Bulgarian Chemical Communications, Volume 56, Issue 3 (pp. 203-207) 2024 *DOI: 10.34049/bcc.56.3.DD-M*

Continuous flow chromium (VI) adsorption onto peach stone- and acrylonitrile-divinylbenzene copolymer-based activated carbons

D. Duranoğlu*, I. Küçük, Ü. Beker

Department of Chemical Engineering, Faculty of Chemical and Metallurgical Engineering, Yildiz Technical University, Davutpasa Campus, 34220, Esenler, Istanbul, Turkey

Received May 24, 2024; Accepted: June 14, 2024

Peach stone-based activated carbon (PS-AC) and acrylonitrile divinyl benzene copolymer-based activated carbon (ANDVB-AC) were evaluated in fixed-bed continuous flow Cr(VI) adsorption studies. The results were compared with those for the commercial activated carbon (CPG-LF). Continuous flow adsorption studies were carried out in a fixed-bed column with various concentrations of a Cr(VI) solution of pH 2. The effect of flow rate on the breakthrough capacity was investigated *via* breakthrough curves. Although total Cr(VI) adsorption capacities were obtained as 122, 58, and 103 mg/g for PS-AC, ANDVB-AC and CPG-LF, respectively, the breakthrough capacities were determined to be 25.0, 35.2, and 30.0 mg/g. When polymer-based AC was used, 61% of the capacity was effectively utilized while with peach stone-based AC, only 21% of the capacity was effectively utilized at a flow rate of 5 mL/min. This difference was attributed to the shorter contact time of the solution in the column and the slower adsorption kinetics of PS-AC. At a lower flow rate (0.96 mL/min) peach stone-AC can be utilized with higher (47%) efficiency. Both peach stone- and polymer- based activated carbons can be effectively utilized in a fixed column under continuous flow with high Cr(VI) adsorption capacities.

Keywords: Chromium; activated carbon; continuous flow adsorption; peach stone; acrylonitrile divinyl benzene

INTRODUCTION

Water sources contaminated with Cr(VI) compounds which are toxic and of carcinogenic nature, should be treated. Due to the superior properties like high specific surface area, porous structure and oxygen-containing surface functional groups, activated carbon (AC) can be effectively used for removal of contaminants from aqueous solutions. Any carbonaceous materials available at low cost, both naturally occurring like agricultural wastes and synthetic like polymers, can be utilized as precursors in the production of activated carbons [1, 2]. Commercial activated carbons are mainly produced from wood, coal and coconut shells. Due to their adsorptive properties, low cost and sustainability, activated carbons prepared from agricultural by-products could be superior compared to conventional activated carbons [3].

Various kinds of biomass have been utilized as activated carbons for Cr(VI) adsorption in a fixed bed column [4-8]. Availability and abundance of precursor are crucial. Peach stone is one of the most abundant agricultural wastes of juice factories. Turkey is the fifth peach manufacturer in the world with a production of 485,000 tons [9]. On the other hand, polymer-derived carbons can be better controlled by the choice of precursor material, including its own porosity, chemical composition, and pore size distribution, as well as by carbonization and activation conditions. Polymer-based activated carbons are more stable and mechanically resistant compared to other biomass-based activated carbons. Moreover, owing to the shape of the beads of the polymer precursor, activated carbon shows good hydrodynamic properties in fixed-bed applications.

The aim of the current study is to investigate Cr(VI) adsorption onto peach stone-based (PS-AC) and acrylonitrile-divinylbenzene copolymer-based activated carbon (ANDVB-AC) in a fixed bed column. Cr(VI) adsorption on different activated carbons was compared *via* breakthrough curves obtained.

EXPERIMENTAL

Fixed bed column studies

Continuous flow adsorption studies were carried out in a fixed-bed column of 13 mm diameter. Different concentrations of a Cr(VI) solution prepared at pH 2 were fed into the fixed-bed polyethylene column using a peristaltic pump until all adsorbent was saturated. In the column experiments, activated carbons dried overnight at 378 K were used. The solution at the column outlet was collected into tubes using a timed fractionated sample collector, then Cr(VI) concentrations were determined at 540 nm wavelength by using Analytic Jena Specord 40 spectrometer after complexing with diphenylcarbazide in acidic medium [10]. Experiments were continued until the concentration

---

* To whom all correspondence should be sent:
E-mail: *dduran@yildiz.edu.tr*

of the collected outlet solution was equal to the concentration of the inlet solution.

Breakthrough curves were obtained by plotting relative concentration of inlet and outlet values against the amount of the outlet solution or bed volume. The bed volume was calculated using Equation 1:

$$Bed\ volume = \frac{V}{(\pi \cdot D^2 \cdot h)/4} \qquad (1)$$

V, D and h values given in Equation 1 show the outlet solution volume (mL), column diameter (cm) and the height of the activated carbon in the column (cm), respectively.

Studies conducted with peach stone-based activated carbon (PS-AC): The PS-AC sample with a particle size of 0.14-0.56 mm was filled into the ion exchange column. The height of activated carbon in the column was 14 mm (0.8 g of PS-AC). The adsorption experiments were carried with four different Cr(VI) concentrations (5 ppm, 15 ppm, 30 ppm and 60 ppm) and a feeding flow rate of 5 mL/min until the column reached saturation. In order to examine the effect of flow rate on the breakthrough point capacity, separate experiments were conducted with a concentration of 30 ppm and a flow rate of 0.96 mL/min.

Studies conducted with polymer-based activated carbon (ANDVB-AC): The activated carbon with a particle size of 0.075-0.29 mm was filled into the ion exchange column. The height of activated carbon in the column was 27.5 mm. The adsorption experiment was carried with a Cr(VI) solution at a concentration of 30 ppm at a feeding flow rate of 5 mL/min until the column reached saturation.

Studies with commercial activated carbon (CPG-LF): The CPG-LF sample with a particle size of 0.14-0.56 mm was filled into the ion exchange column. The height of activated carbon in the column was 14 mm. The adsorption experiment was carried with a 30 ppm Cr(VI) solution at a feeding flow rate of 5 mL/min until the column reached saturation.

MATERIALS

Peach stones (PS) were obtained from a fruit juice factory in Bursa, Turkey. They were converted into activated carbon (PS-AC) *via* steam activation at 1073 K as described in our previous study [11]. Acrylonitrile-divinylbenzene copolymer beads (ANDVB) were prepared by a suspension polymerization method with hexadecane and toluene (1:9 w/w) as diluents. The level of crosslinker was set at 40 wt%. Full details of the polymerization are given in ref. [12]. The activation of ANDVB beads was performed in three successive stages; air oxidation at 573K, then carbonization at 673 K for 4 h and finally at 1123 K for 1 h under nitrogen flow. Detailed production conditions of polymer-based activated carbon (ANDVB-AC) were previously reported [11]. Commercial activated carbon (Chemviron Carbon, CPG-LF) was used for the comparison of the adsorption results. Some characteristics of polymer-based ACs are given in Table 1. N_2 adsorption measurements were performed using Quantachrome Autosorb-1-C surface analyser. Nitrogen adsorption-desorption isotherms of the AC samples produced within the scope of the study are given in Figure 1. Visual inspection of adsorption isotherms provides useful information about adsorption and pore structure of the adsorbent. When the figures are examined, it is seen that the nitrogen adsorption of all carbon samples obeys a Type I isotherm. Microporous adsorbents demonstrate a Type I isotherm [13]. At small values of P/P_0, the micropores are filled with adsorbed gas and then the curve flattens. This indicates that adsorption does not continue after the micropores are filled. SEM images obtained from JEOL JSM-633SF model field emission scanning electron microscope, are also shown in Figure 1. The porous structure of produced carbons is clearly seen from the figure.

Table 1,. Characteristics of activated carbons

Properties	PS-AC	ANDVB-AC	CPG-LF
BET surface area (m^2/g)	608	579	693
Pore volume (cm^3/g)	0.341	0.300	0.351
Micropore volume (cm^3/g)	0.331	0.234	0.318
Composition (Kjeldahl %N; %N; %C; %H; %O)	0.15; 0.22; 93.18; 0.94; 5.67	4.69; 4.49; 82.29; 1.38; 11.85	0.50; 0.86; 91.37; 0.73; 7.04

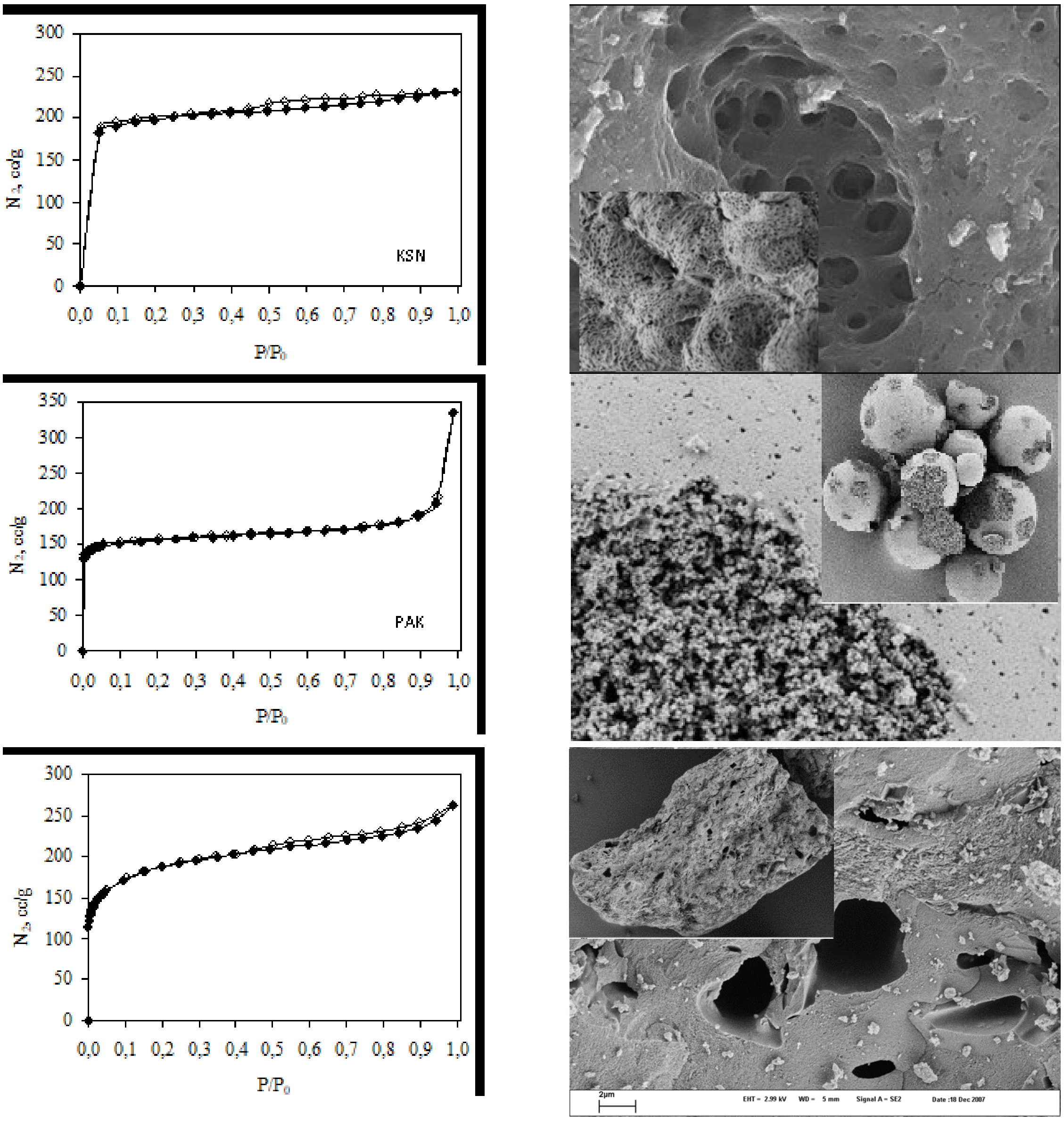

Figure 1. Nitrogen adsorption-desorption isotherms and SEM images of the AC samples

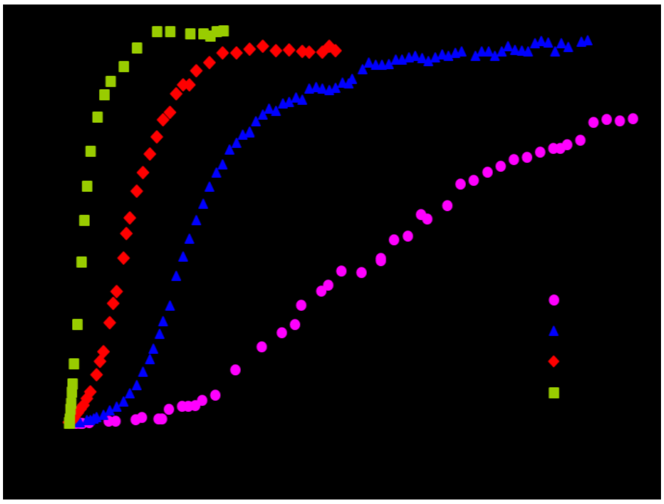

Figure 2. Breakthrough curves obtained with PS-AC activated carbon (PS-AC: 0.8 g; bed volume: 3.4 mL; flow rate: 5 mL/min)

RESULTS AND DISCUSSION

Sorption studies with PS-AC

In order to determine the dynamic behaviour of the adsorption column, the time at which the breakthrough point appears and the shape of the breakthrough curves are very important parameters. Breakthrough curves are usually created by plotting the relative concentration (C/C_0), the ratio of column outlet concentration to inlet concentration, as a function of time or bed volume [14].

The breakthrough curves obtained as a result of adsorption experiments performed with PS-AC at different inlet Cr(VI) concentrations are shown in Figure 2. As seen, the relative concentration of outlet solution is initially very close to zero, then, it increases by further solution passing through the column, i.e. the column reaches a saturation point. The first break points seen in the figure are called breakthrough points. When the inlet Cr(VI) concentration was increased, breakthrough points began to appear earlier. Breakthrough point is seen after approximately 5.3 L of solution (~2800 bed volumes) passes through the column with 5 ppm inlet concentration, while the breakthrough points are 2.2 L, 660 mL and 100 mL (~1200, ~360 and ~55 bed volumes) for the inlet concentrations of 15 ppm, 30 ppm and 60 ppm, respectively. In addition, as can be seen in Figure 2, a much steeper curve was obtained at higher inlet concentrations. The PS-AC column was completely saturated after 4 L of Cr(VI) solution passed through the column when working with an initial concentration of 60 ppm. On the other hand, approximately 40 L of Cr(VI) solution was required to saturate the column for 5 ppm inlet concentration.In order to examine the effect of flow rate on adsorption, the breakthrough point curves obtained at 30 ppm inlet concentration with different flow rates (0.96 mL/min and 5 mL/min) for PS-AC are given in Figure 3. The breakthrough point, which was seen at 660 mL (~360 bed volumes) when the flow rate was 5 mL/min, was observed after 1250 mL (~670 bed volumes) of solution passed through the column at a flow rate of 0.96 mL/min. The breakthrough point curve obtained at a lower flow rate was much steeper, and the column quickly reached saturation. This situation can be explained by the contact time between the solution and activated carbon. While the contact time in the column is 22 seconds at a high flow rate (5 mL/min), this time is 116 seconds at a low flow rate (0.96 mL/min). By 5-fold increasing of the contact time between the activated carbon and the solution, the PS-AC in the column was much more effectively utilized.

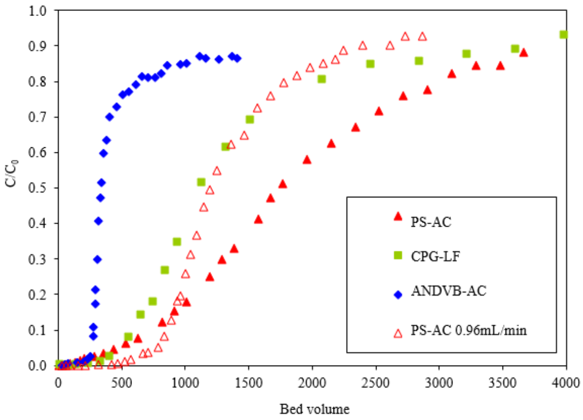

Figure 3. Breakthrough curves obtained with different activated carbons (flow rates: 5 mL/min; Cr(VI) inlet conc: 30 ppm; PS-AC bed volume: 1.84 mL; ANDVB-AC bed volume: 3.94 mL; CPG-LF bed volume: 1.86 mL)

The breakthrough curves obtained as a result of the column sorption study performed with three different activated carbons (PS-AC, ANDVB-AC and commercial CPG-LF) can be seen in Figure 3. When studied under the same conditions, the breakthrough point of the commercial activated carbon occurred when about 430 bed volumes of solution were passed, while the breakthrough points of PS-AC and ANDVB-AC were observed at 360 and 250 bed volumes, respectively. Breakthrough capacity of PS-AC is very close to that of the commercial one whereas ANDVB-AC shows the lowest capacity with a much steeper curve compared to the others. This steeper curve resulted in lower exhaustion capacity, however, higher utility of the capacity.

The amount of substance per unit adsorbent amount at the breakthrough point is called breakthrough point capacity, and this value is lower than the total capacity value. Breakthrough capacity depends on process conditions and is meaningless when these conditions are given without being specified. Total capacity refers to the total amount of substance adsorbed by the column until it reaches saturation and depends on the amount of adsorbent [15]. The total and breakthrough capacities given in Table 2 were calculated from the breakthrough curve graphs. The most suitable profile for the specified operating conditions (30 ppm inlet concentration and 5 mL/min flow rate) was provided by ANDVB-AC. Compared to PS-AC and CPG-LF, although the total capacity of the ANDVB-AC sample is very low, the breakthrough point capacity is high. While 60% of the capacity could be effectively utilized when polymer-based activated carbon (ANDVB-AC) was used, only 21% of the total capacity could be effectively utilized when peach stone-based activated carbon (PS-AC) was used (Table 2).

Table 2. Breakthrough and total capacities, capacity utilizations

AC	Flow rate (mL/min)	Residence time[a] (s)	Breakthrough capacity[b] (mg/mL)	Total capacity[b] (mg/mL)	Breakthrough capacity[c] (mg/g)	Total capacity[c] (mg/g)	Effective capacity utilization[d] (%)
PS-AC	5	22	10.8	52.5	25.0	122	21
ANDVB-AC	5	47	7.1	11.8	35.2	58	60
CPG-LF	5	22	12.9	44.3	30.0	103	30
PS-AC	0.96	116	19.2	41.2	44.6	96	47

[a] Residence time = Bed volume/Flow rate; [b] based on the volume of activated carbon; [c] based on the mass of activated carbon; [d] Effective capacity utilization = (Breakthrough capacity/Total capacity) ×100

This is closely related to the residence time of the solution in the column. The residence time of the solution in ANDVB-AC the column is 47 sec, while when PS-AC and CPG-LF are used, this residence time is about 22 sec. By increasing the residence time in PS-AC from 22 sec to 116 sec sec *via* decreasing the flow rate, the breakthrough point capacity could be increased by 80% and the effective capacity utilization rate could be increased to 47%. In commercial applications of ion exchangers, the breakthrough point capacity is generally 50% of the total capacity for strongly acidic and strongly basic resins and 80% or more for weakly acidic and weakly basic resins. Accordingly, ANDVB-AC and PS-AC (at low flow rate conditions) can be effectively utilized as Cr(VI) adsorbents in fixed-bed columns. In ion exchangers, the ion exchange capacity is usually given per unit resin volume [16]. Adsorption capacity values given in Table 2 are on the basis of both volume and mass. Although ANDVB-AC is superior to PS-AC considering breakthrough point capacities calculated on mass basis, if breakthrough point capacities calculated on volumetric basis are examined, it is seen that PS-AC is more efficient.

CONCLUSION

According to our findings it may be concluded that:

- Peach stone-based AC showed higher Cr(VI) adsorption capacity compared to the others, however, its capacity utilization is low due to the low kinetics in nature. On the other hand, peach stone-based activated carbon can be effectively used with low flow rates.
- Even though polymer-based AC has the lowest total capacity, its capacity utilization is significantly high.

Hence, both peach stone- and polymer-based activated carbons are promising adsorbents for Cr(VI) removal from aqueous solutions in a continuous flow process.

REFERENCES

1. A. A. Attia, B. S. Girgis, N. A. Fathy, *Dyes and Pigments*, **76**, 282 (2008).
2. B. S. Girgis, A. A. Attia, N. A. Fathy, *Colloids and Surfaces A: Physicochemical Engineering Aspects*, **299**, 79 (2007).
3. P. Galiatsatou, M. Metaxas, V. Kasselouri-Rigopoulou, *Mikrochimica Acta,* **136**, 147 (2001).
4. S. Yüksel, R. Orhan, *Arabian Journal for Science and Engineering,* **44**, 5345 (2019).
5. S. M. Yakout, M. R. Hassan, H. A. Omar, *Desalination and Water Treatment*, **170,** 128 (2019).
6. H. Haroon, J. A. Shah, M. S. Khan, T. Alam, R. Khan, S. A. Asad, M. A. Ali, G. Farooq, M. Iqbal, M. Bilal, *J. Water Process Eng.*, **38**, 101577 (2020).
7. A. Ajmani, C. Patra, S. Subbiah, S. Narayanasamy, *J. Environ. Chem. Eng.,* **8**, 103825 (2020).
8. S. Mohanta, M. K. Sahu, P. C. Mishra, A. K. Giri, *Water Science & Technology*, **84**, 55 (2021).
9. Z. G. Göktolga, B. Gözener, O. Karkacıer, *G.O.Ü. Ziraat Fakültesi Dergisi*, **23**, 39 (2006).
10. APHA (American Public Health Association), Standard Methods for Examination of Water and Wastewater, Baltimore, 2005.
11. D. Duranoğlu, A. W. Trochimczuk, U. Beker, *Chem. Eng. J.*, **165,** 56 (2010).
12. A. W. Trochimczuk, M. Streat, B. N. Kolarz, *React. Funct. Polym.*, **46**, 259 (2001).
13. International Union of Pure and Applied Chemistry (IUPAC), Reporting Physisorption Data for Gas/Solid Systems with Special Reference to the Determination of Surface Area and Porosity, **57**, 603, 1985.
14. E. Malkoc, Y. Nuhoglu, M. Dundar, *Journal of Hazardous Materials*, **138**, 142 (2006).
15. F. Helfferich, Ion Exchange, Dover Publications, New York, 1995.
16. F. C. Nachad, J. Schubert, Ion Exchange Technology, Academic Press, New York, J., 1965.