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Comparison Study of Removing Dye from Aqueous Solution Using Triton X-100, Triton X-114 and Egg Shells

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Abstract

A surfactant cloud-point extraction (CPT) process using two different non-ionic surfactants, Triton x-100 and Triton x-114.And adsorption process on egg husk to remove Bromo cresol green dye from aqueous solution have been studied comparatively. The effects of surfactant and dye concentration , pH ,temperature as well as salt and for the adsorption process of egg husk ,the effects of dye concentration, pH , adsorbent dose , temperature and incubation time have been studied .The optimum conditions were obtained for the removal of Bromo cresol green dye. The results showed that up to 60 ppm of Bromo cresol green can quantitatively be removed (97%) by cloud-point extraction process with triton x-100 and (99.3%) with triton x-114 and (95%) by adsorption process with egg husk.

Keyword: Triton x-100; Triton x-114; Cloud point Extraction;Bromocresol green

1. Introduction

Cloud point extraction (CPE) has become an influential and multi-faceted technology for separation, purification and known concentration of organic compounds (such as phenol and its derivatives), dyes and inorganic compounds such as ions toxic to heavy metals [1]. CPE is based on the premise that non-ionic surfactants are created micelles with aqueous solutions to become cloudy upon heating above a temperature known as cloud point temperature (CPT). In a small volume mainly contains more surfactant, it is called the coacervate phase (CP) and the aqueous phase diluted in large quantities includes a small amount of surfactant at the critical micellar concentration (CMC). During the formation of the two phases, the hydrophobic species may be restricted to CP. This process is called (CPE) [1-3]. The use of CPE has many advantages, such as low cost, high safety, simplicity, and low volume of organic solvents, which are generally very toxic [4-7].Although there are many non-ionic surfactants, Triton X-100 and Triton X-114 were used in this study because the derivatives (Triton X) with surfactants were low cost, commercially available, high purity and low toxicity [8]. The actual mechanism of phase separation above CPT is unknown. Several authors have proposed some hypotheses using the phase separation phenomenon. Nelson et al [9]. He suggested that the dielectric constant of water decreases with increasing temperature which reduces the interaction between the hydrophilic part of the surfactant and the water. Thus the dehydration process takes place in the outer layer of the micelles of the non-ionic

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surfactant above CPT [9]. Another suggestion is that the phase separation above CPT is due to micellar attraction since at this lower temperature (less than CPT) the repellent force is prevalent between cells which becomes attractive when the temperature exceeds CPT [10]. Some authors have further suggested that the phase separation mechanism is caused by the increase in micellar volume (increase in the number of aggregations) with temperature [11]. The correlation of solubility domain and solubility site in non-ionic surfactant micelles is not understood. Therefore, some authors have suggested what is relevant to the additional non-ionic agent. That the core is surrounded by a cover of a group of aqueous chains, and dissolution occurs in both the core and the mantle [12]. The non-ionic micelles depend on the ionic property of their solubility. The emergence of additional non-ionic agents is relatively more hydrophobic at higher temperatures due to the equilibrium shift favoring the drying of ether oxygen with approaching the cloud point as the solubility of non-polar materials increases due to an increase in the number of micelles aggregation. As for the polar soluble materials, their solubility decreases due to the drying of the polyoxyethylene chains attached to the core more tightly. These observations claim that nonpolar compounds dissolve in the core of the micelles, while polar soluble substances are present on the mantle. All the temperature effect reported here corresponds to the differences in the available surface area of the dissolved particles in the micelles [12]. The CPE method provides the advantage of using surfactant the ability to extract and pre-concentrate analyzes in one step using a simple procedure. In addition to the advantages of using CPE charts it has several advantages: (1) it has a good ability to dissolve analyzes of different types and nature. (2) Compatibility of the surfactant-rich phase with the micellar or hydro organic mobile phases of the HPLC system. (3) Excluding losses from solvents because it is not necessary to evaporate the solvents. (4) Ease of disposal of solvents. There are limitations imposed on the CPE methodology, including that many surfactants are not available as pure homogeneous preparations and that many surfactants are in the area. Ultraviolet radiation has a high absorption spectrum, which prevents its use in the pre-chromatographic separation step when using spectrophotometric detection for liquid chromatography. Analyzes subject to thermal changes may be subject to degradation at the temperatures required for phase isolation with some surfactants [13].

2. Experimental

2.1. Material

The dye used in this study is Bromo cresol green (MW: 698.04, λma(617 nm), dye content: 97% Thomas Baker Manufacturing India). Triton X-100 (iso-octylphenoxypolyethoxyethanol) MW: 646.87, density at 25 ° C. 1.061 g mL, Thomas Baker Corporation, India Manufacture and Triton X-114 (octyl phenol poly (ethylene glycol ether) MW: 537, Density 25 C. 1.058 g mL, Sigma-Aldrich Corporation, USA. As a non-ionic surfactant, the critical micellar concentration (CMC) of TX-100 and TX-114 is 2.8 (mM) and 2.1 (mM) [14], respectively. The cloud point of TX-100 and TX-114 in solution Aqueous 65 ° C [15] and 37 ° C [16], respectively. Potassium chloride has been purified (MW: 74.56, minimum purity 99%, Thomas Baker Corporation, India) Bretton-Robinson buffer solution at a pH range of 4 Made from a mixture of acetic, phosphoric

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and boric acids, Thomas Baker Corporation, Manufacture India. Chicken eggshells were purchased from local markets.

2.2. Methods

A concentration (500 ppm) for each dye is prepared by dissolving 0.125 g of the dye in deionized water using a 250 ml volumetric vial.The other concentrations are prepared for experiment from the above concentration using the dilution law.Take 20 ml of the dye at the specified concentration and 5 ml of Bretton Robinson PVR , Which was prepared from (mixing equal volumes and a concentration of 0.04 m of acetic acid, phosphoric acid and boric acid and titrated with sodium hydroxide at a concentration of 0.2 M to reach a pH of 4) [17]. Add 10 ml of salt.10 mL of (2M) electrolyte salt (KCl) are added. The solution is transferred to a 50 ml glass cylinder. To the solution of surfactants, a volume of 0.5 ml is added and the volume of the solution with distilled deionized water is added to a volume of 50 ml. The glass cylinder is placed in a thermostatic vibrating water bath at a selected temperature for a period of (30 minutes).After the expiry of the above time, the glass cylinder is placed in an ice bath for a period of (5 minutes). The solution is separated by a centrifuge for a period of (10 minutes) at (3500 cycles per minute) into two layers (aqueous solution and a cloud point layer).The absorbance of the aqueous solution of the dye is measured at its maximum wavelength by means of UV-Vis spectroscopy.The residual dye concentration after removal is obtained by calculating the titration curve for each stain for the purpose the residual dye concentration after removal is obtained by calculating the titration curve for each stain for the purpose of calculating removal efficiency. Of calculating removal efficiency.The eggshell was washed with its membrane using water, dried at room temperature, and kept at 35°C to prevent damage to samples before using. The eggshell was ground with an electric grinder and a sieve was used to obtain the required particle size (150 µm). Next, use the product from the eggshell as the adsorption study.

3. Results and discussion

For cloud point extraction, the extraction efficiency was known from the equation below: extraction efficiency = (1- Cd / C0) x 100 where C0 and Cd are the initial and dilute concentration of Bromo cresol green, respectively. The absorption spectra of bromo cresol green showed the maximum absorption range at the greatest wavelength (617 nm). Therefore all measurements were made at this wavelength. The effects of different operating conditions from dye separation were investigated and the optimal concentrations of CPE determined.

3.1Effect of concentration on efficiency the removal

The results obtained showed that changing the initial concentration of bromo cresol green dye at the wavelength (617 nm) with a constant volume of Triton X 100 was at a percentage of the removal efficiency (cloud point extraction) 90% at the concentration of (20 ppm) while it became At a concentration of (80 PPM) 93%, it was equal to the previous concentration. Whereas, the percentage of removal efficiency (cloud point extraction) with a constant volume of Triton X 114 was 69% at (20ppm), while it became

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at (80ppm) 82%.CMC increase of non-ionic surfactants in aqueous solution due to an imbalance of water structure [18]. This increases the hydration of the hydrophilic group of the surfactant [18]. In this study, bromo cresol green pigment contains an active functional group similar to that of urea. Therefore, it can be assumed that in the presence of a dye (at a constant surfactant concentration), the CMC of the non-ionic surfactant increases. This means that the concentration of the number of micelles decreases with increasing dye concentration. Therefore, increasing the concentration of the feed dye only increases the insoluble dye which will increase its concentration in the dilute phase and thus reduce the extraction efficiency. The presence of the dye increases CMC resulting in fewer micelle thus reducing volume. But this decrease is more than offset by the moisturizing effect of the dye, which leads to the formation of larger particles [19].As for the removal rate for adsorption of the dye on the eggshells, it was 72% at the concentration of (20 ppm) and became 56% at the concentration of (40 ppm), and at the concentration (60 ppm) the percentage was 42% while the percentage was 28% at the concentration of (80 ppm) for the same weight as the adsorbent. Where it is noticed that the percentage of removal gradually decreases with the increase in the concentration of the dye. The reason for this is that the number of active sites that are available on the surface of the adsorbent of the eggshell is insufficient with the increase in the initial concentration of the dye, and thus the amount of dye that can be removed decreases [20]. The competition of dye molecules on a fixed number of active sites from the adsorbent surface leads to saturation of the effective sites of the adsorbent surface with dye molecules [21, 22]. The experiment was conducted under a constant weight of 1 g of adsorbent and at a temperature (25◦ C) and at a time (60min) with Change the initial focus of the dye (20 – 80 pmm).As shown in the figure 1.

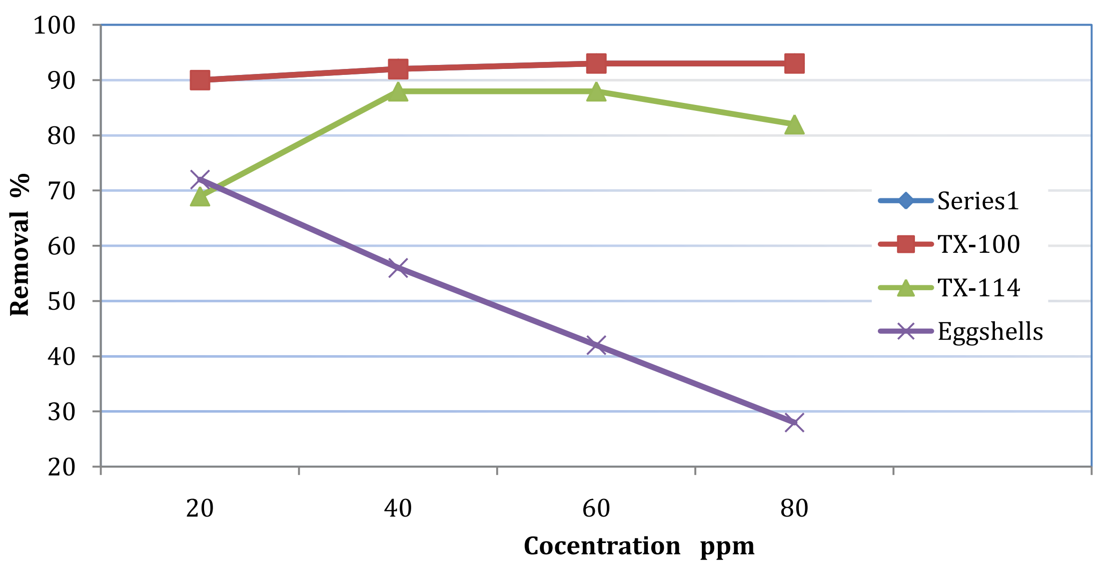

Figure 1. Effect of concentration on efficiency the removal of bromo cresol green (Conditions: 20 mL of solution containing different concentration of dye (20, 40, 60

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and 80 ppm), 10 ml, 0.2M, of KCl and 5ml from 0.5 ml of Bretton Robinson PH 4 and 0.5 ml of triton x-100, triton x-114 and 1g of eggshells.The volume is supplemented with distilled water. equilibration temp 75 oC, for triton (TX-100, TX-114) and 25Oc for eggshlls equilibration time 20 min, centrifuge time 10 min and centrifuge rates 3500 rpm).

3.2 Effect of volume triton and Egg shell weight on removal

This study demonstrated the effect of the volume of surfactant depressant by extracting the cloud point using a fixed concentration of Bromo cresol green dye (60 ppm) with two types of surfactants, namely (Triton X- 100) and (Triton X-114) volumes (0.5, 1 ,1.5 ,2 ,2.5 ml) of surfactant, When other parameters are constant, such as temperature, removal time, electrolyte salt concentration and pH.Where as, the results were that the optimum percentage of removal at the volume of (2.0 ml) is 97% with respect to TritonX-100.Whereas, the percentage of removable TritonX-114 was (99.3%) at volume (1.5 ml). Since the molecular weight of the dye is the same when removing with a surface tension reducer, the removal ratio (separation) mainly depends on the value of CMC the surface tension reducer, so the CMC lower it is, it is useful for removal operations on the basis of molecular weight as a general rule value of CMC (Triton X-114) is (0.2mM),while value of CMC (Triton X-100) is (0.24 Mm)[23 , 24] .As for the effect of the weight of the adsorbent surface on the adsorption capacity of (Bromo cresol green) on the eggshell, where different weights of the surface of the adsorbate (1, 2, 3, 4, 5 g) are tested. Where it was observed that the adsorption capacity of the dye is affected by the weight of the adsorbent surface. At (5 g) from the weight of the adsorption surface, we find the highest percentage of the adsorption capacity (51%). The explanation for this is that the dye removal efficiency increases with increasing the adsorbent dose due to the increase in the surface area of the absorbent and the number of adsorption sites for the dye [25]. As shown in the figure 2.

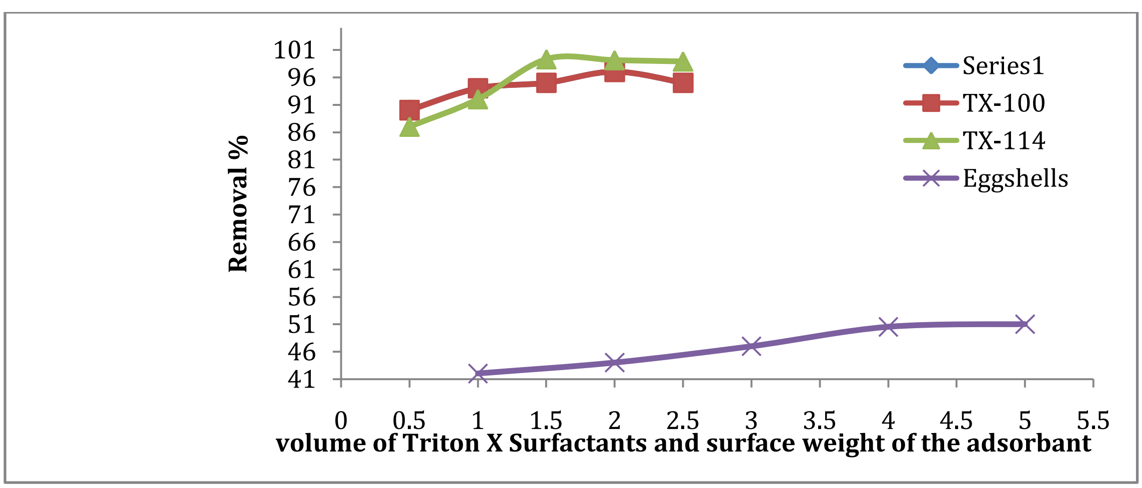

Figure : 2 Effect of volume triton and Egg shell weight on removal.

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3.3. Effect of time

The effect of removal time on the percentage of dye removal from aqueous solutions using surfactant tensile reducer. The study took different times, ranging between (20, 30, 40, 50 min) with Triton X-100 and Triton X-114. The results showed that the maximum percentage of dye removal was 97% at time (20 min) using surfactantTriton X-100While the percentage of removal at time (50 min) was 94.8%. Whereas, the results showed that using surfactant Triton X-114, the percentage of removal at a time (20 min) was 99.3%, while the percentage of removal of pigment decreased to 72.3% at a time (50 min). The reason for this is that the increase in the removal time increases the enthalpy of the dye and the surfactant, and this leads to a decrease in the wetting of the hydrophobic part of the surfactant and the increase in its concentration ratio and the return of the dye to increase the percentage of dissolution in the dilute solution since the dissolved dye molecules are randomly removed on the mantle of a water chain Thus, the percentage of removal decreases, since the ratio depends on the initial concentration and the dilute concentration [26].The effect of contact time on adsorption of bromo cresol green dye on the surface of eggshells at time intervals ranging between (15 ,30 ,45 and 60 min) at temperature (25◦C), volume of 50 ml, constant concentration of dye, (60 ppm) , constant weight of eggshell (5 g) and the incubator speed was 120 rpm Where the percentage was 35% at the contact time of (15 min), and the percentage became 77% at the contact time of (60 min). We found that there is an increase in the percentage of dye adsorption with increasing time, and the reason for this is due to the availability of active sites at the beginning and the need for adsorption to time to occur [27].As shown in Figure 3.

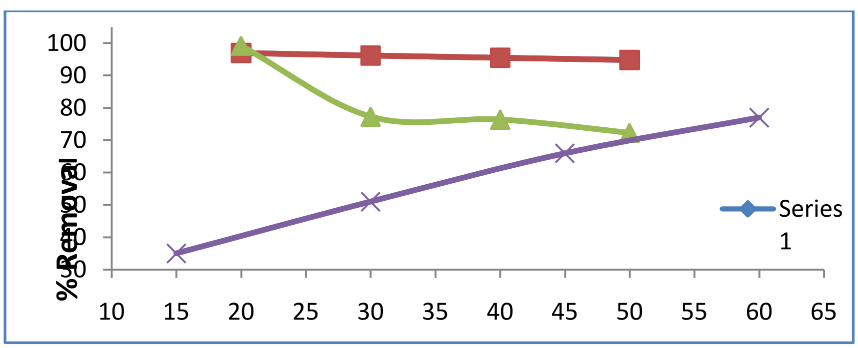

Figure:3 Time (min)

3.4 Effect change of the temperatur

In this study, the effect of changing the temperature of the vibrating water bath on removing the dye was done in this study using a fixed volume of surfactant and a specific concentration (60 ppm).Where the results showed that the percentage of removal when using Triton X-100 was 87% at a temperature of 60◦C and the removal percentage began to rise to reach 97% at a temperature of 75◦C, but it began to decrease to 92.3% when the temperature rose to 80◦C, with the removal time fixed for all samples.While the results showed when using Triton X-114 with the same conditions as the previous experiment, where the percentage of removal was 91.2% at a temperature of 40◦C, and it was noticed that the removal rate increased to reach 99.3% when the temperature reached 50◦C, but the removal rate began to decrease after this degree to reach 83% when it reached The temperature to 80◦C. The occurrence of the results in this situation is due to the fact that the increase in temperature above the temperature of the cloud point serves to loosen the hydrogen bonds and increase the collection process Triton X-100 and Triton X-114 of the surface active substance micelles and spread in the aqueous solution. An optimal convergence of the micelles is the formation of the cloud point layer, which reduces the size of the rich phase of the surfactant to be smaller and higher in density. The higher the temperature over the cloud point temperature of the solution, the higher the removal efficiency until the optimum removal temperature is reached [28]. The optimum removal rate leads to increased proliferation of micelles and dispersion of the cloud point layer, thus reducing the removal rate [29]. While the experimental results showed that the effect of temperature on the percentage of adsorption of the dye with eggshells was 77% at a temperature of 25◦C and the percentage increased to 85% at a temperature of 40◦C, but when the temperature increased, the percentage decreased to 60% at a temperature of 50◦C, and the explanation for this is that the increase in The temperature enlarged the size of the pores and increased the rate of adsorption of the dye to increase the penetration of the dye into the eggshells, as the temperature range created new sites for adsorption to reach the maximum adsorption at a certain temperature [30]. As for the reason for the decrease in the percentage of adsorption when continuing to increase the temperature, this is due to the rapid spread of the adsorbent and adsorbent particles on the surface of the material, which leads to a decrease in the attraction and the separation of the bonds between the surface and the adsorbent molecule [31,32].As shown in Figure 4 below:

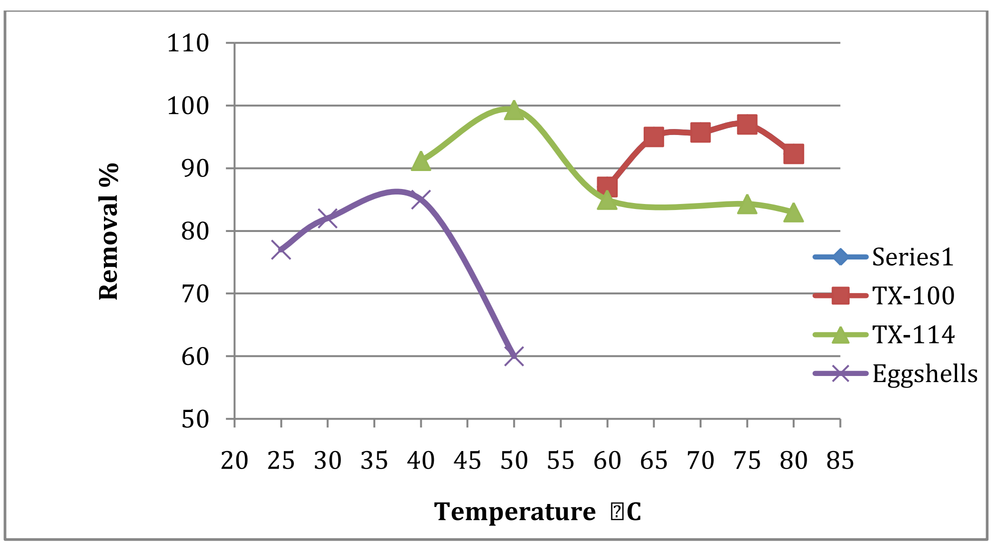

Figure 4: Effect change of the temperature

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3.5 Effect of electrolyte salt volume on the removal

Salt KCl at a concentration of (2 M) was used only with experiments in which surfactants were used for the depigmentation process, and it was not used with the adsorption of eggshells due to the difference in the dye removal mechanism from aqueous solution.The effects of the electrolyte using (potassium chloride) on the percentage of removal of dye from the solution can be summarized by the consistency of other factors (dye concentration, surfactant size, pH, temperature, removal time). It was noticed that the percentage of removal using Triton X-100 as a surfactant was 94% when using 8 ml of salt and increased to 97% with a volume of 10 ml salt and decreased to 94.6% at 14 ml. While when using Triton X-114 as a surfactant, the percentage of removal was 81.4% when the volume of salt was 8 ml and the percentage increased to 99.3% when the volume of 10 ml of salt was used, and when using more than the volume of salt, the percentage of removal decreased and became 80.7% at a volume of 14 ml. The explanation for this is that the increase in the volume of salt in the solution reduces the cloud point of the surfactant and promotes the drying of the ethoxy groups on the directed surface of the micelles as well as the concentration of micelles by the coacevate phase and the strengthening of the dissolved cells. Therefore, coacevate phase decreases with increasing salt concentration and more water to the dilution phase for a certain concentration. Increasing salt concentration does not affect removal, but works in the opposite way by decreasing removal efficiency [33]. As shown in Figure 5.

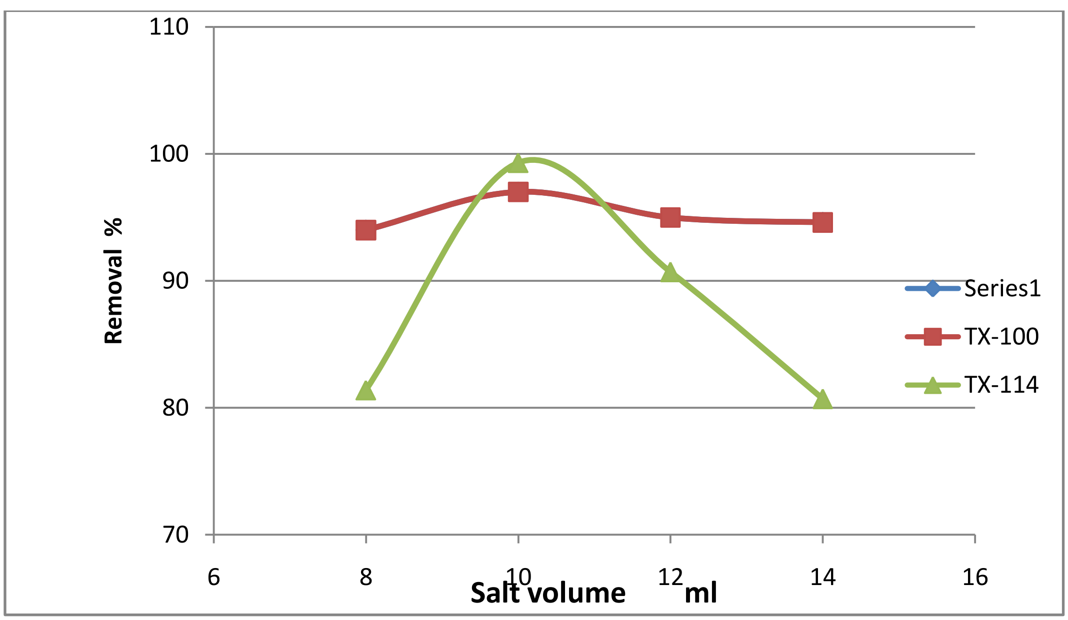

Figure 5: Effect of electrolyte salt volume on the removal

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3.6.Effect of pH

The study showed the effect of the acidic function on the percentage of removal of Bromo cresol green dye, 5 mL of solution Britton -Robinson with different pH ranges were added to the sample solution to maintain the desired pH (pH = 4, 7 , 10), where the results showed when using Triton X-100 as a surfactant that the percentage of removal was 97% when the medium of the solution was acidic (pH 4) and became 60% when it The medium of the solution was neutral (pH 7) and decreased further to become 49% when the medium of the solution was alkaline (pH 10). As for when using Triton X-114 as a surfactant, the results showed that the percentage is 99.3% when the medium is acidic (pH 4) and decreases to 50% when the medium is neutral (pH 7) and decreases further to reach 40% when the medium is basic (pH 10).The explanation for this is that the pH range affects CPE for all types of ionized substances that are performed CPE where each substance has an optimal pH range and the quantitative analytical extraction is on this basis by dissolving the uncharged form from the analyzes and incorporating it into the micelles [34].As for the effect of the acidic function on the adsorption of the dye at values of (PH=4 ,10), where the results showed that the percentage of adsorption at PH4 was 95% while the percentage was 65% at PH10. The explanation for this is that the increase in adsorption in the acidic medium is the tendency of the dye to bond with the surface of the peel Eggs have more than their tendency to bind with solvent particles. In the basic medium, we notice the disappearance of the negative charges of the dye ability to adsorb the dye ions is weak due to the increase in the repulsion force between the identical charges of the ions, that is, electrostatic repulsion of the dye with the surface [35]. As shown in Figure 6.

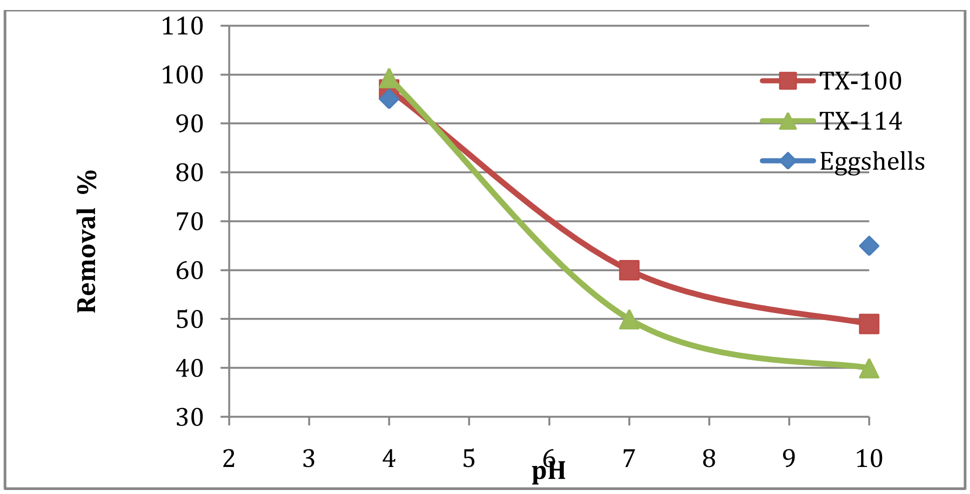

Figure 6: Effect of pH

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4. Conclusions

Surfactants are amphibious surfactants that help dissolve organic and inorganic compounds with organic solvents and water. The surfactants reduce the interfacial surface tension supra- CPE at the phase boundaries. Their role as an extractor and non-ionic coupling agent in extracting the liquid phase was the focus of this study. The study proved that the use of surfactant Triton X-100 and Triton X-114 was the most efficient, effective and evolutionary method of adsorption on eggshells to separate Pigment pollutants from aqueous solutions. Further research is necessary on surfactant-based removal methods to neutralize other concurrent conditions and materials that can be utilized in wastewater removal operations under a variety of experimental conditions.

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