Sustainable Chemistry and Pharmacy 7 (2018) 9–16

Contents lists available at ScienceDirect

Sustainable Chemistry and Pharmacy

journal homepage: www.elsevier.com/locate/scp

# Adsorption of hexavalent chromium in aqueous solution on activated carbon prepared from apple peels

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ARTICLE INFO

*Keywords:*
Adsorption
Chromium(VI)
Activated carbon
Apple peels

ABSTRACT

In the present study, activated carbon prepared from apple peels (ACAP) was used to remove chromium (VI) from aqueous solution. The characterization of this ACAP has been performed using different analytical techniques such as FTIR and SEM. The adsorption parameters studied were: pH [2- 7], adsorbent dose [0.025–0.15 g/50 mL], initial Cr(VI) concentration [10–50 mg/L] and temperature [10–40 °C]. Maximum Cr(VI) adsorption of 36.01 mg/g was achieved using Cr(VI) concentration of 50 mg/L, pH of 2, adsorbent dose of 0.05 g/50 mL, contact time of 4 h and temperature of 28 °C. This ACAP gave a Cr(VI) adsorption capacity better than a commercial activated carbon. The experimental data fitted well to Freundlich isotherm ($R^2$ = 0.99) and kinetics followed the pseudo-second order model. Thermodynamic parameters, $\Delta G < 0$, $\Delta H^\circ = 1.99$ (Kcal/mol) and $\Delta S^\circ = 0.0079$ (Kcal/K mol) indicate that the adsorption process is spontaneous and endothermic.

## 1. Introduction

The industrial revolution has ameliorated the living standards of life, whereas it causes the pollution of the environment due to the release of untreated effluents. Various industrial processes such as mineral processing, metal mining, tanning in the leather industry, dyeing in textile industry and pigment manufacture, contribute in the discharge of pollutants which can be classified as inorganic (heavy metals, sulphates, nitrates, etc.), organic (dyes, phenols, pesticides, etc.) and biological (viruses, bacteria, etc.). Therefore, several technologies have been employed for wastewater treatment (Gupta et al., 2012). Among these techniques we cite precipitation (Maurer and Boller, 1999), coagulation (Kennedy et al., 1992), flotation (Rubio et al., 2002), reduction (Cao et al., 1999), aerobic and anaerobic treatment (Seshadri et al., 1994), micro- and ultra-filtration (Choo et al., 2008), ion exchange (Rock and Stevens, 1975), oxidation (Karthikeyan et al., 2012), photocatalysis which is one of advanced oxidation processes, utilized particularly for organic pollutants degradation (Saravanan et al., 2016; Gupta et al., 2011; Saleh and Gupta, 2011) and Adsorption (Gupta et al., 2013; Mohammadi et al., 2011; Mittal et al., 2010; Tahir et al., 2016; Gupta and Saleh, 2013; Enniya and Jourani, 2017).

In this paper, we are interested in heavy metals removal, an important origin of water pollution because of their toxicity (Grevatt, 1998). For this reason the elimination of heavy metals from wastewater has become extremely necessary before their discharge into the aquatic system. Until now, a variety of methods have been developed to deal with heavy metals from aqueous media, including reduction (Shi et al., 1999), precipitation (Kongsricharoern and Polprasert, 1995), membrane filtration (Yang et al., 2003), biological methods (Sahinkaya et al., 2012), ion exchange (Yang et al., 2014) and adsorption. However, adsorption is a preferred method due to its high efficiency, simplicity and low cost for eliminating metal ions (Gupta et al., 1998, 2015). Several studies have been undertaken to evaluate the adsorption of Cr(VI) (Dehghani et al., 2016), Zr(VI) (Bhatti et al., 2016), U(VI) (Kausar et al., 2017), Cu(II) (Mushtaq et al., 2016), Pb(II) (Nadeem et al., 2016; Gupta et al., 2011; Saleh and Gupta, 2012), Zn and Ni (Rashid et al., 2016) and Cd (Gupta and Nayak, 2012).

Chromium is one of the most harmful heavy metals in wastewater. It has been used in several industries such as tanning, painting, dyeing, explosives, ceramics and wood processing as well as in the paper industry. Chromium exists in both trivalent (Cr(III)) and hexavalent (Cr (VI)) forms. The hexavalent chromium is the most toxic one (Elmerzouki, 2009). The toxicity of Chromium was evaluated, the mutagenic and cytogenetic effects of chromium have been reported (Iqbal, 2016).

Recently, a diversity of cheap materials have been examined as

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https://doi.org/10.1016/j.scp.2017.11.003
Received 28 September 2017; Received in revised form 14 November 2017; Accepted 16 November 2017
Available online 05 December 2017
2352-5541/ 

adsorbents for the removal of Cr(VI) from aqueous solutions. Some of the low-cost adsorbents include treated waste newspaper (Dehghani et al., 2016), apricot kernel activated carbon (Demirbas et al., 2004), sugarcane bagasse (Garg et al., 2007), longan seed activated carbon (Yang et al., 2015), native and immobilized sugarcane bagasse (Ullah et al., 2013) and animal charcoal (Hyder et al., 2015). Activated carbons have been highly investigated for the adsorption of Cr(VI) in terms of their high specific surface and important pore volume (Yang et al., 2015).

Apple is one of the popular fruit in the world, with an annual global production that exceeded 69 million tons in 2008–2009 (Food and Agriculture Organization (FAO)). Apple peels are produced in large amounts as a biowaste from food processing industries. Between 17 and 21 million tons of apple waste are produced every year (Dhillon et al., 2013). Apple pomace and essentially apple peels are very rich in polyphenols, cellulose, hemicellulose, pectin, and lignin. These contain functional groups like -CO, -COO, -OH and $-NH_2$ which are largely responsible for the adsorption of metals (Gardea-Torresdey et al., 1990), thereafter apple peels can be exploited in Cr(VI) adsorption.

In the present study, the attempts have been made to remove chromium (VI) ion from aqueous solution using an activated carbon prepared from apple peels as a low-cost adsorbent. Besides, the effect of pH, initial Cr(VI) concentration, adsorbent dose, contact time and temperature was studied. Kinetics, isotherm and thermodynamic studies were also performed.

## 2. Materials and methods

### *2.1. Adsorbent preparation*

The apple peels activated carbon was prepared according to the following procedure. Apples (Golden Delicious) were purchased from the local market. They were peeled and the peels free from pulp were dried at 60 °C for 24 h. The dried apple peels were mixed with concentrated phosphoric acid ($H_3PO_4$ 85%) in 2.7:1 ratio ($H_3PO_4$ volume (mL)/Dried Apple peels mass (g)) and activated in a muffle furnace maintained at 619 °C for 56 min. This activated material was washed several times with distilled water to remove the free acid. Then, it was dried at 80 °C until a constant weight is obtained. The activated carbon prepared from apple peels (ACAP) is stored in a closed container at room temperature.

### *2.2. Fourier transform infrared (FTIR) spectroscopy analysis*

Fourier transform infrared (FTIR) analysis was applied to determine the functional groups present on the surface of ACAP and in order to understand the mechanism of Cr(VI) adsorption, using FTIR spectroscope (Bruker-Tensor 27). The spectra were recorded from 4000 to 500 $cm^{-1}$.

### *2.3. Scanning electron microscopy (SEM)*

Surface morphology of the activated carbon prepared from apple peels was studied using scanning electron microscope (FEI Quanta 200) in order to make a comparison with Apple peels surface before the treatment.

### *2.4. Adsorption experiments*

A stock solution (1000 mg/L) of Cr(VI) was prepared by dissolving $K_2Cr_2O_7$ into distilled water. The test solution of Cr(VI) used in each study was prepared by diluting the stock solution. The pH value for test solution was adjusted by 0.1 N HCl or 0.1 N NaOH solutions. Adsorption experiments have been carried out by introducing a quantity of ACAP in Erlenmeyer flasks containing Cr(VI) solution at specified initial concentration and at a constant temperature. The mixture was agitated using a magnetic stirrer at a constant stirring speed (400 rpm). A number of experimental variables such as pH (2–7), Cr(VI) concentration (10–50 mg/L), adsorbent dose (0.025–0.15 mg/50 mL) and temperature (10–40 °C) had been studied to investigate the Cr(VI) removal process. The presented results are the average of three measurements ± standard deviations.

Samples of the solution were withdrawn at various time intervals and centrifuged at 2000 rpm for two minutes.

The supernatant absorbance is measured using the spectrophotometer at 554 nm after complexation using the diphenylcarbazide solution according to the procedure described in detail by Klimaviciute et al. (2010).

The removal percentage (%R) of Cr(VI) is calculated as follows:

$$\%R = \frac{C_i - C_e}{C_i} \times 100 \quad (1)$$

$C_i$ (mg/L) is the initial concentration of Cr(VI) and $C_e$ (mg/L) is the Cr(VI) concentration at equilibrium.

The adsorption capacity of Cr(VI) is given by the following formula:

$$q_t = \frac{(C_i - C_t) \times V}{m} \quad (2)$$

$q_t$ (mg/g) is the amount adsorbed at time t (min), $C_t$ (mg/L) is the Cr (VI) concentration at time t, V (L) is the volume of Cr(VI) solution and m (g) is the mass of the adsorbent used.

## 3. Results and discussion

### *3.1. Comparison of Cr(VI) adsorption on different prepared adsorbents*

In order to compare the adsorption capacity of the hexavalent chromium on different adsorbents prepared in our laboratory:

-Raw apple peels (Raw AP).
-Dried apple peels at 60 °C for 24 h ($AP_{60,24}$).
-Apple peels treated with NaOH ($AP_{NaOH}$) which was prepared as follows. Apple peels were dried at 60 °C for 24 h. The dried apple peels were treated with 0.1 N sodium hydroxide (NaOH) solution for 24 h with an impregnation ratio (Apple peels/NaOH) of 1:5 (mass/volume). The sample was then washed thoroughly with distilled water until the neutralization. Then, it was dried in the oven at 80 °C for 24 h.
-Activated carbon prepared from apple peels (ACAP) as described in paragraph 2.1.
-Commercial activated carbon ($AC_{Com}$).

Experiments were carried out at the following conditions: 50 mL of Cr(VI) solution at a concentration of 50 mg/L, 0.05 g of adsorbent and a contact time of 2 h. Results are shown in Table 1.

As we can see in the Table 1, ACAP gives an adsorption capacity of 18.78 mg/g, which is higher to the all other adsorbents including the commercial activated carbon with a capacity of adsorption of 9.55 mg/g.

**Table 1**
Adsorption capacities of Cr(VI) on different prepared adsorbent (Cr(VI) solution volume 50 mL, Cr(VI) concentration 50 mg/L, adsorbent dose 0.05 g, stirring speed 400 rpm and contact time 2 h).

| Prepared adsorbent | Adsorption capacity (mg/g) |
|---|---|
| Raw apple peels | 0.62 |
| $AP_{60,24}$ | 4.61 |
| $AP_{NaOH}$ | 3.95 |
| ACAP | 18.78 |
| $AC_{com}$ | 9.55 |