INVESTIGATION OF THE USE OF ADSORPTION, CERAMIC MEMBRANE, HYBRID SYSTEMS IN Cr(VI) REMOVAL

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Abstract: In this study, Cr(VI) removal from aqueous solutions by adsorption-ceramic membrane hybrid system was investigated. For this aim batch adsorption, batch ceramic membrane and adsorption-ceramic membrane hybrid systems experiments were conducted. *Platanus orientalis* (sycamore fruit) treated with 1 M H_2SO_4 was used as adsorbent in adsorption experiments. Ceramic membranes produced by İLKSEM Engineering Incorporated Company were used in the experiments. Membranes produced from different materials have different pore sizes. Cr(VI) removal yield was obtained as 90.1% by adsorption (contact time 3 hours)- ceramic membrane hybrid system.

INTRODUCTION

Chromium is at the top of the list of toxic pollutants in the wastewater commonly generated in the industry. The chromium is most commonly seen in chromium(VI) or chromium(III) in aqueous solutions. Chromium(VI) compounds are considered to be 100-1000 times more toxic than chromium(III) compounds (1).

The main methods used to remove chromium(VI) from waters and wastewater; chemical precipitation, ion exchange and adsorption processes. Ceramic membranes are used to remove suspended solids, microorganisms, heavy metals, radioactive materials, pesticides, and pre-treatment water and wastewater treatment prior to reverse osmosis. Ceramic membranes are also preferred in the treatment of wastewater treatment plant drainage water. The term hybrid membrane processes can be explained as applying one or more membrane processes together with conventional treatment systems to improve feed and product quality (2, 3). The main purpose of these systems is to increase the purification as much as possible.

Cr(VI) removal by adsorption was investigated onto different material such as *Ocimum americanum* L. seed pods, biomass of microalgae *Scenedesmus* sp., chestnut shells by different investigators (1, 4-6).

Ceramic membrane preparation, characterization and performance evaluation studies were conducted at different studies (7-11).

In this study, Cr(VI) removal from aqueous solution by adsorption on to *Platanus orientalis* treated with 1M H_2SO_4, ceramic membrane filtration and adsorption – ceramic membrane

filtration hybrid systems were investigated. *Platanus orientalis* was used as adsorbent in the study for the first time. Ceramic membranes produced by İLKSEM Engineering Incorporated Company were used in experiments. The results are presented and discussed.

EXPERIMENTAL

Cr(VI) solutions were prepared from 1000 mg/L $K_2Cr_2O_7$ stock solution. Cr(VI) concentrations were determined by diphenyl carbazide method using standard methods with a UV/Vis spectrophotometer (Shimadzu UV-120-01) (12).

Adsorption experiments
Platanus orientalis was used as the adsorbent. It was broken (all of the part was used) and dried at 100 °C for 24 hours and treated by 1M H_2SO_4. For this aim, 3 g of the adsorbent was mixed with 50 mL of the acid solution at about 80–90 °C for 2 hours on a hotplate/magnetic stirrer and then filtered from filter paper. Adsorbent particles on filter paper were washed with 50 mL of distilled water and then dried at 105 °C in an oven.

In the study, batch adsorption experiments were conducted. Shaker water bath (Memmert) was used for constant temperature for batch adsorption experiments. After adsorption mixture was filtered and Cr(VI) concentration was analyzed in the filtrate, equilibrium concentrations were determined.

To determine the effect of initial concentration, 50 mL solutions at the initial concentrations of 75, 100, 150, 200, 250, and 300 mg/L, were prepared using 1000 mg/L stock $K_2Cr_2O_7$ solution. For each initial concentration, 25 mL of solution was placed on 0.5 g of *Platanus orientalis*. The mixture was shaken for 24 hours at 25 °C and 140 rpm in a shaker water bath and filtered through filter paper. Cr(VI) was analyzed in filtrates by a UV/Vis spectrophotometer.

In order to determine the effect of contact time on Cr(VI) adsorption, 10 g of acid-treated *Platanus orientalis* was weighed into the beaker and placed into a 500 mL of a 100 mg Cr(VI) / L solution. It was kept on the magnetic stirrer for 24 hours at a stirring rate of 700 rpm. Samples (5 mL) were taken at certain time intervals and Cr(VI) concentrations were analyzed.

Ceramic Membrane Experiments
Different ceramic membranes coded as K1, K4, and K7, produced by İLKSEM Engineering Incorporated Company, were used in ceramic membrane filtration experiments. Properties of ceramic membranes which effect on chromium(VI) were determined. Strength was tested Gabriella CRS1650, density, water absorption percent were tested by Archimedes scales. Porosity was determined Quantochrome Nova Win 2 BET equipment. According to the membrane codes properties of ceramic membranes were given in Table 1.

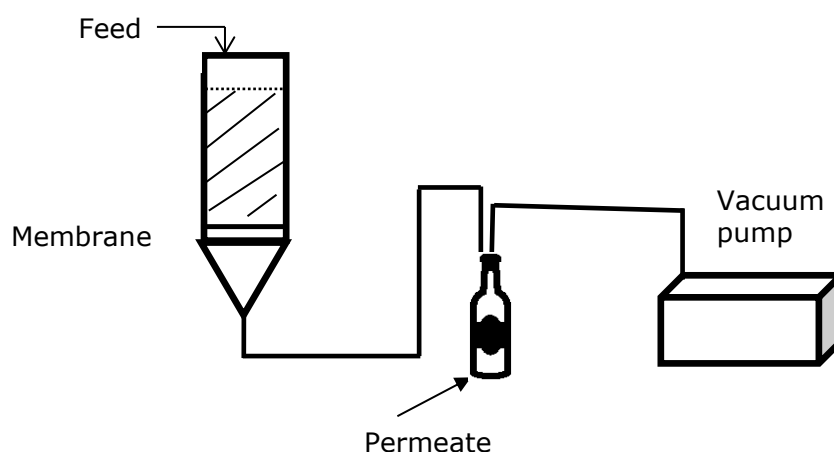Ceramic membrane filtration experimental set up was given in Figure 1.

Figure 1. Ceramic membrane filtration experimental set-up.

The filtration times for 100 mL solution (100 mg / L Cr(VI)) were determined to calculate permeate fluxes.

Table 1. Properties of the ceramic membranes used in experiments (Vacuum pressure: 0.06 MPa, Membrane diameter 5.2 cm, Membrane Thickness: 0.3).

Membrane	Sintering Temperature (ºC)	Strength (MPa)	Water absorption (%)	Porosity (%)	Density (g/cm³)
K1	1200	6.3	28	44	1.58
K4	1250	3,3	24	40	1.64
K7	1100	7.7	37	46	1.26

Adsorption – Ceramic Membrane Hybrid System Experiments

In hybrid system experiments, firstly, batch adsorption experiments were carried out at 25 ºC using 0.5 g of the adsorbent and 100 mg/L initial concentration of Cr(VI) solution. Adsorption was terminated at the end of the contact time for 3 hours, and then the filtrate was passed through the ceramic membrane.

RESULTS AND DISCUSSIONS

Adsorption continuing until equilibrium is formed between the amount of adsorbed matter (mg / g) and the concentration of the substance remaining in the solution. This equilibrium can be mathematically explained by the adsorption isotherms. The adsorption isotherms define the relationship between solute concentration at the constant temperature and the amount adsorbed by the adsorbent. These values are the values at equilibrium. The equilibrium adsorption isotherm is of fundamental importance in the design of adsorption system. In order to determine adsorption isotherm for Cr(VI) adsorption onto *Platanus orientalis* treated with acid, 25 mL solution at the initial concentrations of 75, 100, 150, 200, 250, 300 mg/L $K_2Cr_2O_7$ solution and 0.5 g of the adsorbent were used in batch adsorption experiment. Cr(VI) removals (%) were calculated from the equation below.

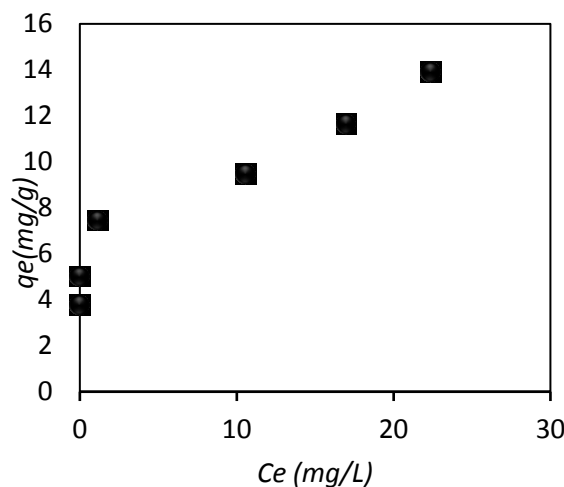$$Cr(VI) \ Removal \ (\%) = \frac{C_o - C_e}{C_o} . 100 \qquad (Eq. \ 1)$$

C_e = Equilibrium Cr(VI) concentration in solution (mg/L)
C_o = Initial Cr(VI) concentration in solution (mg/L)

Adsorption isotherm is given in Figure 2.

According to the Figure 2 Langmuir and Freundlich isotherms may be applicable to the adsorption data. So in this study, the suitability of the data to Langmuir and Freundlich isotherms was investigated. Linearized form of the the Langmuir isotherm can be expressed as given equation (1).

$$\frac{C_e}{q_e} = \frac{1}{bq_{max}} + \frac{C_e}{q_{max}} \qquad (Eq. \ 2)$$

Where q_{max} (mg/g) and b (L/mg) are the Langmuir constants related to the adsorption capacity and energy of adsorption, respectively. The amount of Cr(VI) adsorbed by the *Platanus orientalis*, q_e(mg/g), calculated given below equation:

$$q_e = (C_o - C_e)V/w \qquad (Eq. \ 3)$$

Where V : initial volume of Cr(VI) solution (L) w: weight of the adsorbent (g). In order to find Langmuir isotherm constants C_e/q_e vs C_e is plotted. Values of q_{max} and b were calculated from the slope and intercept of the linear plots. Calculated isotherm constants were given in Table 2.

Figure 2. Adsorption isotherm for Cr(VI) removal from aqueous solutions onto *Platanus orientalis* treated with 1 M H_2SO_4.

Freundlich isotherm is appropriate for the adsorption on to heterogeneous surfaces. This isotherm defines the surface heterogeneity. Freundlich isotherm given in the equation below is based on the assumption that the concentration of adsorbed on the adsorbent surface increases with the increase in the adsorbed concentration (1). According to the Figure 2 it can be said that this assumption is valid.

$$q_e = K_f . C_e^{\frac{1}{n}} \qquad \text{(Eq. 4)}$$

where K_f and n are Freundlich adsorption isotherm constants, affecting the adsorption capacity and intensity of adsorption. Linearized form of Freundlich isotherm is given below:

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \qquad \text{(Eq. 5)}$$

Values of n and K_f were calculated from the slope and intercept of the plots of log q_e versus log C_e. The calculated isotherm constants are given in Table 2.

Table 2. Langmuir and Freundlich models isotherm constants for Cr(VI) adsorption onto *Platanus orientalis* treated with 1 M H_2SO_4.

Langmuir Isotherm			Freundlich Isotherm		
b(L/mg)	q_{max}(mg/g)	R^2	n	k_f(L/g)	R^2
1.09	13.04	0.965	3.32	5.068	0.822

When the regression coefficients (R^2) obtained for the isotherms were taken into consideration, Langmuir isotherm was found to be more suitable and the capacity of the adsorbent was determined as 13.04 mg/g. If Freundlich constant *n* is greater than unity, this indicates a desired adsorption. Langmuir constant q_{max}, the adsorption capacity, is maximum amount of Cr(VI) adsorption with complete monolayer coverage on the adsorbent surface. Langmuir constant *b* indicates the strength of the link between Cr(VI) ions and the adsorbent.

It was observed that these concentrations were fixed after a certain period of time. This period was determined as the equilibrium time (18 hours) for the used adsorbent. At the beginning, it was seen that removal percent increased rapidly. This situation can be explained by the saturation of the active regions after the equilibrium is reached.

100% removal was obtained for 24 hours contact time, by adsorption at the concentration of 100 mg/L Cr(VI).

BET and SEM analysis were performed for raw and treated *Platanus orientalis*. BET surface areas, pore volumes and pore size distribution were determined by using Quantachrome, Autosorb 1C an automatic adsorption instrument at 77 K. The adsorbate was N_2. Prior to gas adsorption measurement, the carbon was degassed at 300 °C in the vacuum for 3 h. BET method was applied to calculate the pore volume and surface area. Results for BET analysis were given in Table 3. Surface morphology was investigated by (SEM) (JEOL JSM-5600LV Scanning Electron microscopy). Samples were taken different part of adsorbent and coated Au/Pd. SEM images of *Platanus orientalis* were given in Figure 3.

Table 3. BET analysis results

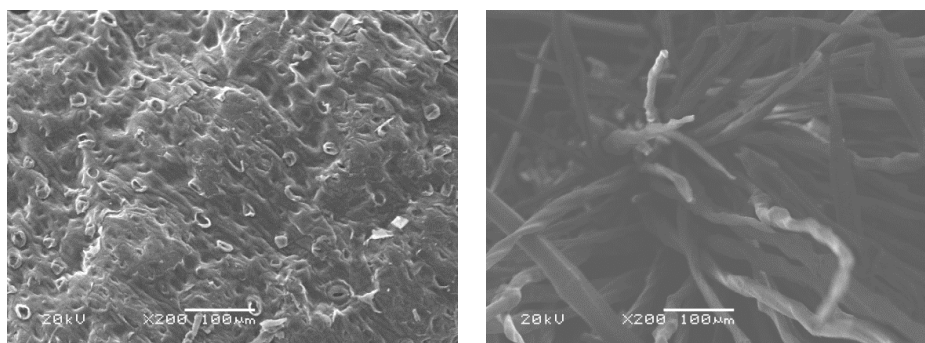| Property	Raw *Platanus orientalis*	*Platanus orientalis* treated by acid
SBET(m^2/g)	10.06	24.35
V_{Tot}(cc/g)	0.0194	0.056
Average pore size(A)	60.82	217
V_{mic}(cc/g)	0	0

Figure 3. Left: SEM image for Raw *Platanus orientalis.* Right: SEM image for *Platanus orientalis* treated by acid.

Pore size increased for acid-treated *Platanus orientalis* (Table 3) compare to the raw sample. Two of the adsorbents did not have micropores. Total pore volume for acid-treated *Platanus orientalis* was greater than the raw sample. Surface area was increased with increasing pore size and total volume of pores. According to the Figure 3a it can be said Raw Platanus Orientalis have cellulosic nature. According to the Figure 3b pore size growth was observed for acid treated Platanus Orientalis. It can be said that The BET and SEM analysis were found to support each other (Table 3 and Figure 3). This porous structure is thought to contribute to adsorption.

Ceramic Membrane filtration experiment Cr(VI) rejection percent was calculated from below equation:

$$Cr(VI)\ rejection\ (\%) = \frac{C_f - C_p}{C_f} \times 100 \qquad (Eq.\ 6)$$

where C_p : Permeate Cr(VI) concentration (mg/L)
C_f : Cr(VI) concentration in the feed (mg/L)

Permeate fluxes were calculated from Equation (7).

$$J = m/A.t \qquad (Eq.\ 7)$$

Where J: Permeate flux $(\frac{g}{cm^2 s})$
m: Amount of filtered solution (g)
t: Filtration time(s)
A: Membrane area (cm^2).

For the ceramic membrane filtration experiment, the rejection percent of Cr(VI) and permeate flux values are given in Table 4.

Table 4. Results of ceramic membrane experiments

Membrane	Cr(VI) Rejection (%)	Permeate Flux, q $(\frac{g}{cm^2 s})$
K1	6.92	0.0077
K4	16.46	0.0108
K7	3.34	0.0035

A maximum of 16.46% Cr(VI) rejection from a 100 mg / L solution was obtained with K4 coded ceramic membrane. Compared with the properties of the other membranes, it was determined that the membrane used had the highest removal of the membrane with the lowest water absorption capacity and porosity.

In the hybrid system experiments, firstly, batch adsorption experiments were carried out at 25 °C using 0.5 g of adsorbent and 100 mg/L initial concentration of Cr(VI) solution. In the adsorption method, the equilibrium time was 18 hours which was considered to be long for industrial application. So adsorption was terminated at the end of the contact time for 3 hours (removal 76 %), and then the filtrate was passed through the ceramic membrane and 90.1% total removal was achieved.

The purpose of the use of the adsorption ceramic membrane hybrid system as the method is that the concentration of Cr(VI) in wastewaters is lowered to the discharge standards of Turkish Water Pollution Control Act (generally 0.5 mg/L in a 2 hour composite sample). In the hybrid system, the contact time was maintained for 3 hours and 90.1% removal was achieved. So it can be suggested that method is appropriate for this purpose.

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