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Solid phase extraction performance of polyurethane foam coated with Curcumin or Dithizone

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ABSTRACT

Polyurethane foam (PUF) was physically functionalized with curcumin and dithizone to adsorb Fe³⁺ ions, applying the off-line solid phase extraction procedure. The concentrations of the metals have been determined using the molecular spectroscopy. Various factors including, the pH of the sample solution and the time of extraction were examined. The adsorption mechanism of metal ions onto coated PUF was tested using the Morris-Weber and Lagergren equations. The capacity sequence of the sorbent was in the order dithizone-PUF > curcumin-PUF.

Introduction

The ability to separate and determine trace amounts of elements in different types of samples is important [Oliveira and Lemos, 2012]. There is always a need for sample preparation for the sample by means of dissolution, pre-concentration and/or separation of trace elements before their analysis to avoid interference and to improve sensitivity of the analytical methods [Durukan et al., 2011]. Many separation techniques are frequently used to overcome interferences from matrix elements and to improve detection limits through concentration of the analyte [PYRZYNSKA, 2007], providing more reproducible results, decrease the use of organic solvents, provide cleaner extracts for instrumental measurements, saving time, and less cost [Bader, 2009] [Bader, 2011]. Various methods of separation and pre-concentration have been used, such as solid-phase extraction (SPE), liquid-liquid extraction (LLE), cloud-point extraction (CPE) or co-precipitation. Several authors have chosen SPE due to its high pre-concentration factor, simplicity, low cost and ease of automation [6]. Furthermore, SPE usually does not require organic solvents, many of which are toxic [Lemos et al., 2007; Lemos et al., 2010; Bader et al., 2014; Bader et al., 2014; Liu et al. 2021; Wu et al. 2021].

Solid Phase Extraction

Solid phase extraction (SPE) is an extraction method that uses a solid phase and a liquid phase to isolate analyte from the matrix in a solution [Żwir-Ferenc, 2006].

It is an effective sample preparation method for separation and enrichment of analyte from interfering compounds by transferring the analytes to solid sorbent and then recovered by elution.

SPE has been used in many areas, including environmental, pharmaceutical, clinical, food, and industrial chemistry. Over time, various SPE formats and sorbents have been developed to facilitate the process of different sample types and to extend the scope of the method [Chen et al., 2009].

PUF as SPE Sorbent:

Polyurethane foam in analytical chemistry—a historical overview

Polyurethane foam (PUF) is a good sorbent material in SPE, and it has been the subject of several review articles [Lemos et al., 2007]. Since Bowen investigated the absorption properties of PUFs in 1970 the interest about these materials has increased significantly, and they have been used as a solid sorbent for pre-concentration and separation of a wide variety of inorganic and organic compounds in different media [Aristidis et al., 2002].

One year later, untreated PUF was proposed for sorption of organic contaminants from water using a batch technique. Braun and Farag published the first applications of PUF for chromatographic separation in 1972. These studies resulted in a number of papers, involving the use of unloaded and loaded PUF (polyether and polyester type) in separation and pre-concentration procedures for the determination of inorganic and organic species using different analytical techniques [Lemos et al., 2007].

Physical and chemical characteristics of polyurethane foams

The physical and chemical properties of PUF are a direct function of the preparation process. Figure 1 shows the typical structure of PUF in its original form i.e., in the form in which it is used for sorption purposes. Unloaded PUF only adsorbs metal ions after complex formation. Organic and inorganic ligands can be used for this operation.

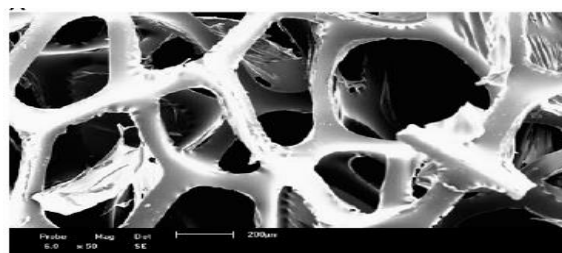


Figure 1. Scanning electron micrographs of PUF

Various factors determine the chemical and physical properties of PUF: functional groups, bond strength, crosslink density and flexibility. The regulation of the crosslink density allows the urethane polymer molecule to vary from the uncross-linked linear polymers (fibers and thermoplastics) to a moderate cross-linking (elastomers, flexible coatings and foams) and finally to the very highly cross-linked structures (rigid thermosetting resins and foams [Benning, 1969]).

Experimental

Instrumentation and Equipments

A CECIL – CE 7400 (Aquarius), UV-Visible double beam spectrophotometer was used for determination of metal concentrations. The pH measurements were made by a AZ pH-Meter 761.

Procedure

Preparation of the sorbent

Polyurethane cubes have been cut and cleaned with distilled water then with acetone and immersed in a solution of 10^{-2} M dithizone or curcumin acetone for few minutes. The sorbent cubes have been squeezed kept to dry at room temperature for approximately 30 minutes to complete the solvent evaporation.

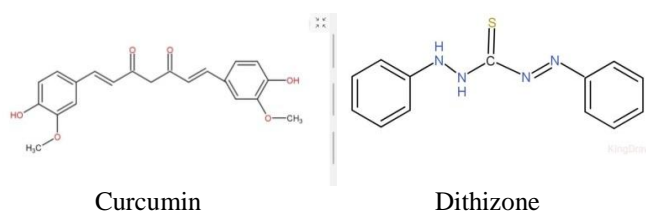


Fig 2: Chemical structure of curcumin and dithizone

General procedure for metal determination

After adjustment of metal sample solutions to pH 5-5.5 given volumes up to 100ml were shake with coated cubes for about 30min. After a washing step with 3ml deionized water.

The adsorbed metal was eluted with 10ml of 2mol/L HNO₃. The concentration of metal ions in the eluate was determined by spectrophotometry using thiocyanate ion as a reagent in acidic medium.

Effect of pH on metal adsorption

For this study, the pH values of the element for 100 ml solutions were adjusted within the range of 1-10 using HNO₃ or NaOH then the general procedure has been applied.

Effect of sample volume

Studies were also performed with metal solutions with different sizes to find the possibility to enrich solutions at low concentrations with a high concentration factor. A series of 50,100,250, and 500 solutions spiked with the same amount of Fe(III) have been tested.

Capacity of the sorbents

In order to study the adsorptive capacity of coated PUF for metals. 100ml of 20ppm metal solution at pH 5.00 was passed through the column and then eluted with 10ml 2M HNO₃ and diluted to 100ml and determined. The absolute amount of the metal is then calculated in the final solution

which is the maximum amount adsorbed on the surface of the sorbent.

Results and discussion

Effect of pH on metal adsorption

The Fe(III) uptake by the sorbent as a function of pH value of the solution is presented in Figure 3.1. The recovery of the analytes was calculated from the ratio of the concentration found and the concentration calculated theoretically as following

$$\text{Recovery\%} = \left(\frac{\text{Analyte concentration in eluent}}{\text{Analyte concentration in eluent}} \right)$$

The pH of the metal ion water solution is an important factor to control the sorption process. The pH of the solution affects the adsorbent capacity, the metal adsorption typically increases with increase of pH; and the mechanism of metal ions binding, by changing it from ion exchange and/or adsorption at acidic region to adsorption and/or complexation and possible precipitation at the basic region [Minceva et. al., 2008]

The formation of a stable chelating complex requires that the chelating agent of a Lewis base has a functional group. The group could donate its electron pair to metal ions, and it is an advantage for the agent if it has a negative charge. Dithizone is utilized as chelating agents through two amino groups and two donating electron pairs, so it can form stable chelates with many different metal ions [In et. al., 2008]

The pH values of the element solutions were adjusted within the range of 1-10 using HNO₃ or NH₄OH. The optimum retention pH range of the sample solution was 4.5-5.5.

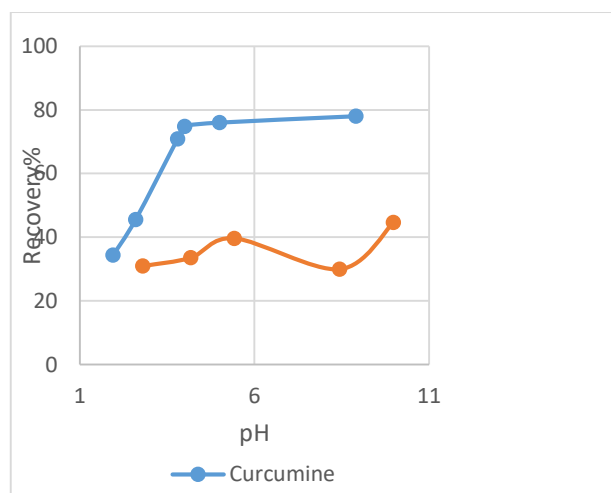


Figure 3: Effect of pH on iron adsorption

The adsorption process depends on the reaction between chelating groups of the used organic ligands with the Fe (III) ion

Diphenylthiocarbazone (Dithizone) is a sulfur-containing organic ligand that bond to heavy metals to form a hydrophobic complex, and the presence of a substance that enhances the hydrophilic character of the formed complex will cause a decrease in the extraction efficiency. This phenomenon appears when solid phase extraction process based on the reverse-phase mechanism [Otoniel D et. al., 2004].

The differences in the capacity and the maximum recovery between dithizone-PUF and curcumin-PUF sorbents toward iron ion indicates that, the adsorption depends mainly on the reaction between the metal ion and the chelating groups.

The higher capacity of Dithizone-PUF toward iron ions can be attributed to the small size of the ligand, since D is relatively smaller than Curcumin therefore more D will connect to the PUF than C.

Effect of sample volume

The effect of changes in the volume of sample solution passed through the column on the recovery of metal ions was investigated in order to determine an applicable sample volume or a minimum analyte concentration. To get a high pre-concentration factor, a large volume of sample solution is required. From Figure 3.2 the recovery values were quantitative up to 100ml in case of curcumin-PUF.

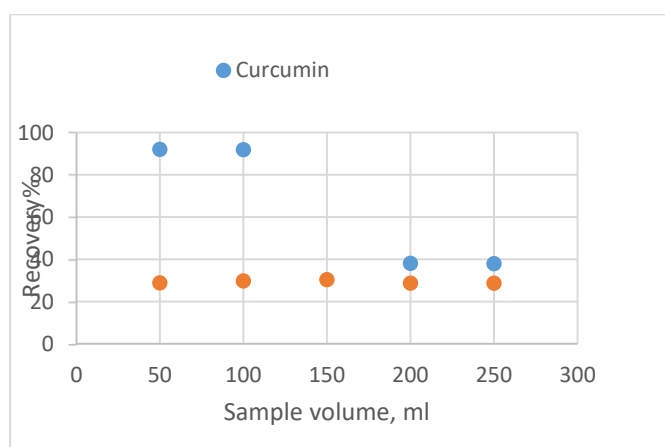


Figure 4: Effect of sample volume on Dithizone – PUF and Curcumin-PUF

Capacity of the sorbents

Adsorption capacity is an important factor to evaluate the sorbent, as it determines how much solid phase is required for a given solution. The pre-concentration and determination of the analyte is possible if the total load of the analyte is less than the sorption capacity.

The capacities of the used sorbents towards metal ions used are shown in Table 3.1

Table (1): Sorbent capacity of Dithizone – PUF and Curcumin-PUF toward

Average capacity per one gram sorbent	microg/g	mmol/g
Dithizone - PUF	252	4.50
Curcumin - PUF	26	0.46

Experimental values of the capacity allow us to discuss the dependence of the chromatographic efficiency on both the properties of the stationary phase and the solutes to be separated and the experimental conditions.

Sorption kinetics

The adsorption process depends on the effective collisions between the solid-phase (PUF) and the metal ions, which is

enhanced with the shaking of the solution. Even with the efficient shaking, certain time is required to achieve maximum transfer of metal ions from liquid to the solid-phase.

The influence of shaking time on the percentage of sorption is recognized of significant importance to determine the possible discrimination order of the sorbent behavior towards Fe^{3+} ion.

The percentage sorption of metal ion was calculated from the relation:

$$\text{sorption} = \left(\frac{C_0 - C}{C_0} \right) \times 100$$

Where C_0 and C are the initial and remaining concentrations ($mg\ l^{-1}$) of the metal ion respectively.

It is evident from the results represented in Fig. 3.3 that the equilibrium between Fe^{3+} ions and the phase coated with dithizone is faster than that coated with curcumin. An equilibration time of about 10 min was sufficient to achieve sorption of Fe^{3+} with Dithizone-PUF and 50 min in case Curcumin-PUF sorbent.

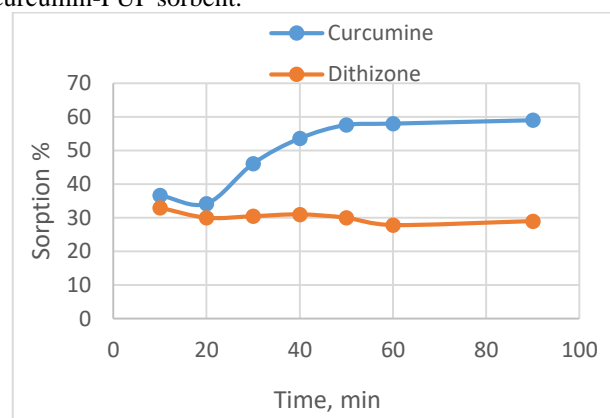


Fig. 5: Rate of sorption of Fe^{3+} with Dithizone-PUF and Curcumin-PUF sorbent

The PUF material is highly porous with spherical and symmetrical macropores and micropores. Sorption into the macropores is rapid and characteristic of film diffusion, because the macropores are relatively large compared with the small molecular size of the solute and readily accessible to the solute, but in contrast, the micropores and the size of the solute molecule are similar. Diffusion in such pores would be severely hindered due to steric interaction, so that the subsequent slow approach to equilibrium would be characteristic of an intra-particle diffusion process [Burham et. al., 2014].

The interpretation of adsorption data of adsorbate can be achieved by applying the diffusion equations on the diffusion process and mass action phenomenon.

The controlled by The slowest step controlling the rate of the adsorption process, would be either diffusion or intra particle diffusion.

The surface adsorption is usually a fast step because solute molecules have a very little chance to diffuse into the adsorption particles, sorption may be attributed to film diffusion, and the process of adsorption occurs at the macropores of the adsorbent, while time dependent sorption process may be film diffusion or intra particle diffusion.

The adsorption of metal ions onto Dithizone-PUF and Curcumin-PUF sorbents was tested by using the Morris-Weber equation in the form [Bader et al. 2018]

$$q_t = k_i (t)^{1/2} \dots \dots \dots \text{equation 1}$$

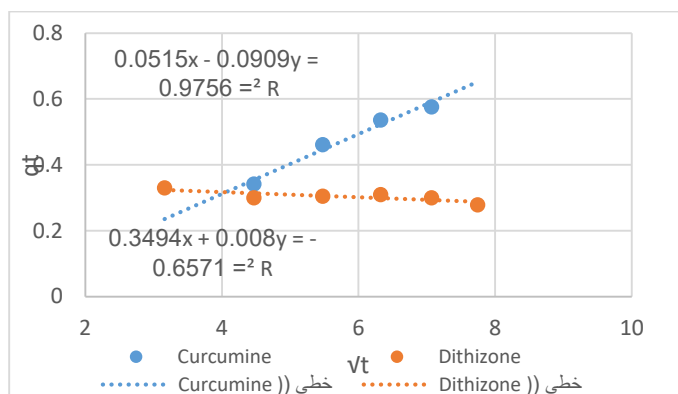


Fig 6: Morris-Weber plot for sorption of Fe^{3+} on Dithizone-PUF and Curcumin-PUF sorbent

Where q_t is the amount of ion adsorbed at time t and k_i is the adsorption rate. The straight line of the plot q_t vs $(t)^{1/2}$ in cases Curcumin-PUF with high R^2 (0.975) indicates the intra particle transport phenomena and time dependent mechanism. In case of Dithizone-PUF the rate was stable and this can be attributed to mass action phenomenon mechanism.

The second model is first order Lagergren equation. It was applied for mass action phenomenon and which is given below:

$$\log(1 - q_t/q_e) = -k_1 t / 2.303$$

or

$$\ln(1 - F) = -k_1 t$$

where k_1 is the rate constant of the sorption process, and $F = q_t/q_e$.

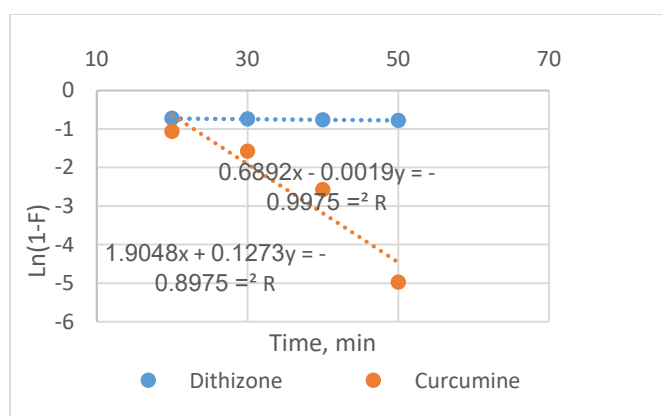


Fig 7: Lagergren plot for sorption of Fe^{3+} on Dithizone-PUF and Curcumin-PUF sorbent

The plots of $\log(1 - F)$ Vs t for Dithizone-PUF was straight with high R^2 0.99 (Figure 7), indicates that mass action phenomenon are controlling the mechanism following first order process. [Journal of chinese chemical society., 2007] In the diffusion process, the slope of the curve depends upon the particle size, film thickness and concentration of the solute in solution.

The sorption kinetics of β -Nap-PUF toward Ni^{2+} , Cu^{2+} , Ag^+ , and Hg^{2+} have been studied by [Moawed et. al, 2005]. The obtained kinetic data were treated according to mass action process, which means a first-order reaction depending on time. The results show that the rate constant for adsorption depends mainly on the reaction between the metal ion and the chelating groups of β -Nap-PUF.

[Bader et al. 2018] have studied the adsorption of Fe^{3+} , Cu^{2+} , Cr^{3+} , Co^{2+} and Mn^{2+} on PUF chemically modified with β -Naphthol. For Cu^{2+} , Cr^{3+} and Mn^{2+} mass action phenomenon was controlling the mechanism following first order process. In case of Mn , the results indicates the intra particle transport phenomena.

Conclusions

Polyurethane foam (PUF) coated with curcumin and dithizone can be used as solid phase extraction sorbent to adsorb Fe^{3+} ions from aqueous solutions. The concentration factor of the metals using curcumin-PUF sorbent was greater than dithizone-PUF. Multiple extraction with dithizone-PUF is required. The capacity sequence of the sorbent was in the order dithizone-PUF > curcumin-PUF.

The adsorption mechanism of $Fe(III)$ on curcumin-PUF was intra particle transport phenomena and time dependent mechanism and in case of dithizone-PUF was mass action phenomenon.

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