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Optimization of extraction conditions for some phenolic pollutants

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Abstract

The aim of this study is to arrive at a reliable protocol for the extraction of phenolic compounds from industrial wastewater, and as a first step to achieve this, a water sample consisting of four phenolic compounds (phenol, Ortho-nitrophenol, 4,2-Dinitrophenol, paranitrophenol) was prepared at known concentrations, Thus, simulating industrial wastewater, The effect of a set of factors (type of solvent, volume of solvent, pH) on the yield of the process for extracting phenolic compounds from these waters has been studied and tested. We chose four solvents, namely petroleum ether, cyclohexane, chloroform and dichloromethane and tested three different volumes of the extraction solvent (6 ml, 15 ml, 30 mL); as for pH, we chose the values 2, 4, 7, 10. We calculated the phenolic index of the samples obtained by the method of colorimetric analysis (4-amino antiprin method) using an ultraviolet spectrophotometer. Through the yield values obtained, we concluded that the extraction yield increases with the increase in volume of the extraction solvent and the acidity of the media, however, dichloromethane had the best yield, reaching 96 % at pH=2.

Keywords: Liquid-liquid extraction, phenolic compounds, industrial waters, organic solvents, pH, colorimetric analysis, ultraviolet and visible spetrophotometer

1. Introduction

Various industrial activities consume huge amounts of water every day, which leads to an increase in industrial wastewater containing a range of pollutants and toxic substances (organic and inorganic compounds) that are discharged into channels mixed with urban and domestic wastewater. Organic pollutants are the most and the most dangerous. Some of its substances are carcinogenic or mutagenic, and some of the most widespread types are phenols, hydrocarbons, dyes, detergents and pesticides, and most of them come from effluents of the main industrial activities such as oil refining, coal mines, organic synthesis, pesticide manufacturing, textile industry and pulp industry. It is known that most industrial activities do not comply with industrial drainage controls, and water treatment plants for the most part use traditional methods of water purification, which do not eliminate industrial pollutants [Mesrouk, H and al,2012, Mesrouk, H and al,2014, Namane , A, and al, 2008, Bai, J and al ,2007]. Phenolic compounds are one of the residues of industrial activities, as a result of their use in the production of some substances such as medicines, dyes, polymer preservatives, antioxidants, dyes, pesticides, Petroleum, wood additives, chlorination plants and paper... etc. The presence of phenols in effluents, even in trace amounts, poses significant problems because these compounds, especially chloro-and nitrophenols, are toxic to living organisms including humans. Many of them are classified in the black list of substances hazardous to human health and living organisms prepared by the World Health Organization, which are found in industrial wastewater (according to previous studies in this field) in high concentrations, exceeding international standards. To find a solution to this environmental problem, our work will be limited to contributing to improving the conditions for extracting some of these phenolic pollutants from laboratory-prepared water that mimics industrial wastewater in terms of characteristics[Tziotzios, G,and al ,2007, Jean-Claude Boeglin, Contreras, E.M, and al 2008 ,Shourian, M and al,2009].

2. Material and methods

Preparation of contaminated (phenolic) water

Instead of using real wastewater taken from industrial wastewater estuaries, we used laboratory-prepared water with known ingredients and concentrations to facilitate the study and to avoid the presence of other substances that may give us false results. We mixed equal amounts of four compounds selected from among the phenolic compounds considered by the EPA and the European Union as priority pollutants in toxicity, namely: (phenol, Ortho-nitrophenol, 2,4-Dinitrophenol, paranitrophenol), To obtain phenolic water samples with a total concentration of 100 mg / l, this choice is based on the results obtained through previous work, which give us values for the concentration of phenolic compounds in industrial wastewater approximating this value for the selected concentration[Mesrouk, H and al,2012, Mesrouk, H and al,2014, Leybros, J ,1984, Outil, N ,2008, Touil, Y. *and al* 2021]. The table 1 shows the concentrations used:

Table 1. Concentrations of phenolic compounds used for the preparation of contaminated water.

Compound	Phenol	2,4-dinitrophenol	4-nitrophenol	2-nitrophenol
Concentration (mg/l)	25	25	25	25

3. Extraction

One of the important chemical processes for separating substances from each other is one of the most common methods of chemical separation processes, which is a simple method that extracts and separates a variety of organic molecules from aqueous solutions. In this work, we relied on liquid extraction, i.e. we used organic solvents to extract phenolic substances from an aqueous medium. among the most commonly used solvents for this purpose are ethyl acetate, diisopropyl ether, butyl acetate, diethyl ether, n-hexane, dichloromethane, trichloromethane..... [Elboughdiri, N and al,2009, Centre d'expertise en analyse environnementale du Québec,2009]

Selection of the studied parameters of the extraction process

There are many factors that affect the efficiency of the extraction process, and to obtain the best results from this process, we have chosen the most important of them and to study the impact of its change on the yield values in order to develop a specific and effective protocol to extract phenolic compounds from water, we can apply it on real samples of industrial wastewater, The table (2) summarizes all the factors studied:

Table 2. The studied factors influencing the liquid -liquid extraction process.

Solvent	Volume of solvent (ml)	pH
Chloroform	6/15/30	2/4/7/10
Dichloromethane	6/15/30	2/4/7/10
Petroleum Ether	6/15/30	2/4/7/10
Cyclohexane	6/15/30	2/4/7/10

4. Extraction protocol

We take a volume of 150 ml of the solution prepared at a concentration of 100 mg / l, pour it into the decanting ampoule and add to it the desired volume of solvent for each experiment (6, 15, 30 ml), We re-extract twice in each experiment with the same volume of solvent, we separate the organic phase from the aqueous phase, we repeat the experiment three times. In the same way and with the same volume, we re-extract, changing each time the pH of the phenolic water (2, 4, 7, 10) by adding drops of sulfuric acid solution (9 N) or soda (10 N) depending on the case. We follow the same steps with a change of solvent each time.

5. Analysis

To study the effect of changing the values of factors related to the extraction process on the yield. We calculate the extraction yield for each experiment by measuring the phenolic index of water phases.

Colorimetric analysis by the 4-amino antipyrine method:

Phenols with amino-4-antipyrin in an alkaline medium and in the presence of potassium ferricyanide give a color measured by an ultraviolet and visible spectroscopy device (of brand UNICAM). In the first step, the sample is distilled (if the sample is turbid and contains other substances). In the second step, the sample is mixed with an alkaline solution (pH near 10), potassium ferricyanide and with an 4-aminoantipyrine solution to form a colored compound. The absorbance is measured at 505 nm and compared with a calibration curve, obtained using phenol (C_6H_5OH)[Mesrouk, H and al,2012, Centre d’expertise en analyse environnementale du Québec,2009].

6. Calibration curve

After having prepared the mother solution of phenol at a concentration of 1 g / L, we carried out a sequential extension to obtain the solution at a concentration of 10 mg / L, where we prepared the solutions at the desired concentrations (1-10 mg/ L) to plot the calibration curve, following the steps indicated in the table (3)

Table 3. The method of preparing the solutions used to draw a calibration curve.

Becher number	T	1	2	3	4	5	6	7	8	9	10	11
Phenol solution 10(mg/l)(ml)	0	0.25	5	10	15	20	25	30	35	40	45	50
Distilled water (ml)	50	47.5	45	40	35	30	25	20	15	10	5	0
Tampon solution pH=9.5 (ml)	2	2	2	2	2	2	2	2	2	2	2	2
4-amino-antipyrine solution (mL)	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Potassium ferecyanide solution (ml)	1	1	1	1	1	1	1	1	1	1	1	1
Phenol concentration (mg/l)	0	0.5	1	2	3	4	5	6	7	8	9	10

The solutions are left for five minutes until the color is formed, then a sufficient amount is placed in the bottle intended for reading by the ultraviolet spectrophotometer. And this is after setting the wavelength to 505 nm. We record the absorbance values of all the solutions to draw a calibration curve. We follow the same steps to assay the aqueous phases of the samples in order to obtain the phenolic index.

7. Calculation of the extraction yield

After drawing the calibration curve, we extract the various coefficients of the obtained linear curve (slope, correction coefficient, linear equation), and use them to calculate the values of the phenolic index of the water phases of the studied samples. Using the absorptivity values obtained by the same steps mentioned earlier. We calculate the extraction yield using the following relation:

$$y = \frac{norganic}{ntotal} \times 100$$

y: Extraction yield.

$n_{organic}$: amount of moles of phenolic compounds in the organic phase.

n_{total}: total amount of moles of phenolic compounds.

8. Results and discussion

Changes in the yield values of the extraction of phenolic compounds from water by changing the process conditions, represented by the solvent (methane dichloride, cyclohexane, petroleum ether, chloroform), solvent Volume (6, 15, 30 ml), pH (2, 4, 7, 10) are shown in the figures (1-8)

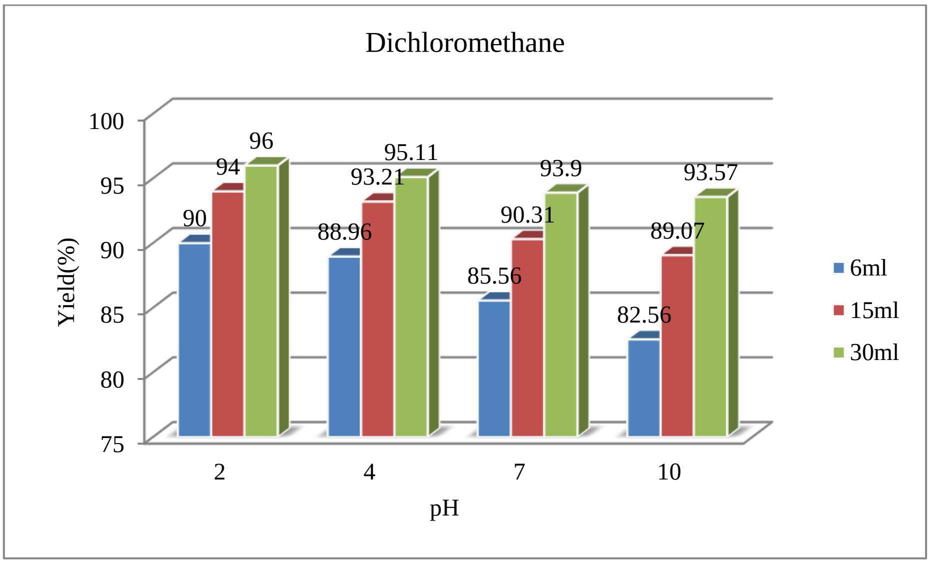


Fig.1. changes in the yield of extraction of phenolic compounds from water by changing the conditions of the experiment using the methane dichloride solvent.

Starting from the results illustrated in (Figure 1), which we obtained using methane dichloride as a solvent to extract the phenolic compounds from the prepared water, we observed the following observations:

- The extraction yield is high, ranging from 82.2 to 96%. The highest recorded value was 96% for water samples with a pH of 2 and extracted with a volume of solvent of 30 ml.

-The extraction yield increases with the increase in volume of extraction solvent used.

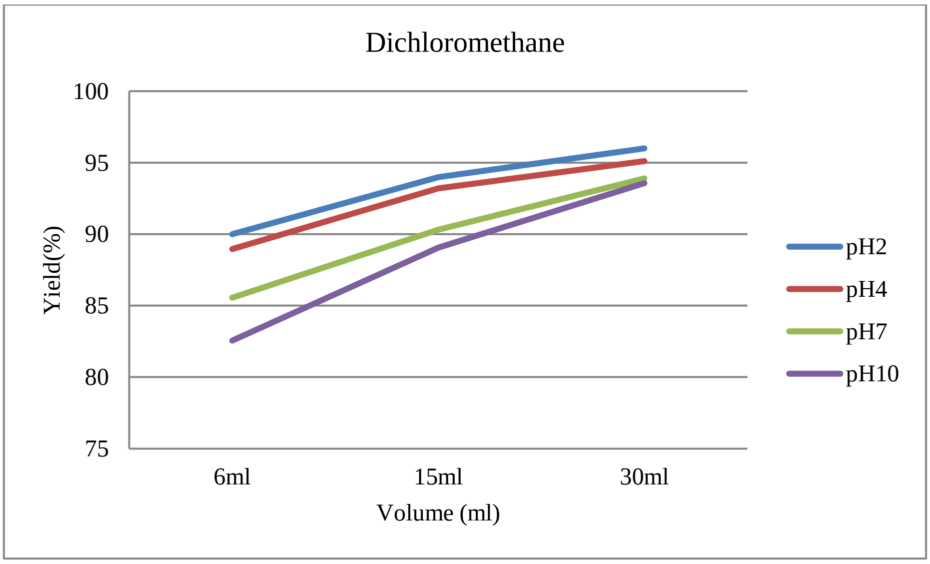


Fig. 2. The extraction yield changed with a change in the volume of the solvent (methane dichloride).

- We observed a decrease in the value of the extraction yield with an increase in the pH value of the medium and vice versa using the same volume of solvent (Fig 2)

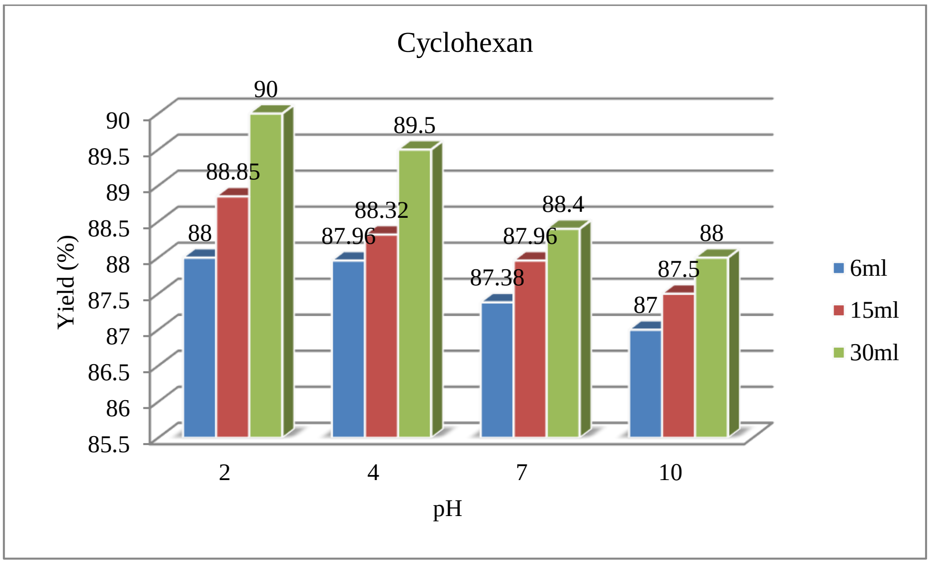


Fig. 3. Changes in the yield of extraction of phenolic compounds from water by changing the conditions of the experiment using the cyclohexane solvent.

From the results shown in (Fig. 3) obtained by using cyclohexane as a solvent to extract phenolic compounds from the prepared water, we observed the following:

- The extraction yield is high, ranging from 87 to 90 %. The highest value recorded was for samples with a pH of 2 and extracted with a solvent volume of 30 ml. It is noted that all the yield values were close and there are only minor changes from one experiment to another.

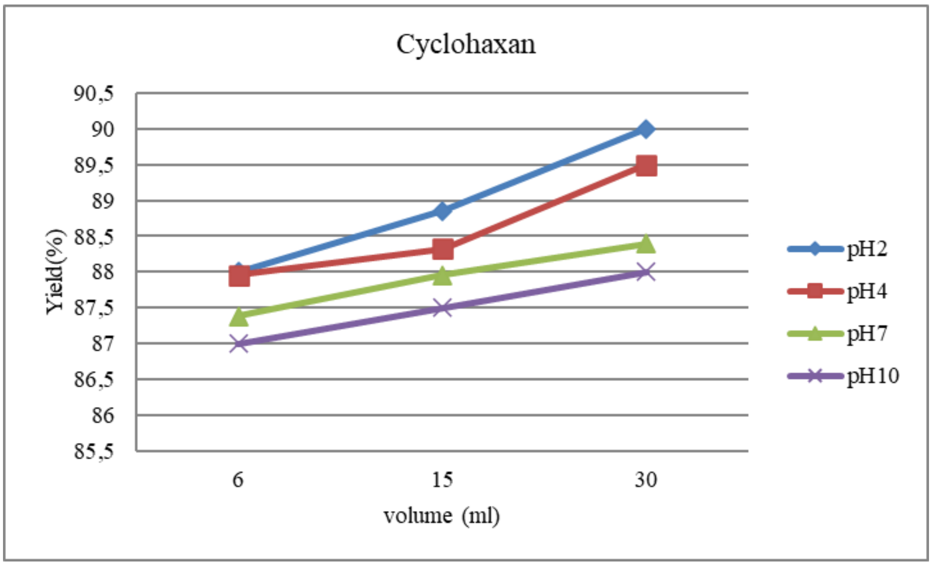


Fig. 4. The extraction yield changed with the volume change of the solvent (cyclohexane).

- The greater the volume of cyclohexane used in the extraction process, the greater the value of the yield obtained, and we have observed this for all pH values in (Fig. 4).

- We observed a decrease in the value of the extraction yield with an increase in the pH value of the medium and vice versa using the same volume of solvent and the same quality of Water (fig. 4).

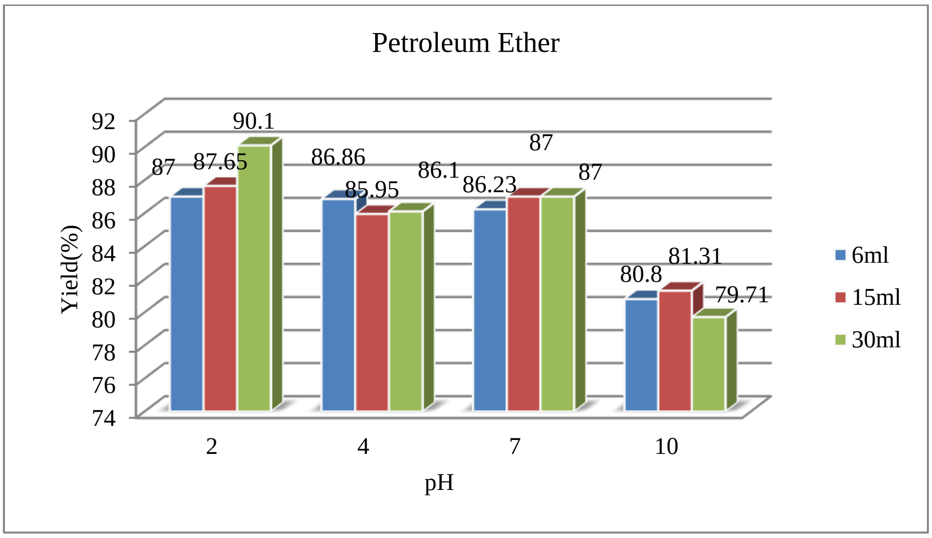


Fig. 5. Changes in the yield of extraction of phenolic compounds from water by changing the conditions of the experiment using the solvent petroleum ether.

From the results shown in (Fig. 5) obtained by using petroleum ether as a solvent to extract phenolic compounds from the prepared water, we observed the following:

- The extraction yield is high, ranging from 79.71 to 90.1 %. The highest value recorded was for samples with a pH of 2 and extracted with a solvent volume of 30 ml. It is noticeable that all the yield values were close and there are only minor changes from one experiment to another.

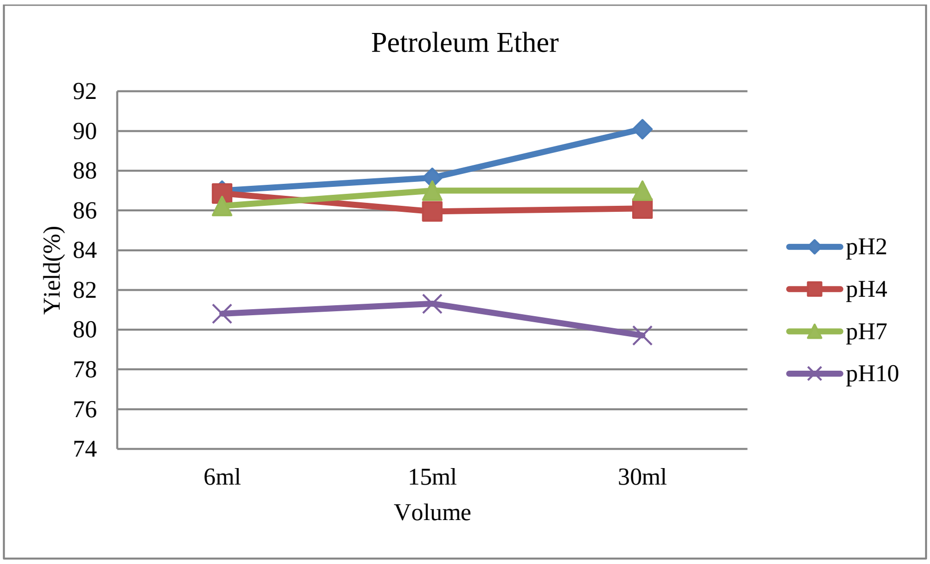


Fig. 6. The change in the extraction yield with a change in the volume of the solvent (petroleum ether).

- The effect of volume change was not clear for this solvent, as the yield values were close, and we observed this for all pH values in (Fig. 6).

- We observed a decrease in the value of the extraction yield with an increase in the pH value of the medium and vice versa using the same volume of solvent.

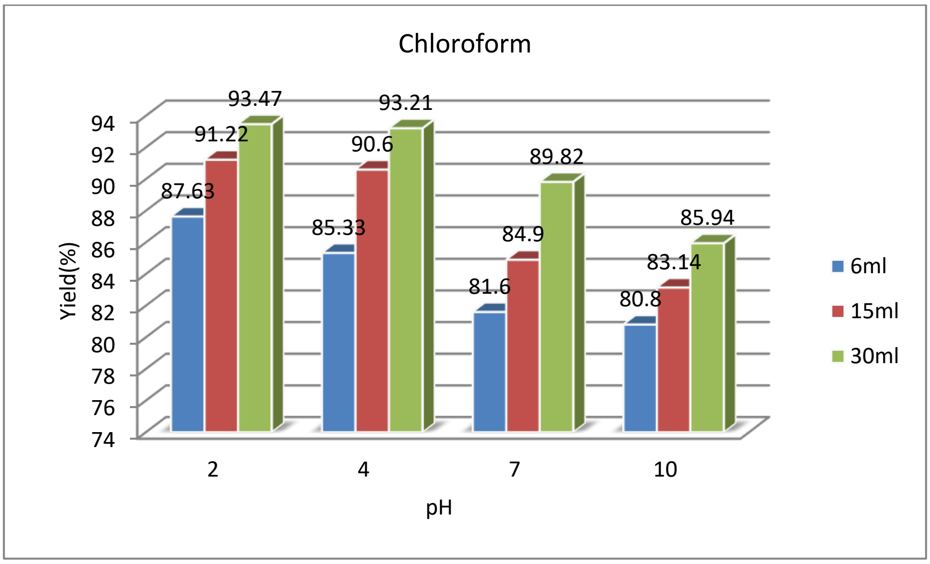


Fig.7. Changes in the yield of extraction of phenolic compounds from water by changing the conditions of the experiment using the solvent chloroform.

From the results shown in (Fig7) obtained by using chloroform as a solvent to extract phenolic compounds from the prepared water, we observed the following:

- The extraction yield is high ranging from 80.8 to 93.47 %. The highest value recorded was for samples with a pH of 2 and extracted with a solvent volume of 30 ml.

- The greater the volume of chloroform used in the extraction process, the higher the value of the yield obtained, and we have observed this for all pH values in (Fig 7).

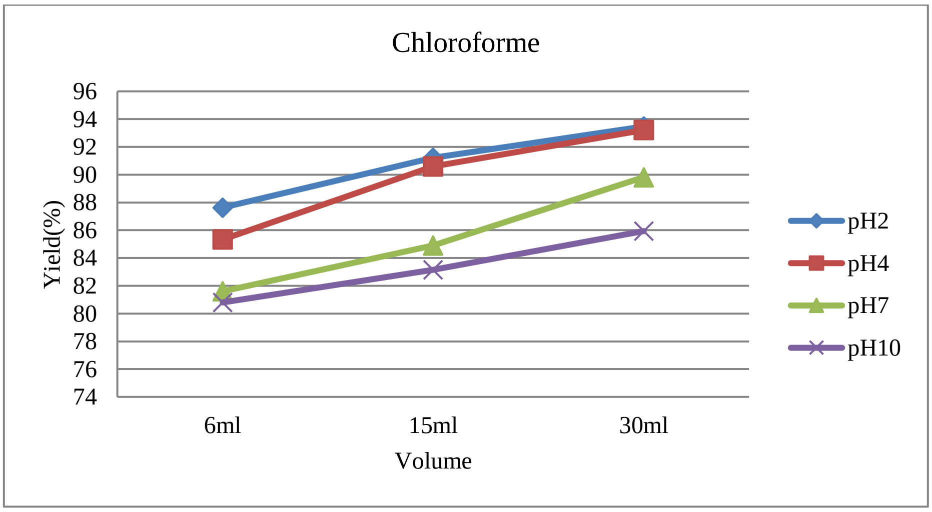


Fig. 8. The extraction yield changed with a change in the volume of the solvent (chloroform).

- We observed a decrease in the value of the extraction yield with an increase in the pH value of the medium and vice versa using the same volume of solvent, for PH 2 and 4 we noticed a significant convergence of the yield values for each volume of solvent used. (Fig.8)

9. Discussion

We can summarize all the results obtained as follows:

- The best yield of 96% was recorded for pH 2 of the sample extracted with 30 ml of methane dichloride.

- We recorded the highest extraction yield values for pH 2 (this is the smallest value used), and for a volume of 30 ml.

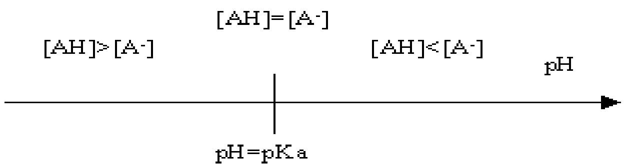
- Classification of solvents by extraction yield values:

$$Y_{DCM} > Y_{TCM} > Y_{cyclohexane} > Y_{\text{Ether Petroleum}}$$

It is clear, this arrangement has a relationship with the polarity, that is to say the extraction yield increases with the increase of solvent polarity, this is due to the fact that phenolic compounds are rather polar compounds and this causes them to dissolve more and more in polar solvents, which increases the extraction yield.

- The results of changing the solvent volume clearly showed that the extraction yield increases with increasing solvent volume and reached its peak at 30 ml. This makes us expect that perhaps if we take a larger volume, we will get higher yield values, which may reach 100% for some solvents. With the exception of the petroleum ether solvent, the effect of changing the volume has not been clearly shown to us, we explain that this yield may be the maximum that we can get even with a change and increase in volume.

1. - The results of the pH change carried out at the base medium (pH=10), moderate (pH=7), acidic medium (pH=4) and highly acidic (2=pH) showed a clear effect, as the yield was decreasing with increasing pH values, and the best yield values were obtained for pH values 2 (where the value was the lowest used for the same experiment). We explain this with the following diagram, which shows how the molecule in the medium founded by hydrogen is less than the pH constant, its molecular form is predominant over its ionic form, and therefore it is easy to extract it with an organic solvent, and vice versa in the case of a pH greater than its pH, where its predominant form is the ionic form, knowing that the pKa of the extracted phenolic compounds phenol, 4,2-Dinitrophenol, paranitrophenol, orthonitrophenol respectively are 9.95, 4.09, 7.08, 7.22[Zafra, A and al ,2005, Lahbabi, N, and al,2009, Debellefontaine, H, and al ,1992, Kamenev, R and al, 2003, Lin, K, and al,2009].



10. Conclusions

One of the environmental problems currently posed is water pollution with various chemicals as a result of increased industrial activity with disrespect and adherence to the controls of this type of activity from not throwing waste directly into sewage channels without treatment, with many areas containing only ordinary filtering stations that cannot cope with this type of material. As a contribution from us, in this work we managed to obtain an approximate and non-final, reliable protocol on the process of extracting phenolic compounds from industrial water.

The study was conducted on a laboratory-prepared water sample, which is a mixture of four phenolic compounds (phenol, Ortho-nitrophenol, 2,4-Dinitrophenol, paranitrophenol), and testing a set of factors affecting the extraction process (solvent, solvent volume, pH); we obtained the best yield equal to 96% for a water sample at pH=2 using the extraction solvent dichloromethane. The study and testing of the best conditions of the previously mentioned factors for the process of extracting liquid gave the following results:

- The best solvent for extracting phenolic compounds from water is dichloromethane, which gave us the best yield values.
- Extraction yield values increase with increasing extraction volume.
- Therefore, The yield values increase with increasing acidity of the medium, towards pH values lower than the values of the ionization constant.
- According to the results obtained, we can take dichloromethane as the best solvent and use it in the application to the real sample (industrial water sample).
- We expect that any increase in the volume of the solvent and a decrease in the pH, i.e. a more acidic medium, will give us better yield results, which we expect to reach a peak of 100% for the extraction of phenol from industrial water.

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