Characterization of P(Hema-Gma)-Ida Membrane to Adsorbing Leather Dye

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***Abstract*—Different chemical substances and too much water are used during leather production. Therefore, the waste water load of the leather industry is harmful to the environment. One of the pollution source is the production of leather coloring process is a further need to focus on the removal of dye waste waters subject. These water-soluble dyes have a small organic molecular size. Besides the environmental hazards that these dyes cannot be underestimated, they also have harmful effects on human health.**

In this study, poly (hydroxyethyl methacrylate-glycidyl methacrylate) p (HEMA-GMA) hydrogel membranes were synthesized by UV polymerization method. The hydrogel synthesized is modified with imino diacetic acid (IDA) and then chelated with trivalent chromium ions. The chelating capacity of the membranes were determined according to the time, pH and concentration parameters. Dynamic swelling test, elemental analysis, ninhydrin analysis and adsorption, desorption and reusability performances of membranes were also determined. As a result of the analyzes, it was understood that the hydrogel membrane had high adsorption capacity. The adsorption capacity of the p (HEMA-GMA) -IDA-Cr (III) hydrogel membrane did not decrease even after 5 desorption. At the end of the fifth cycle, the membrane was found to have a dye-binding capacity of about 92%. According to these results, the reusable property of the membrane also makes it cost effective as well as effective adsorption.

***Keywords*—Adsorption, desorption, dye, leather, p(HEMA-GMA)-IDA**

I. INTRODUCTION

Nowadays dyeing process which is one step of the leather manufacturing plant of leather is a process which increases the waste water pollution. Discharged dyestuffs break both the aesthetic image in the water and cause aberrations in the aquatic life. Dyes prevent the passage of sunlight, making it difficult for photosynthetic creatures in the water. Thus, the ecological balance in the water is damaged [1, 2].

Adsorption, an important purification method, especially for the removal of dyestuffs and heavy metal ions from aqueous media [3]. In this method, the contaminated water can be passed slowly through the adsorbent materials such as the strainer or can be activated for a while to remove the pollution of the water. [4, 5].

In this study, poly(hydroxyethyl methacrylate-glycidyl methacrylate) p(HEMA-GMA) hydrogel membranes were synthesized by UV polymerization method. The synthesized hydrogel membranes were modified with imino diacetic acid (IDA) for Cr (III) ion chelation. It was aimed to increase the adsorption of Acid Black 210 dyes with Cr (III) ions. After the characterization of the hydrogel membrane, the optimization of the Acid Black 210 dyes was carried out under different ambient conditions. Furthermore, desorption conditions and membrane reusability of the dye adsorbed by the synthesized membrane have been determined. In order to see the applicability of the work, the Acid Black 210 dyes were adsorbed and desorbed

II. MATERIALS AND METHODS

Acid black 210 was purchased from Coriacido Black T (Stahl holdings b.v.) HEMA, GMA, monomers, IDA and other chemical substances obtained from Sigma Aldrich and Merck.

Synthesis and modification of hydrogels were carried out according to Aslan *et al*. study. [6].

The dynamic swelling test of dried p (HEMA), p(HEMA-GMA)-IDA and p(HEMA-GMA)-IDA-Cr(III) hydrogel membranes was calculated using the following equation 1.

$$\% S=[(Mwet-Mdry)/Mdry]x100 \quad (1)$$

The equilibrium percent is the swelling value,% S is the experimental value, and the swelling capacity is calculated according to the following equation. The S (%) is the swelling ratio, Mwet is the wet weight of the membrane, and Mdry is the weight prior to the swelling analysis of the membrane.

After chelating the p(HEMA-GMA)-IDA hydrogel membrane with Cr (III), the amount of Cr (III) in the membrane was determined by elemental analysis. Elemental analyzes of p (HEMA-GMA)-IDA and p(HEMA-GMA)-IDA-Cr(III) hydrogel membranes were performed with a Philips XL 30S FEG brand scanning electron microscope EDX detector (EDAX).

1 ml ninhydrin solution (solution prepared with 0.35 g ninhydrin added 100 ml of ethanol) was added to 5 ml of sample. The mixture in the tube was boiled for 4 minutes with gentle stirring, before cooled to room temperature. The amount of IDA bound to the membrane was determined at 570 nm at the end of the process

Acid Black 210 dye adsorption conditions were determined by comparing non-derivatized p(HEMA) membranes and derivatized p(HEMA-GMA)-IDA-Cr(III) membrane systems. The adsorption capacity of the membranes for Acid Black 210

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dyes was determined by measuring at 435 nm in a UV-visible spectrophotometer.

An ethanol water mixture (1:3 v/v) was used as a chaotropic agent (desorption agent) for acid dye desorption from Acid Black 210-bound p(HEMA-GMA)-IDA-Cr(III) membrane system. In the desorption step, Acid Black 210 adsorbed p(HEMA-GMA)-IDA-Cr (III) membranes were stirred at 200 rpm for 2 hours at 25 °C in desorption medium. The amount of desorbed dye in desorption was determined in UV-visible spectrophotometer at 435 nm. In addition, in order to determine whether any Cr (III) ion in the membrane is desorbed, additional measurements were made at 601 nm where the chromium ions peaked in the desorption medium. After the desorption cycle has been repeated at least 5 times in optimizing conditions, the amount of adsorbed dye was determined in mg/g and the post-cycling performance losses were investigated. The desorption amount is calculated by the following equation 2.

Desorption (%)=[Desorbed dye (mg)/Adsorbed dye (mg)]x100 (2)

III. RESULTS AND DISCUSSIONS

Dynamic swelling test results of % hydrogels of p(HEMA), p(HEMA-GMA), p(HEMA-GMA)-IDA and p(HEMA-GMA)-IDA-Cr(III) membranes are given in Table 1. When the results are analyzed, p(HEMA) has a high dynamic swelling rate due to the -OH groups in the hydrogel membrane structure. However, after the addition of groups to the structure of the p (HEMA) hydrogel membrane, water uptake and adsorption decreased considerably.

Table I: Dynamic Swelling Test Results

Hydrogel Membrane	**S(%)**
p(HEMA-GMA)-IDA-Cr(III)	51.9
p(HEMA-GMA)-IDA	55
p(HEMA-GMA)	50
p(HEMA)	245.5

The results of elemental analysis measurements between p(HEMA-GMA)-IDA membrane and p(HEMA-GMA)-IDA-Cr(III) membrane are shown in Table 2. According to the results of elemental analysis, the p(HEMA-GMA)-IDA membrane consists of 66.02% C and 33.98% O elements, whereas the N atom in the structure of iminodiacetic acid (IDA) was not found.

Table II: Elemental Analysis Results

Element	**p(HEMA-GMA) -IDA**		**p(HEMA-GMA) -IDA-Cr(III)**	
	Wt %	**Atomic %**	**Wt %**	**Atomic %**
C	59.33	66.02	57.45	64.39
N	0.00	0.00	0.00	0.00
O	40.67	33.98	42.22	35.52
Cr	-	-	0.33	0.09
Total	100.00	100.00	100.00	100.00

As a result of the ninhydrin assay, p (HEMA-GMA) -IDA hydrogel membrane was detected 1125.7 mg/g (8.46 mmole/g) IDA at 570 nm with UV-Visible Spectrofotometer. According to these results, it was understood that p(HEMA-GMA)-IDA hydrogel membrane could chelate Cr(III) ion with 2 carboxyl groups (COOH) of IDA molecule.

p(HEMA-GMA) hydrogel membrane with Cr(III) ion chelating made in different conditions optimization studies were performed. As a result, a maximum of 30 000 ppm $Cr_2(SO_4)$ was bound to the membrane at pH 4 and 25 °C for 120 minutes. The Acid Black 210 dye adsorption studies of p(HEMA-GMA)-IDA-Cr(III) hydrogel membranes prepared under these conditions were compared with the unmodified p(HEMA) hydrogel membranes (Table 3).

Table III: Acid Black 210 Adsorption Values

$Cr_2(SO_4)$ (ppm)	**p(HEMA-GMA) -IDA-Cr(III) Q(mg/g)**	**p(HEMA) Q(mg/g)**
500	8.73	-
1000	70.52	3.38
2000	249.46	-
3000	313.35	43.035
4000	394.45	-
5000	675.47	59.20
7500	885.14	155.987
10000	885.0	151.003

Table 4 shows the desorption cycles of the p(HEMA-GMA)-IDA-Cr(III) hydrogel membrane. Approximately 90% of Acid Black 210 dyes were desorbed from the p(HEMA-GMA)-IDA-Cr(III) hydrogel membrane system.

Table IV: Desorption Cycles Of Membrane

Cycle	**Desorption Q(mg/g)**	**Desorption Q(%)**
1	385.27	97.91
2	385.93	97.83
3	388.19	100.04
4	380.82	91.10
5	388.24	100.25

IV. CONCLUSION

As a result, the p(HEMA-GMA)-IDA hydrogel membrane system can be used as an effective adsorption method. The advantage of this membrane system is that the production process is cheap, easy, large surface area, high adsorption capacity and repeatability. It has therefore been demonstrated in the future that hydrogel membrane systems can be incorporated into dyeing wastewater treatment systems.

In the future, the adsorption and desorption capacities of different heavy metals and different dyes can be investigated.

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The adsorption capacity and properties of hydrogel membrane systems can be studied comparatively in single ion and competitive wastewater environments. In addition, if financial support can be provided; suitable membrane synthesis environments can be provided by switching from small systems to large purification systems.

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