A new insight into the restriction of Cr(VI) removal performance of activated carbon under neutral pH condition

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ABSTRACT

Activated carbon has been widely used to remove hazardous Cr(VI), however, the impact of Cr₂O₃ precipitate on gradually declined removal ability as pH increased has received little attention. Herein, to investigate the effect of Cr₂O₃, SEM-EDX (scanning electron microscope-energy dispersive X-ray analysis) coupling elements mapping of chromium loaded powder activated carbon (PAC) revealed that a chromium layer was formed on the PAC exterior after being treated with Cr(VI) at pH 7. XPS (X-ray photoelectron spectroscopy) study confirmed that 69.93% and 39.91% Cr₂O₃ precipitated on the PAC surface at pH 7 and pH 3, respectively, corresponding to 17.77 mg/g and 20 mg/g removal capacity. Exhausted PAC had a removal efficiency of 92.43% after Cr₂O₃ being washed by H₂SO₄ solution, which was much higher than the removal efficiency of 51.27 % after NaOH washing. This further verified the intrinsically developed Cr₂O₃ precipitate on PAC under neutral conditions limited the durability of PAC as an adsorbent. Consecutive elution assessments confirmed that adsorption and reduction ability both declined as pH increased. Raman spectroscopy and C 1s spectra of materials demonstrated two distinct Cr(VI) removal mechanisms under pH 3 and pH 7. In conclusion, the exhausted AC after Cr(VI) adsorption can be rejuvenated after the surface coated Cr₂O₃ being washed by the acid solution which can expand the longevity of AC and recover Cr(III).

Key words: activated carbon, adsorption, chromium, neutral conditions, passivation, reduction

HIGHLIGHT

• In this work, we scrutinized the mechanism of poor removal capacity of commercial activated carbon on toxic heavy metal Cr(VI) under neutral pH conditions. Differing from the most accepted view that electrostatic repulsion is the main consideration, our study suggested that the relatively more Cr₂O₃ precipitate on the surface of activated carbon under higher pH led to the low Cr(VI) sequestration capability.

GRAPHICAL ABSTRACT

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1. INTRODUCTION

Chromium abounds in nature and is highly toxic in the form of \( \text{CrO}_4^{2-} \) and \( \text{Cr}_2\text{O}_7^{2-} \) through bioaccumulation (Li et al. 2018). The chromium pollution of water, land, and environment has attracted the interest of experts as electroplating plants, stainless steel manufacturing plants, leather manufacturing plants, and refractory plants have progressively appeared (Wang et al. 2019; Aparicio et al. 2021; Samuel et al. 2021). Cr(III) presents less mobility, toxicity, and solubility than Cr(VI) and generates sparingly soluble chromium hydroxides (Dognani et al. 2019). The reduction of Cr(VI) to Cr(III) is rapid at acidic conditions, meanwhile, the readily available electron is required for the reduction process (Deng et al. 2020; Fang et al. 2021b). It is well known that removing Cr(VI) from water by reduction and precipitation is a viable option (Barrera-Díaz et al. 2012; Qian et al. 2019; Wu et al. 2019; Zeng et al. 2019). Conventional reducing agents are sulfur and iron salts (Zhang et al. 2021a, 2021b), post-treated effluent contained sulfate, and iron salts would contaminate water and soil. Furthermore, the mandatory wastewater discharge would result in high costs.

The bulk of published studies on Cr(VI) removal by low-cost and readily accessible activated carbon (AC) demonstrated that removal capacity was greater in acidic conditions than alkaline conditions. This suggests that the Cr(VI) elimination is strongly pH-dependent (Al-Othman et al. 2012; Zhou et al. 2016; Valentín-Reyes et al. 2019). The removal efficiency of Cr(VI) by activated carbon prepared from teakwood sawdust was 100% at pH 2 while it was below 20% at pH 10 (Ramirez et al. 2020). Table 1 shows the capacity of several ACs to remove Cr(VI) in acidic and alkaline environments. At low pH, the removal capacity was favored because the positively charged surface of Cr(VI) advanced the adsorption of anion Cr(VI) (Norouzi et al. 2018). It is worth noting that the pH-speciation of Cr(VI) reveals that HCrO₄⁻ dominated below pH 6, whereas CrO₄²⁻ dominates above pH 7 (Rakhunde et al. 2012). Furthermore, prior studies have found that positively charged AC produced by protonation at a low pH value tends to attract chromate anions, which is thought to be the main mechanism for Cr(VI) adsorption (Mohan et al. 2005). It was discovered that as pH dropped, the reduction and adsorption process enhanced simultaneously.

To our understanding, there have been few investigations on systematic chromium adsorption and reduction study when pH rises over 7, to shed light on a substantial drop in AC performance. Most studies have only focused on the unfavorable effect of electrostatic repulsion between chromate anions and negatively charged AC surface at high pH values (Niazi et al. 2018; Ma et al. 2019; Liu et al. 2020). Besides, an earlier study failed to elucidate the removal paths at pH higher than 6 because the surface negatively charged bamboo bark-based AC that unfavored the adsorption of Cr(VI) anions, hence the reduction process of Cr(VI) to Cr(III) at high pH was omitted (Zhang et al. 2015). Cr(III) speciation as a function of pH was depicted clearly by Lopez-Valdivieso’s study showing that Cr(OH)₃(s) predominates at pH over 6.4 (Fang et al. 2021a). The effect on the removal of Cr(VI) under alkaline conditions of the AC surface loaded Cr(III) precipitate was especially neglected. Early reported studies on the synthesis of eskolaite (α-Cr₂O₃) nanoparticles through AC following adsorption of Cr(VI) have shown that Cr₂O₃ was the reduced species of Cr(VI) on AC (Cruz-Espinoza et al. 2012; Ibarra-Galván et al. 2014). Recently study showed that the Cr₂O₃ reduced the adsorption rate of Cr(VI) significantly (Wang et al. 2020).

| Table 1 | Comparison of Cr(VI) removal under different pH by various carbon materials |
|---------|------------------|------------------|------------------|
| Carbon materials | Acid condition | Alkali condition | References |
| AC derived from Posidonia Oceanica seagrass | 30.5 (pH 3) | 0 (pH >4) | Asimakopoulos et al. (2021) |
| Biochar derived from corn straw | 125 (pH 2) | 50 (pH 6) | Qu et al. (2021) |
| Powdered AC | 46 (pH 2) | 8 (pH 7) | Sangkarak et al. (2020) |
| Biochar derived from waste glue residue | 206.7 (pH 2) | 90 (pH 6) | Shi et al. (2020) |
| AC prepared by calcination wheat bran | 22 (pH 2) | 0 (pH 10) | Ogata et al. (2020) |
| Commercial AC | 21 (pH 2.5) | 13 (pH 5.5) | Wu et al. (2020) |
| KOH activated porous corn straw | 98.3 (pH 3) | 33.7 (pH 7) | Ma et al. (2019) |
| AC derived from an acrylonitrile-divinylbenzene copolymer | 80 (pH 2) | 9 (pH 8) | Duranoğlu et al. (2012) |
Compared to the consensus that the electrostatic repulsion led to the poor Cr(VI) removal efficiency of AC at alkaline conditions, the effect of AC surface coated Cr$_2$O$_3$ precipitate on removal performance was not fully understood. This work aimed to study the effect of powdered AC (PAC) surface formed Cr$_2$O$_3$ precipitate on Cr(VI) removal, SEM-EDX (scanning electron microscope-energy dispersive X-ray analysis), and XPS (X-ray photoelectron spectroscopy) were used to investigate the surface morphology and the chemical properties. Desorption and regeneration experiments were used to confirm the role of Cr$_2$O$_3$. The insight gained from this study would help to expand the longevity of AC and the recovery of Cr via AC.

2. MATERIALS AND METHODS

2.1. Characterization of PAC particle
To scrutinize the composition of loaded-chromium on PAC after Cr(VI) removal, three types of de-passivation agents were examined to desorb the adsorbed/reduced chromium on PAC. The formation process of the chromium layer on PAC at pH 3 and 7 was inspected by carrying out consecutive desorption tests following each Cr(VI) adsorption. SEM-EDX (JSM-6610LV, JEOL, Japan) and XPS (K-Alpha, Thermo Scientific, USA) were employed to characterize the distribution of chromium and the chemical species of Cr and C on PAC at pH 3 and 7, respectively. The difference of removal mechanisms under the two pH values was delineated by XPS and Raman spectroscopy (DXR, Thermo Scientific, USA).

2.2. Materials
All the chemicals were analytical grade and the aqueous solutions were prepared with deionized water through Barnstead pure II water purification system (Thermo Scientific, USA). Potassium dichromate (K$_2$Cr$_2$O$_7$) was purchased from J.T.Baker and used for preparing 1,000 mg/L Cr(VI) as a stock solution. 1.0 M H$_2$SO$_4$ and 1.0 M NaOH were used to adjust the pH of the aqueous solutions. H$_2$SO$_4$, NaOH, KCl, and 1,5-diphenylcarbazide were provided by J.T.Baker. Commercial available AC was provided by Calgon company, its chemical composition was 97% carbon and 3% inorganic residual. The AC was treated by ball milling and obtained a PAC with an average size of 4 μm, a specific surface area of 929 m$^2$/g, and a pore radius of 15.9 Å, PAC used in this study was reported in our previous work (Fang et al. 2021b). Following the grinding step, the PAC was dried and stored in a desiccator.

2.3. Comparison of Cr(VI) removal at different pH
A comparison was conducted for the PAC removal efficiency at pH 3, 7, and 9 (Jiang et al. 2014). The desired mass of PAC (5 g) was mixed with deionized water (100 mL) for 1 h, then the pH was adjusted to 3, 7, and 9 using 1.0 M H$_2$SO$_4$ and NaOH aqueous solutions and monitoring the pH with an Orion 3 star pH meter (Thermo Scientific, USA). 0.2829 g K$_2$Cr$_2$O$_7$ reagent was added to the PAC suspension to prepare a 1,000 mg/L solution once the pH was stable. To follow the Cr(VI) uptake a 200 μL aliquot was withdrawn from the aqueous solution at 3, 5, 9, 15, 30, 60, 360, 1,440 min. The withdrawn aliquot was centrifuged in a centrifuge (Allegra™ 21, Beckman coulter, USA) for 15 min prior to analysis. The Cr(VI) removal capacity was calculated through Equation (1) (Krishna Kumar et al. 2019), wherein $\Gamma$ (mg/g) is the removal capacity, $C_0$ (mg/L) is the initial concentrations and $C_t$ is the concentration at time t, V (L) and M (g) are the volume of solution and dose of PAC, respectively.

$$\Gamma = \frac{(C_0 - C_t)V}{M}$$

2.4. Selection of desorption agents
Three kinds of desorption agents were evaluated to determine their effectiveness for desorbing the adsorbed chromium species on PAC. Analytical grade K$_2$Cr$_2$O$_7$ acted as a precursor of the chromium layer on PAC. To obtain adequate loaded chromium on PAC for assessment, consecutive uptake experiments were undertaken. 5.0 g PAC was mixed with 1,000 mg/L Cr(VI) aqueous solution at a fixed pH of 7 in a glass volumetric flask. This suspension was stirred magnetically (Thermo scientific, USA) at 100 rpm to prevent deteriorating of the chromium layer formed on the PAC. A 200 μL sample was withdrawn from the suspension at 0.25, 0.5, 1, 3, 5, 7, 9, 12, 15, 30, 60, 120, 1,440 min to determine the concentration of Cr(VI), then the suspension was filtered to collect the PAC, which was rinsed with deionized water, and dried before the following removal experiments. Consecutive removal steps were performed with 1,000 mg/L Cr(VI).
Dried chromium-load PAC after four repetitive adsorption runs was used for the desorption testing. All the batch experiments were conducted in duplicate under ambient conditions. The adsorption capacity at equilibrium for Cr on PAC was expressed as Equation (2)

\[
q_p = \sum (1000 - C_{e_i})V_i/M_i
\]  

where \( q_p \) (mg/g) is the content of chromium on PAC, \( C_{e_i} \) (mg/L), \( V_i \) (mL) and \( M_i \) (g) \( (i = 1, 2, 3, 4) \) are the equilibrium concentration, solution volume and mass of PAC of each removal cycle, respectively.

To desorb the loaded chromium from the PAC, 0.2M KCl, 0.2M H₂SO₄ and 0.1M NaOH were employed. 0.5 g chromium-loaded PAC was mixed with 50 ml of the desorption agent solution in a glass volumetric flask and stirred at 200 rpm, the concentration of desorbed chromium after 1, 3, 5, 7, 9, 24, 30, 48, 72, 96, 148 h was determined, the efficiency of desorption was determined through Equation (3).

\[
\eta = 100 \times (C_t/V)/(q_pM)
\]  

where \( \eta \) (%) is desorption efficiency, \( C_t \) (mg/L) is the dissolved chromium concentration at t time, \( V \) (L) and \( M \) (g) are the volumes of desorption solution and dose of PAC correspondingly. In addition, the performance of PAC treated with Cr(VI) after desorption with different chemical agents was evaluated.

2.5. The formation process of chromium layer at pH 3 and 7

To ascertain the route of the chromium layer formed on PAC, the chromium speciation after consecutive adsorption runs was analyzed with selected desorption agents (0.2M H₂SO₄ and 0.1M NaOH solution). Four desorption tests followed four successive removal cycles were performed and the increment content of loaded chromium on PAC between two successive adsorption runs was determined by Equation (4).

\[
\Delta q = (C_{i_i} - C_i)V/M
\]  

where \( \Delta q \) (mg/g) is the increased content of chromium on PAC, \( C_{i_i} \) and \( C_i \) (mg/L) are the equilibrium concentration of desorbed chromium after the two successive elution tests, \( V \) (ml) and \( M \) (g) are the volume of desorption solution and the dose of PAC after adsorption of Cr(VI).

The adsorption capacity of PAC loaded with chromium on Cr(VI) after the last elution assessment was examined, and all the adsorption experiments were conducted with 1,000 mg/L Cr(VI).

2.6. Analytical method

A colorimetric approach employing 1,5-diphenylcarbazide and a UV-Visible spectrophotometer (Thermo Scientific, USA) coupled with a 1 cm quartz cell was used to determine Cr(VI). 100 µL filtered solution was diluted to 10 ml and mixed with 0.1 mL 49% H₂SO₄, 0.1 mL 42.5% H₃PO₄, and 0.4 mL 0.2% 1,5-diphenylcarbazide solution, sequentially. The mixed solution stood for 10 min and was then measured by a UV-Visible spectrophotometer under 540 nm. The absorbance of deionized water was used as a reference. With prepared 0, 0.02, 0.05, 0.1, 0.2, 0.4, 0.6, 0.8, and 1.0 mg/L Cr(VI), a standard curve of concentration versus absorbance was constructed, this standard curve was used to determine the Cr(VI) concentration of the sample. The total concentration of aqueous Cr was analyzed by atomic absorption spectrometry (AAS, Varian Spectra 220FS), a 50 µL filtered solution was diluted to 10 mL and then sprayed into the flame of air-acetylene. The chromium ground state atoms formed under a high-temperature flame produce selective absorption of the 357.9 nm characteristic spectrum of chromium hollow cathode lamps, and the absorbance value is proportional to the concentration of Cr. The standard curve of total Cr was built in the same way as Cr(VI), and the concentration of total was determined by the standard curve as well. The presence of soluble Cr species in the solution was Cr(III) and Cr(VI), the concentration of aqueous Cr(III) was confirmed by the difference between total Cr and Cr(VI).
3. RESULTS AND DISCUSSION

3.1. Particle characterization

3.1.1. Surface morphology

The surface morphology of PAC after Cr(VI) adsorption under pH 7 was characterized by SEM-EDX and elements mapping. As seen in Figure 1, a chromium layer adsorbed mostly on the PAC surface. A similar observation was reported recently (Wang et al. 2020).

3.1.2. XPS spectra analysis

To further inspect the chemical species of Cr on the surface of PAC, the XPS analysis was employed. Figure 2(a) and 2(b) showed the XPS spectra, which were fitted and deconvoluted into multiple peaks by CasaXPS (version 2.3.23). The peak referenced as C 1s at 284.8 eV, the Shirley type was designated as the background subtraction. As presented in Figure 2(a), the Cr 2p peak due to Cr(VI), denoted that the Cr(VI) was adsorbed onto PAC. The XPS spectrum of PAC after being treated with Cr(VI) at pH 3 (PAC-pH 3) and 7 (PAC-pH 7) was built as presented in Figure 2(b). The Cr 2p region of the photo-electron spectrum was both detected for PAC-pH 3 and PAC-pH 7, which was consistent with the EDX spectrum shown in Figure 1. Cr 2p involves two energy levels, 2p 1/2 and 2p 3/2. The XPS spectrum of PAC-pH 3 can be divided into the Cr1, Cr2, and Cr3 peaks, where the binding energies (BE) value of Cr1 peak of PAC-pH 3 was 587.5 eV, which was very close to that of Cr2O3 (587.4 eV ± 0.2) (Grohmann et al. 1995). The BE for Cr2 and Cr3 of PAC-pH 3 were 579.2 and 577.8 eV, respectively, which can be attributed to Cr(VI) (Murphy et al. 2009; Ren et al. 2016; Zhang et al. 2019). Two contributions of Cr1 and Cr2 for the Cr 2p region of PAC-pH 7 were 587.7 and 578.0 eV, matching well with the binding energy for Cr(VI) and Cr2O3 (Biesinger et al. 2004; Ren et al. 2016; Chen et al. 2019). Due to XPS detection depth was no more than 4 nm from the sample surface, it can be said that the chromium layers on the surface of PAC-pH 3 were mainly constituted by Cr(VI) and PAC-pH 7 was mainly constituted by Cr2O3 (Chowdhury et al. 2012). Consistent with the present results, previous studies have demonstrated that the reduction and adsorption participated principally in the Cr(VI) removal on biomass (Wu et al. 2010; Cui et al. 2011). Moreover, the peak area ratio (Cr1 versus total peaks) as determined by CasaXPS was

Figure 1 | SEM-EDX micrographs (a and b) and SEM coupling with elements mappings (c and d) of PAC after Cr(VI) adsorption at pH 7.
69.93% and 39.91% Cr$_2$O$_3$(s) on the surfaces of PAC-pH 7 and PAC-pH 3, respectively. This higher content of Cr$_2$O$_3$ on PAC-pH 7 clearly evidenced that more Cr$_2$O$_3$ formed on the PAC at pH 7 than at pH 3, impeding the diffusion of Cr(VI) into the PAC, leading to a lower level of Cr(VI) removal. Besides, the ratio of O/C on PAC, PAC-pH 3, and PAC-pH 7 were 0.075, 0.113, and 0.157, respectively (Table 2). This indicates more O on the PAC after adsorption at pH 7 than at pH 3, due to more Cr$_2$O$_3$ precipitate. As noted in Table 2, the ratio of Cr/C on PAC-pH 3 was higher than that on PAC-pH 7, which further substantiated that Cr(VI) removal efficiency under pH 3 was superior to that under pH 7 and indicated that not only there was Cr$_2$O$_3$ on the PAC surface but also Cr(VI).

The surface functional groups of PAC before and after Cr(VI) adsorption were investigated using high resolution C 1 s spectra. The deconvolution of C 1 s produced four peaks, as shown in Figure 3. For PAC, there were four components: C=C (284.8 eV), C-O-C/C-OH (285.5 eV), C-O (286.7 eV), and COOR (286.7 eV) (Jieying et al. 2014). Similarly, the four peaks for PAC-pH 3 were assigned to C=C (284.8 eV), C-OH (285.8 eV), C-O (286.5 eV), and COOR (288.7 eV) (Jia & Wang 2015; Ma et al. 2018). Meanwhile, the four peaks for PAC-pH 7 were allocated to C=C (284.8 eV), C-OH (285.8 eV), C-O (286.5 eV), and COOR (289.5 eV) (Chen et al. 2020). The relative percentages of C-OH for PAC, PAC-pH 3, and PAC-pH 7 were 23.62%, 6.77%, and 6.53%, respectively, which suggested that the group of C-OH contributed to the removal of Cr(VI). The oxidation of C-OH to C-O by Cr(VI) caused the increase of the C-O group (Su et al. 2019). Nonetheless, following Cr(VI) adsorption at pH 3, the relative percentage of COOR on PAC rose from 15.22% to 20.56% and dropped to 10.41% after Cr(VI) adsorption at pH 7. This inconsistency may be due to Cr(VI) oxidized the surface of PAC at pH 3 and introduced more COOR groups (Yin et al. 2019), while the Cr(VI) exhibited weak oxidative capacity at higher pH (Gangadharan & Nambi 2014), and the removal of Cr(VI) under pH 7 consumed the COOR groups through the complex.

### 3.1.3. Raman spectra analysis

Raman spectroscopy investigation was carried out to evaluate the degree of structural order in carbonaceous PACs, as well as to investigate the difference in Cr(VI) removal mechanisms at pH 3 and pH 7. As depicted in Figure 4, the two sharp and strong bands are associated with the D-band (1,319 cm$^{-1}$, defect with sp$^3$ bonding) and G-band (1,563 cm$^{-1}$, graphitization with sp$^2$ bonding) (Cuesta et al. 1994). The intensity ratio of D-band (I_D) versus G-band (I_G) is often used to assess the degree

| Materials | O/C | Cr/C |
|-----------|-----|------|
| PAC       | 0.075 | 0.000 |
| PAC-pH 3  | 0.113 | 0.005 |
| PAC-pH 7  | 0.157 | 0.004 |
The value of \( I_D/I_G \) declined from 1.12 to 1.10 after treatment at pH 3 but increased from 1.12 to 1.14 after treatment at pH 7. As a result, the existence of defects in PAC was strengthened under pH 7, while at pH 3, a well-organized carbon structure formed. This divergence could be explained by the different Cr(VI) adsorption mechanisms at pH 3 and 7. In general, the reduction of surface oxygen-containing functional groups resulted in the increase of amorphous carbon at pH 7 (Cong et al. 2012; Yang et al. 2013; Li et al. 2016; Wang et al. 2017), while the oxidation of hybridized carbon atoms caused structural order to grow at pH 3 (Osswald et al. 2006).
3.2. Adsorption performance of PAC at pH 3 and 7

Figure 5 shows a comparison of adsorption performance at pH 3, 7, and 9 for 1,000 mg/L initial concentration of Cr(VI). Adsorption at those three pH values both reached pseudo-equilibrium immediately after 10 mins. Removal capacities for PAC at pH 7 and 3 were 16.8 mg/g and 20 mg/g, respectively, equivalent to 83.86% and nearly 100% removal efficiency. And adsorption capacity under pH 9 was 7.8 mg/g which was much lower than that at pH 3 and 7. It indicated that the removal performance of PAC on Cr(VI) was higher at low pH, PAC is probably protonated and attracted more anionic Cr(VI).

3.3. Desorption performance of Cr-loaded PAC with chemical agents

The desorption of chromium from the Cr-loaded PAC was evaluated using various chemical agents including H2SO4, KCl, and NaOH. Abundant chromium-loaded PAC was prepared at pH 7. As shown in Figure 6, the Cr(VI) elimination experiment using PAC was repeated four times. The duration time for every removal cycle was 24 hours. The next removal cycle began once the previous cycle was completed. After four consecutive repetitive adsorption cycles, the content of chromium on PAC...
reached 48.6 mg/g. The results of the desorption analysis using the three reagents are shown in Figure 7. It is noted that only Cr(III) was dissolved in H₂SO₄ aqueous solutions, whereas Cr(VI) was only desorbed in NaOH aqueous solutions. Negligible Cr(III) or Cr(VI) were detected in the KCl solution when compared to acidic and alkaline aqueous solutions. These findings agree well with Ouki & Neufeld’s (1997) findings that 3 g/L Cr(III) and 8.4 g/L Cr(VI) were recovered when exhausted carbon was regenerated under acidic and alkaline conditions, respectively (Ouki & Neufeld 1997). Due to the great stability of the adsorbed chromium on the PAC, desorption of Cr(VI) and Cr(III) from the Cr-loaded PAC with deionized water was minimal. Our results are also in line with those of Jing et al. (2011), who found that the desorption rate of Cr-loaded AC was low with distilled water (Jing et al. 2011).

As shown in Figure 6(a), Cr(III) precipitate dissolved gradually in 0.2 M H₂SO₄, and 13.0% Cr(III) precipitate was removed under acidic conditions, this process was depicted by Equation (5).

\[
\text{Cr}_2\text{O}_3 + 6\text{H}^+ \rightarrow 2\text{Cr}^{3+} + 3\text{H}_2\text{O} \tag{5}
\]

With the NaOH aqueous solution (Figure 6(c)), 21.3% Cr(VI) was desorbed, which was higher than the dissolved Cr(III) by the H₂SO₄ aqueous solution. This seems to contradict the XPS conclusion that less Cr(VI) adsorbed on PAC-pH 7 surface. A possible explanation for this might be that more internal adsorbed Cr(VI) in PAC particles were desorbed by alkaline elution. Cr(VI) adsorbed on AC was previously shown to be bound to the surface functional groups (Singha et al. 2013). An ion-exchange mechanism could explain the desorption of adsorbed CrO₄²⁻ (the dominant chromium species under alkaline conditions) on surface functional groups by NaOH aqueous solutions, the OH⁻ ions substitute for CrO₄²⁻ anions, as demonstrated in Equation (6) (Daneshvar et al. 2019).

\[
\text{PAC} - (\text{COOH})_2 \cdots \text{CrO}_4^{2-} (s) + 2\text{OH}^- \rightarrow \text{PAC} - (\text{COOH})(s) + \text{CrO}_4^{2-} + \text{H}_2\text{O} \tag{6}
\]

These findings could be useful in the development of a selective recovery method of Cr(III) and Cr(VI) using acid and alkali aqueous solutions.

3.4. Formation process of chromium layer at pH 3 and 7

To clarify the influence of pH on the development process of chromium layer on PAC, H₂SO₄ and NaOH desorption agents were used to determine the content of Cr(III) and Cr(VI) adsorbed on PAC-pH 5 and PAC-pH 7. Figure 8 compares the results

**Figure 7** | The effect of chemical agents on desorption performance of Cr-loaded PAC (a) H₂SO₄ (b) KCl (c) NaOH (d) H₂O (0.2M KCl, 0.2M H₂SO₄, 0.1M NaOH, 1 g/100 mL Cr-loaded PAC, 298 K).
obtained from elution tests of PAC-pH 3 and PAC-pH 7 after three consecutive adsorption cycles. It is apparent from the figure that the increment of adsorbed Cr(VI) is higher than reduced Cr(III) at each cycle for both PAC-pH 3 and PAC-pH 7. Hence it is conceivable to suggest that the adsorption process prevailed for Cr(VI) elimination. This finding was also reported by Daneshvar et al. (2019). Another significant observation was that for PAC-pH 3 and PAC-pH 7, the adsorbed Cr(VI) and reduced Cr(III) decreased as the cycles progressed. PAC-pH 3 showed higher Cr(VI) adsorption and reduction capacity. This may be due to the more generated Cr(III) precipitate accumulating on the PAC surface over time at the neutral condition, sheltering the PAC active sites from Cr(VI) adsorption.

3.5. Performance of Cr-loaded PAC after desorption

The performance of the PAC for Cr adsorption was assessed after chromium was desorbed from the PAC using the H$_2$SO$_4$ and NaOH. Re-adsorption experiments were conducted following the third cycle desorption step. As can be seen in Figure 9, 92.43% removal efficiency of Cr(VI) was achieved by PAC-pH 7 after washing with H$_2$SO$_4$, whereas only 51.72% removal was attained using NaOH aqueous. Therefore, it can be inferred that the Cr(III) precipitate is mainly responsible for the poor performance of PAC under neutral conditions. The removal performance after acid washing (92.43%) was higher than the preliminary removal efficiency (83.86%); this result indicated that the acid desorption procedure modified PAC.

Figure 8 | The increment of chromium loaded on PAC as consecutive Cr(VI) removal cycle (295 K, 50 g/L).

Figure 9 | The activity of chromium-loaded PAC-pH 7 after treated with H$_2$SO$_4$ and NaOH (1,000 mg/L Cr(VI), pH 7).
properties and introduced surface functional groups. These results are consistent with those of Guolin Huang et al. (2009), who improved AC’s Cr(VI) removal capacity by modifying it with nitric acid (Huang et al. 2009). As a result, it is proved that PAC’s limited removal capability for Cr(VI) at pH 7 was mostly due to Cr(III) precipitate that formed on the surface of PAC. This finding backs with the XPS results in that chromium oxide piled up mostly on PAC under neutral conditions. The sulfuric acid proved to be a potential chemical agent for the regeneration of Cr-loaded PAC after treating water contaminated with Cr(VI).

4. CONCLUSIONS

This study aimed to determine the mechanism of the limited sequestration capability of PAC on Cr(VI) under neutral conditions compared to acidic conditions. SEM-EDX substantiated that a chromium layer was formed on PAC, while XPS spectra corroborated the higher Cr$_2$O$_3$ content on PAC under alkaline conditions, resulting in poor Cr(VI) removal performance. Conversely, a lower Cr$_2$O$_3$ content on PAC under acid conditions is related to the higher Cr(VI) removal capacity. Desorption tests with H$_2$SO$_4$ and NaOH solution revealed that the precipitated Cr$_2$O$_3$ and adsorbed Cr(VI) can be selectively desorbed, proving that adsorption and reduction processes contributed significantly to the Cr(VI) removal. Consecutive desorption assays proved that the reduction and adsorption capability at 7 declined with time and were both lower than at pH 3. This is due to Cr(III) precipitate and adsorbed Cr(VI) blocking active sites. The superior performance of Cr(VI) removal of Cr-loaded PAC after desorption by H$_2$SO$_4$ further confirmed that the restricted removal performance under neutral conditions was ascribed to the formation of Cr$_2$O$_3$ passivation layer on the surface of PAC particle. The insights gained from this work may be of assistance to the recycling of chromium from exhausted AC and extend the lifespan of AC.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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