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PRECONCENTRATION OF ALIZARIN DYE USING BETA-CYCLODEXTRIN EPICHLOROHYDRIN POLYMER AS A SOLID PHASE EXTRACTANT.

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ABSTRACT

The β-Cyclodextrin epichlorohydrin cross-linked polymer (β-CDP) was synthesized and used as a solid phase extraction material to preconcentrate alizarin dye with UV-Vis spectrophotometer. This method is based on the adsorption of alizarin on β-CDP. The residual concentration of the dye was determined spectrophotometrically. The various parameters that were studied are pH; shaking time, sample volume etc. The % recovery of alizarin dye was found to be ≥ 95%. The proposed method has been applied for the determination of alizarin in various samples.

KEYWORDS: β-cyclodextrin epichlorohydrin polymer (β-CDP), alizarin dye, preconcentration, solid phase extraction, spectrophotometry.

1. INTRODUCTION

Coloring materials are usually classified as dyes or pigments. Dyes are Chemically bound to a substrate such as a textile, whereas pigments require another substance, called a binder, to help them adhere to the substrate. The human body may have served as the first substrate for dyes, but textiles or fabrics have been the most common over the ages. In addition to textile fibers, dyes have been applied to paper, wood, food, cosmetics, fur, and leather. Alizarin originally derived from the roots of plants of the madder genus is a red dye used as first natural pigment to be duplicated synthetically. It is the main ingredient for the manufacture of the madder lake pigments known to painters as Rose madder and Alizarin crimson. This dye stains calcium present in tissues and bones. In clinical practice, it is used to stain synovial fluid. Alizarin has also been used in studies involving bone growth, osteoporosis, and bone marrow, calcium deposits in the vascular system, cellular signaling, gene expression and

tissue engineering. However alizarin is very hazardous in case of ingestion, eye contact (irritant), and inhalation. It is thus toxic to lungs, mucous membranes. Repeated or prolonged exposure of alizarin through skin may cause inflammation, pre dermatitis condition. Entry of alizarin dye into blood through cuts, wounds causes harmful effects. Long term exposure to high dust concentrations may cause changes in lung function i.e. pneumoconiosis. Alizarin dye has carcinogenic effect[1] and is related to other respiratory problems. The concentration of this dye must therefore be controlled due to toxic effects on human health. Different separation and preconcentration techniques are used for removal of dyes in the solution. Various analytical methods have been reported using HPLC, capillary electrophoresis, ion chromatography, voltammetry, spectrophotometry and TLC. Some reported methods require complicated instrumentation interferences from others. Therefore, Spectrophotometry due to its higher sensitivity, low cost, low interference level and its excellent detection limits is widely used for the determination of dye.[2-4] Thus, alizarin dye has been determined spectrophotometrically in various samples after preconcentration using β-CDP as a solid phase extractant.

Self-assembling phenomena attract considerable attention as they are basic issues for supramolecular chemistry like formation of host-guest molecules.[5-10] Complexation of hydrophobic guest by macromolecular hosts is a widely found phenomenon in chemistry. Beta-Cyclodextrins (β-CDs)[11-12] well known host molecules that consists of glucose units that are joined by α-(1, 4) glycosidic linkages at C_1 and C_4 to form cyclic structure.[13-15] β-Cyclodextrin polymer (β-CDP) is a new type of sorbent useful for the preconcentration of dyes, organic pollutants, heavy metals, acids, alcohols etc.[16] in water. These substrates form stable complexes with CD's.[17-19] Synthesis of water insoluble β-CDP was done by cross linking the hydroxyl group with various cross-linkers such as epichlorohydrin,[20-24] glutaraldehydes, diisocyanates, succinyl chloride etc.[25-29] Epichlorohydrin is widely used in chemistry and industry because of its high reaction activity and it is the most popular croslinking agent for β –CDP synthesis.

2. EXPERIMENTAL

Reagents and Equipments

All absorbance measurements were done using Shimadzu-1800 UV-vis spectrophotometer with 10mm quartz cell. Measurements of pH were made with digital century Cp-901 pH

meter using a combined glass electrode. Shakings were done using PERFIT INDIA shaking water bath.

Reagents

All the reagents used were of analR grade unless otherwise stated. Double distilled water was used throughout the experimental work.

Synthesis of β-Cyclodextrin polymer

40gm of beta-Cyclodextrin, 10gm of soluble starch and 100ml of 20% sodium hydroxide were added in a beaker. The mixture was vigorously stirred at 50-60°C for an appropriate period until the reactants were dissolved. A total of 60ml of Epichlorohydrin was added drop wise into the solution and β-CDP was formed in 30min. After washing with double distilled water 5-6 times, the obtained polymer were dried at 100°C and then stored at room temperature in dessicator.

A stock solution of alizarin was prepared by dissolving 0.3gm in 100.0ml standard flask and further dilutions were made as per required.

The buffer solutions of pH range 1.0-3.0 were prepared by mixing different amounts of 0.2M hydrochloric acid/0.2M acetic acid and buffer solutions of pH range 3.5-6.5 were prepared by mixing different amounts of 0.2M sodium acetate/0.2M acetic acid. Buffer solutions of pH range 7.0-10.0 were prepared by mixing 0.5M ammonia/0.5M ammonium chloride.

Procedure

An aliquot containing 28.8µg/ml of standard solution were taken in 50.0ml of stoppered flask and 2.5ml of buffer of pH 4.0 and 0.25gm of β-CDP were added. The mixture was kept for about 5.0min to equilibrate and then made up to 25.0ml with double distilled water. After the mixture was shaken mechanically for 120.0min at a rotation rate of 140rpm at room temperature. Then a definite volume of supernatant was extracted and determined spectrophotometrically.

3. RESULTS AND DISCUSION

Optimization of conditions

Effect of pH

The effect of pH on the complexation of alizarin dye with the polymer was studied over a wide pH range of 1.0-7.0 at a constant polymer concentration. Then the preconcentration

procedure as described above was applied. %recovery was maximum at pH 4.0. Hence experimental work was carried out at pH 4.0.

Effect of sample volume

In order to explore the possibility of enriching low concentation of analytes from large volume of solution, the effect of sample volume on %recovery of alizarin was studied by varying total volume from 5.0-50.0ml. It was observed from resulted spectra that% recovery remains constant upto 35.0ml and then decreases. Therefore, 25.0ml sample volume was adopted for the preconcentration of analyte from sample solutions.

Effect of amount of β-CD polymer

The amount of β-CDP is another parameter that affects %recovery of alizarin dye. A quantitative removal cannot be achieved when the β-CDP is less than optimum amount. In order to optimize the smallest amount of the polymer, the polymer amount was varied from 50.0mg-350.0mg. It was found that % recovery was maximum for 250.0mg and after that it becomes constant. Therefore, 250.0mg of β-CDP was selected for working experiment.

Effect of shaking time

Effect of shaking time is an important parameter that affects possibility of applications of β-CDP for %recovery of alizarin dye.Different shaking times ranging from 10-140min were studied. It was found that %recovery increases as the time of shaking increases from 10.0min–120min and then becomes constant for higher shaking times at room temperature. Based on these results shaking time of 120.0min was adopted for further experiments

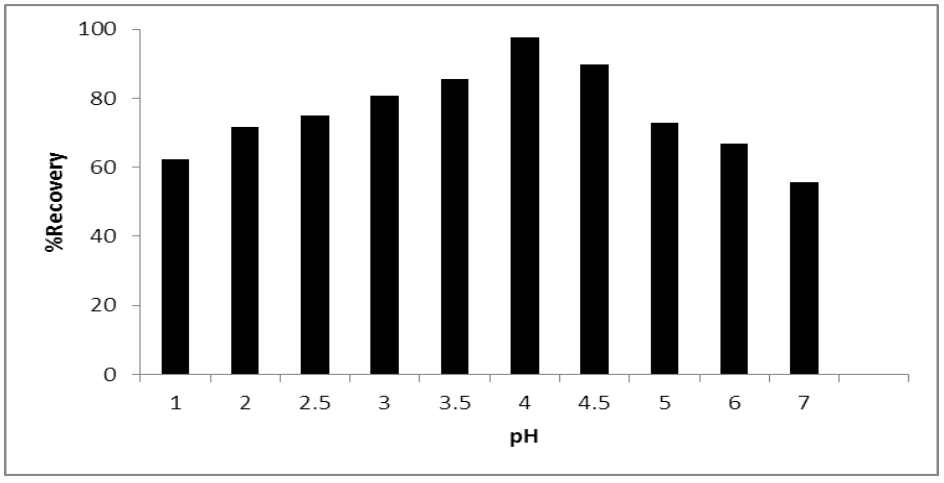

Fig.1: Effect of pH on %recovery of alizarin.

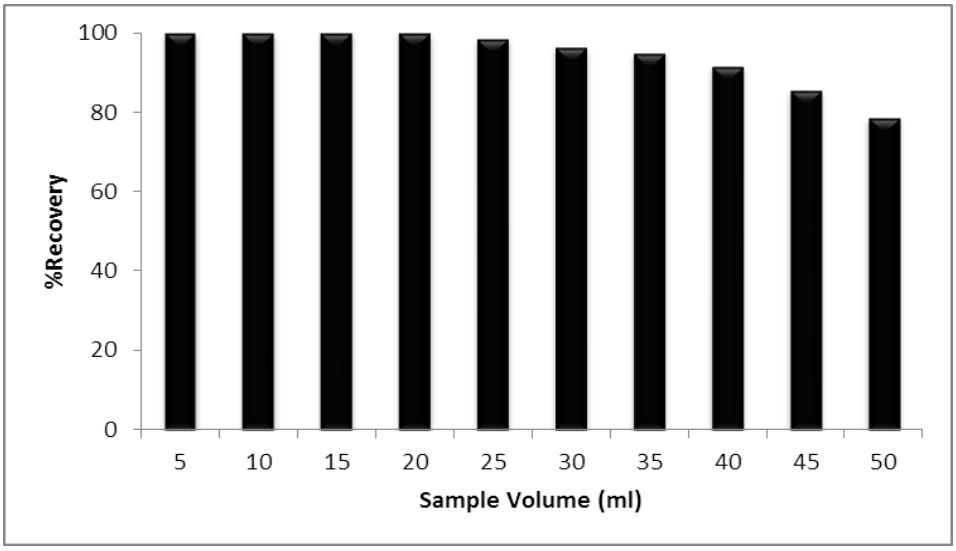

Fig.2: Effect of sample volume on %recovery of alizarin.

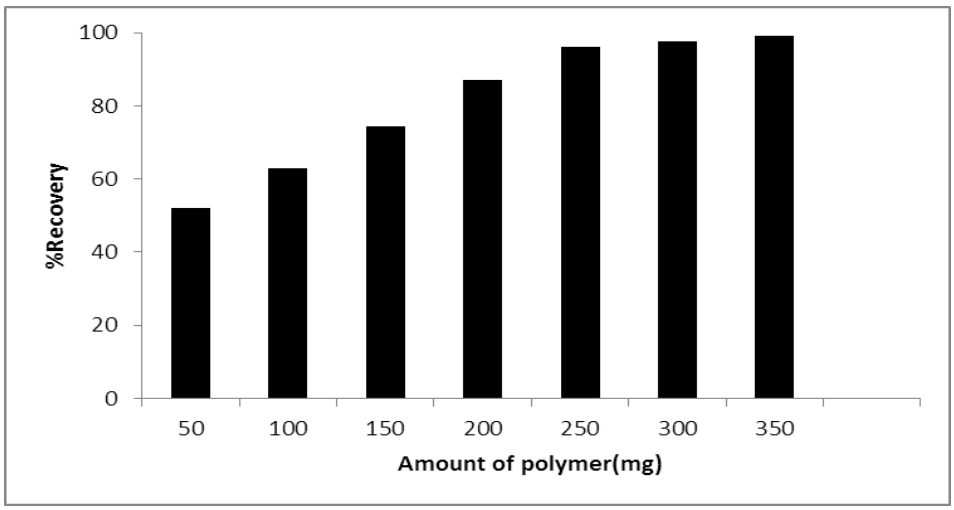

Fig.3: Effect of amount of adsorbent on %recovery of alizarin.

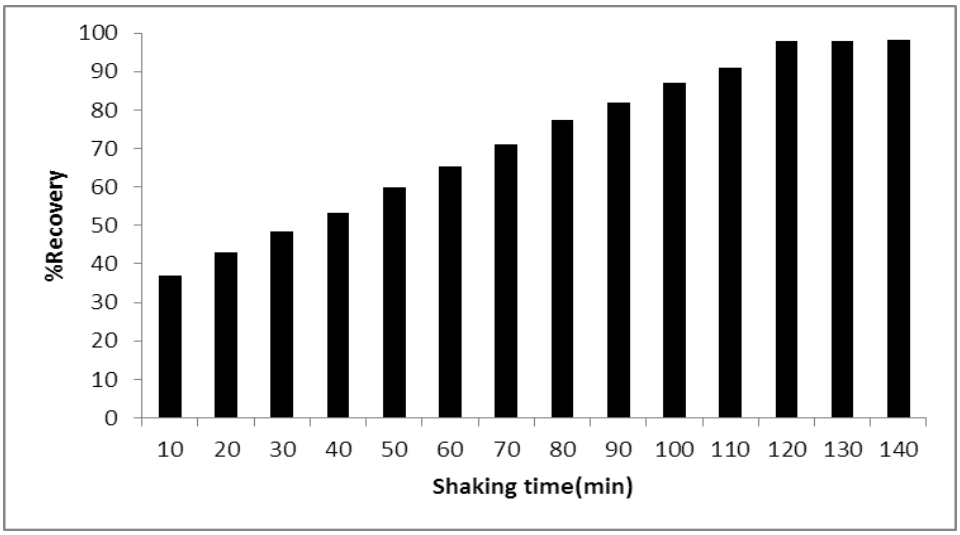

Fig.4: Effect of shaking time on%recovery of alizarin.

4. APPLICATIONS

The developed procedure has been applied for the determination of alizarin dye in spiked samples. Results are shown below in the table:

Table 1: Showing determination of Alizarin in spiked samples.

Sample	Added (µg/ml)	Found (µg/ml)	Recovery (%)
Alizarin Ink*	0.00	0.86	---------
	0.96	0.93	96.0%
Alizarin Crimson**	0.00	0.98	--------
	2.40	2.38	99.0%

*Fischer Chemic Ltd, Chennai, India. **Bhatia Color Company, Gujarat (1975).

5. CONCLUSION

The proposed preconcentration method consists of a simple and low cost procedure which permits quantitative %recovery of alizarin dye from various samples. The synthesis of β-CD polymer is easy with good accuracy, sensitivity and repeatability. The synthesized polymer has a unique stability. In addition, the used colored polymer could be regenerated with 0.1% HCl with more than 95.0% regenerated yield. Thus, solid phase extraction combined spectrophotometry is more useful method of determination of alizarin dye.

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