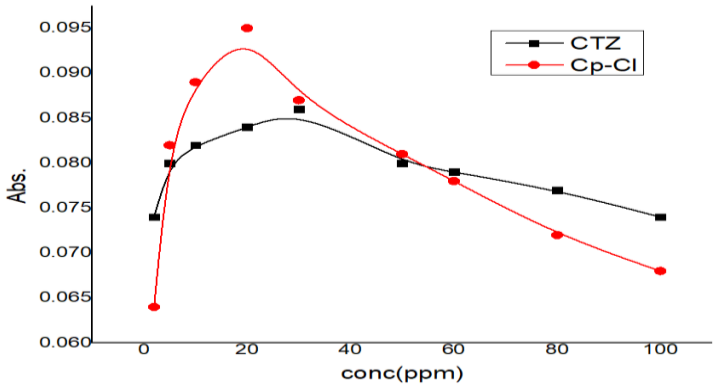

Figure 7. Effects of CTZ and Cp-Cl Drugs Capacity.

III.6. Langmuir and Freundlich Isotherms

In the studies determining the best adsorption isotherm and capacity of the used PUF are the most important factors for evaluating the systems functioning[28]. To fit the data into adsorption models of Langmuir in Figure 8 and Freundlich in Figure 9. Linear form of their general equations 2 and 3 was used and their empirical parameters were presented in Table 1.

$$\left[\frac{C_e}{q_e} = \frac{1}{Q^o b} + \frac{1}{Q^o} C_e\right] \quad (2)$$

$$\left[\log q_e = \log K_f + \frac{1}{n} \log C_e\right] \quad (3)$$

Where

qe: equilibrium adsorbent phase concentration of adsorbate (mg/L)

Ce: equilibrium aqueous phase concentration of adsorbate (mg/L)

Q0: the monolayer adsorption capacity (mg/g)

b: constant related to the free adsorption energy and the reciprocal of the concentration at which half-saturation of the adsorbent is reached

Kf: adsorption capacity and

1/n: adsorption intensity

The equation of Freundlich isotherms usually fits solute adsorption on rough surfaces better than Langmuir isotherms, considering the solid surface heterogeneity and the variable energy distribution of the adsorption sites[29].

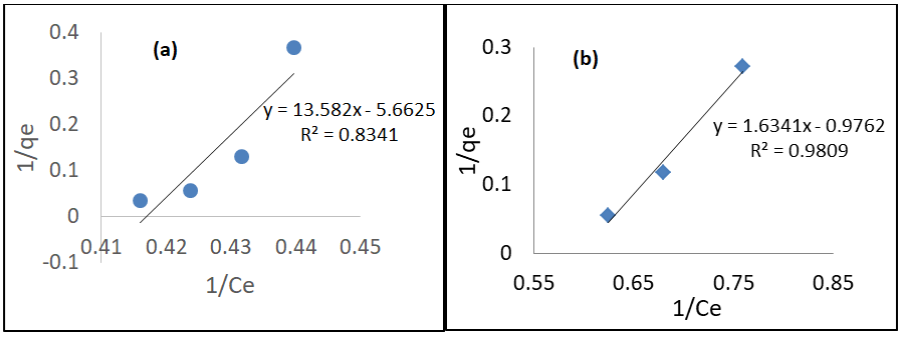

Figure 8. Langmuir Isotherms of (a) CTZ. (b) Cp-Cl

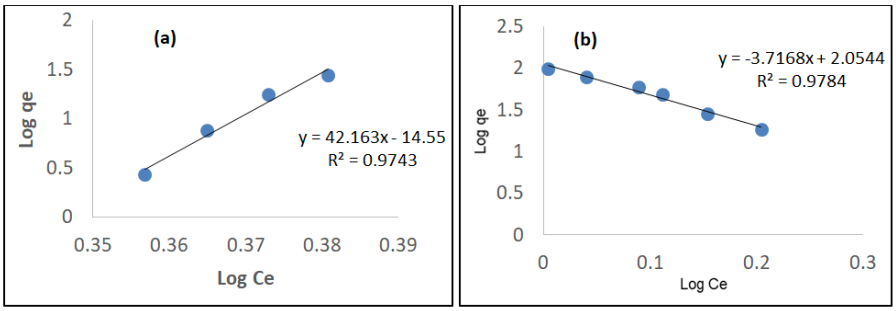

Figure 9. Freundlich Isotherm of (a) CTZ. (b) Cp-Cl

Table 1. Freundlich and Langmuir parameters for CTZ and Cp-Cl removal by PUF.

Drugs	Langmuir Isotherm			Freundlich Isotherm		
	q_m (mg g^{-1})	b (L mg^{-1})	R^2	K_F	n	R^2
CTZ	0.073627	2.398587	0.8341	3.54813E+14	0.023717	0.9743
Cp-Cl	0.611958	1.67394	0.9809	113.3444	0.269049	0.9784

IV. CONCLUSIONS

The study shows that PUF can be used as an effective sorbent for the extraction of drugs from aqueous systems. The present study evaluates the Cetirizine hydrochloride and Cyclopentolate Hydrochloride removal by the use of polyurethane foam. The adsorption performance was strongly affected by parameters such as pH of solution, adsorbent dosage and contact time. The maximum absorption of Cetirizine Hydrochloride drug by polyurethane foam was at 60 min of time, 4.8 pH, 0.6 g, and 30 ppm drug capacity. While in case of Cyclopentolate Hydrochloride drug the maximum absorption by polyurethane foam was at 40 min of time, 7.3 pH, 0.3 g and 20 ppm drug capacity. The value of R2 for Cetirizine Hydrochloride in Freundlich isotherm was (0.9743) and in but in Cyclopentolate Hydrochloride in Langmuir isotherm was (0.9809).

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