Preparation and Utilization of the Precursor Activated Carbon From Carbon Enriched Fuel Oil Fly Ash: Part II Removal and Speciation of Chromium(III & VI) in Wastewater

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Abstract

Activated carbon (AC) prepared from residual fly ash (FA) was activated by combined CO_2-steam gasification and physically modified with procaine hydrochloride (PQ^+Cl^-). Modified AC was used as a low cost and effective solid phase extractor (SPE) for removal, total determination and chemical speciation of chromium(III&VI) in wastewater. Pseudo-second order rate equation is proposed for assigning the kinetics of chromium(VI) sorption in aqueous HCl (1.0 mol L^{-1}) by PQ^+Cl^- modified AC . The data were correlated with surface structure of the SPE. A dual separation mechanism of chromium(VI) as a binary complex ion associate $[PQ^+.CrO_3Cl^-]$ in/on the modified AC via "weak base anion exchanger" and an added component of "surface adsorption" is proposed. At 2 mL min^{-1} flow rate Sorption of spiked chromium(VI) at known concentrations (0.5-20 μg mL-1) from water onto modified AC packed columns at 2 mL min^{-1} was achieved. The sorbed chromium(VI) species were successfully recovered (106.0±2- 110 ±3%, n=3) from AC packed column with NaOH (10 mL, 1.0 mol L^{-1}). Chromium(III) after oxidation to chromium(VI) was also enriched and eluted from the AC packed column and analyzed. Modified PQ^+Cl^- AC packed column was also used for total determination and speciation of chromium(III & VI) species at trace levels in environmental water samples. Good apparent recovery percentage (94.6±6.3-102.0± 8.5 %) of chromium species was achieved confirming the analytical utility of the modified AC-packed column for removal, total determination and speciation of chromium(III & VI) species in environmental water samples.

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Introduction

Heavy metal ions at trace levels in water represents a major of great concern for environmental engineers and chemists[1-3]. Wastewater (Industrial and domestic) affects the health of people and causes severe damage to the environment if not managed properly[4, 5]. Chromium(VI) is highly toxic and it has great mutagenic and genotoxic effects on biological systems whereas chromium(III) is essential trace nutrient[6, 7]. Biological reduction of Cr^{6+} species to intermediates e.g. Cr^{5+} and Cr^{4+} play a crucial role in its toxicity[8]. In drinking water, the permissible concentration level of chromium(VI) reported by WHO set at 0.05 µg L^{-1} [9] whereas USA-Environmental Protection Agency (EPA) guide recommended a level of 100.0 µg/L[10]. Allowable limit of discharge of Cr^{3+} in surface- and seawater varies from 0.5 to 2.0 mg/L, respectively[10]. Manufacturing industries of aluminum, dye, paint, ink and tannery etc are the main sources of Cr^{6+} [11]. Removal and chemical speciation of Cr^{3+} and Cr^{6+} species from wastewater by low cost adsorbent before disposal are of great interest in water due to the bio dependence of Cr(III) oxidation in plants, soil sand sediments[11-17].

The potential risk of FA generated in the local desalination power stations is considered as a solid waste that creates pollution problem in its landfill and surroundings areas[18]. Coal, oil fuel and heavy fuel oil are the most common fuel used in thermal power stations in most countries[19, 20]. Utilization of various fossil fuels e.g. burning coal or heavy fuel oil in power generation plants and seawater desalination units are the major source of bottom ash and fly ash[21]. Fly ashes seemed to too high, their chemical analysis indicated a high level of toxic metals; hence their utilization for the production of the precursor AC as a low cost solid phase extractor (SPE) for removal of heavy metal ions, dyes, phenols, chrysoidine Y, polyaromatic hydrocarbons in wastewater and capture of atmospheric gaseous species e.g. CO_2 has been implemented and /or proposed recently in the literature[21-37]. Large amount of FA is directly discharged as landfills and ash ponds, whereas a percentage (20 %) of FA is used in concrete production, road basement material, waste stabilization/solidification, amendments of soft soil and in geo polymers[37, 38].

In drinking water, the trace level of chromium is not compatible with the limit of detection of numerious spectrochemical methods. Thus, enrichment steps of chromium(VI) are of great importance to enhance the detection of the reported methods[39-45]. Thus, numerous SPE including AC have been published for separation and subsequent speciation of low levels of chromium species[37-59].

Various AC exhibit capacity performance towards chromium(VI) and other inorganic and organic analyte, because of their excellent textural properties (pore pore sizes and structures, large surface areas). Agricultural by-products and FA materials are the major sources for commercial AC[20-27]. Based on the significant growth in Saudi Chemical industries[23, 24], this reports: i) Characterization of AC as an efficient SPE; ii) The sorption profile and kinetics of the uptake of chromium(VI) from aqueous HCl media onto $PQ^+.Cl^-$ modified AC; and finally iii) Determination and speciation of chromium ions (III & VI) by modified AC packed column.

Materials and Methods
Sampling

FA samples (C_1-C_6) were randomly collected from three locations around Rabigh (one of the smallest towns in Saudi Arabia and lies at latitude 23 ^{0} N and longitudes 400 30 'E along the Red Sea coast in the west central part of the Arabian Shield) water desalination power station. Residual FA samples of heavy fuel oil (Vacuum gas oil, Bunker "C") generated from the power station were dried in air for 21 days. FA samples were mixed with HCl (37%v/v) solution at FA waste/HCl weight ratio of 1: 20 (m/v) in a polytetrafluoroethylene beaker for 16-17 h at 25 ^{0}C. The solution mixtures were filtered and washed several times with water. The samples were dried at 105 ^{0}C for one day and finally stored in a desiccators.

Reagents and Materials

Glassware's and polyethylene (LDPE) bottles were washed with con HNO_3, and rinsed with doubly deionized water before use. A.R. grade chemicals were used as received. polyethylene (LDPE) bottles Standard solutions (1000.0 µg mL $^{-1}$) of Cr (VI) and Cr(III) were prepared from BDH (Poole, England) Na_2CrO_4 and $Cr(NO_3)_3$ in de-ionized

water, respectively. Diluted solutions of chromium (0.05- 20 µgmL^{-1}) were prepared from the stock by dilution and was stored in LDPE bottles. BDH H$_2$O$_2$ (30% v/v) was used for oxidizing Cr(III) to chromium(VI) in aqueous alkaline solution[46, 47]. At 25 °C, the solutions were stored in amber glass bottles. The reagent [2-(diethylamino)ethyl 4 aminobenzoate] hydrochloride (1.0 %w/v) commercially named as procaine hydrochloride (PQ$^+$.Cl-) and HCl were prepared individually in water (100 mL).

Apparatus

N$_2$ adsorption measurements were performed at P/P° range 0.005 to 0.99 on a NOVA 2200e instrument (Quntachrome) at liquid nitrogen temperature of the FA and AC samples. A GSL-1800S60, MTI Inc., USA, Richmond, California tube furnace connected to an electric heating boiler was used for the heat treatment of the samples. Nitrogen gas (AHG, 99.99%) was used as an adsorbate. The equipment was connected to a rotary van vacuum pump (Pfeiffer vacuum) to obtain exhaust pressure of 250-1500 mbar and a final pressure ≤ 6.0×10-3 mbar[59]. A Perkin Elmer inductively coupled plasma – optical emission (ICP- OES), Optima 4100 DC (Shelton, CT, USA) and UV-visible (190-1100 nm) spectrometers were operated at the optimized parameters. ICP-OES is optimized daily and operated as recommended for analysis of Cr. The pH measurements were recorded on a Thermo Fisher Scientific Orion model 720 pH Meter (Milford, MA, USA). Milli-Q Waters Plus system (Milford, MA, USA) and digital micropipettes (Volac) were used for preparation of the solutions in deionized water. A mechanical shaker (Chicago, CH, USA) with 10 – 250 rpm shaking rate and glass columns (5.0 cm × 0.5 cm i.d) were used.

Preparation of AC

Dried FA samples (≈3-4 g) were dipped into H$_2$O$_2$ (100 mL, 30%v/v) for 24 h to oxidize the volatile organic impurities , filtered and washed with water. At 100 °C, the samples were heated for 60 min to remove the moisture content, respectively. Heating of the samples were then heated in a tube furnace connected to an electric heating boiler for passing combined CO$_2$ (grade 2.5-B) -steam at 4 psi at absolute pressure inside the tube below 0.12 MPa (Mega Pascal). The furnace was maintained at a

heating rate of 5 °C min^{-1} and 6 psi. Inside the tube, the absolute pressure was always kept below 0.12 MPa (Mega Pascal). Samples were heated between 850-950 °C at 15 °C/min heating rate for 3 h at 120 mL min^{-1} flow rate to a final carbonization process and activation at 950 °C. AC samples were left to cool down, washed with hot distilled water (until the pH is neutral) and dried in the oven at 105 °C for 24 h . The calculated weight loss of FA samples during activation was in the range 16.9-18% m/m.

Preparation of PQ$^+$Cl$^-$ modified AC

Initially, PQ$^+$ .Cl$^-$ reagent was dissolved in 100 mL of deionized in water (1.0% w/v). This solution was shaken with the AC (≈ 5.0 g) with efficient stirring in a jar test for 30 min as reported[59]. The synthesized PQ$^+$.Cl$^-$ treated AC was separated out from the liquid phase after centrifugation, washed at least three times with acetone and water and finally dried for 4 h under N$_2$ gas.

Recommended Procedures
Batch Experiments

In dry LDPE bottle, aqueous solution (100 mL) containing known concentration (20.0µg mL^{-1}) of chromium(VI) at various pH were shaken with accurate weights (0.1 ± 0.001 g) of modified AC at room temperature for 1 h. After shaking, chromium(VI) remained in the aqueous solutions was analyzed spectrophotometrically[57]. At trace level of chromium(VI) lower than the limit of detection (LOD) of DPC method[57], ICP-OES was used. At equilibrium, Sorbed chromium (VI), at equilibrium, qe onto modified AC was determined and the distribution ratio (D) and the extraction percentage (% E) of chromium (VI) uptake were determine[46, 47]. Similarly, the influence of mineral acids, HCl acidity, shaking time, media polarity and surfactant on chromium(VI) sorption was also studied following the same procedures. Triplicate measurements at 25±0.1 °C were performed and the results of % E and D of chromium(VI) sorption were calculated as means ± standard deviation (n=3).

Separation of Chromium(VI) by Modified AC Packed Column

Various concentrations (0.5-20 µg mL^{-1}) of chromium(VI) in aqueous HCl (100 mL, 1.0 mol/L) were percolated through the adsorbent

(0.5± 0.001 g) packed column at 2.0 mL min^{-1} flow rate versus blank. AC packed columns of the blank and sample were washed with HCl solution (100 mL). Chromium(VI) in the effluent solution was then determined spectrophotometry[57] or by ICP-OES via standard curve of Cr. The analyte sorbed analyte on the AC packed column was then stripped with NaOH (10 mL, 1.0 mol/L) and analyzed versus reagent blank.

Separation of Chromium(III)) by Modified AC Packed Column

In aqueous HCl (1.0 mol/L) solution, various known concentrations (0.5-20 µg mL^{-1}) of chromium(III) were transferred to conical flask (50.0 mL). The aliquots were, reacted with H_2O_2 (2 mL, 10% w/v) in alcoholic NaOH (1.0 mol/L), boiled for 20 min, cooled and the solution mixtures were adjusted to pH ~zero by HCl (1.0 -2.0 mol L^{-1}). The solutions were percolated through the modified AC packed column and analyzed for chromium(VI)[57]. Sorbed analyte were stripped from the column with NaOH (1.0 1.0 mol/L) and quantified spectrophotometry[57].

Total Determination and Speciation of Chromium (III & VI) Species

Various solutions (0.5L) of chromium (III) & (VI) mixtures at a total trace levels $\leq$ 0.1 µg mL^{-1} were passed through the modified AC packed column at 2 mL min^{-1} flow rate. Chromium(VI) species in the effluents were analyzed as mentioned for chromium(VI)[57]. Another aliquot samples (0.5L) were oxidized to chromium(VI), percolated through the modified AC packed column and analyzed as mentioned above for chromium(III). The absorbance (A_1) or the ICP-OES signal (I_1) of the first aliquot is a measure of chromium(VI) ions whereas the absorbance (A_2) or the signal intensity (I_2) of the second aliquot is equivalent for the sum of total chromium(III & VI) species in the mixture. Hence, the absorbance (A_2-A_1) or ICP-OES signal (I_2-I_1) intensities is equivalent to of chromium(III) in the aliquots.

Analytical Application

In LDPE bottles, samples of industrial wastewater (1.0 L) were filtered through a 0.45 µm membrane filter (Milex, Millipore Corporation). Samples

were immediately spiked with various amounts (0.05-0.5 µg) of chromium(III & VI), treated with HNO_3-H_2O_2 (100 mL, 1:1 v/v) and boiled for 10 min. The aliquots were centrifuged for 5 min and percolated through adsorbent packed column and analyzed as described for chromium(III). Sorbed Cr species were then stripped with NaOH and analyzed by ICP-OES.

Precision and Accuracy

The precision of the extraction and recovery in the overall procedures, was tested by subjecting three sub samples to the sequential procedure. The limit of detection (LOD) (µg/g of dry ash) was defined as LOD = $3S_{y/x}$/b where $S_{y/x}$ = standard deviation of y- residual and b is the slope of the standard plot. Precision is low as the analyte concentration approaches the LOD and it improves for higher concentrations.

Results and Discussion

FA represents a major issue in the coming decades since electricity generation would remain predominantly heavy fuel and coal-based burning. Thus, FA solid waste is current increasing/year and in 2016, it is expected to increase to 300-400 MT/year. Utilization of power generation FA wastes represents one of the most common problems of thermal power plants for heavy oil and solid fuel burning. Thus, great efforts performed for better utilization and application of FA generated from heavy fuel oil FA for the production of AC adsorbent for use as a SPE for removal and/or minimization of chromium (VI) from wastewaters.

Characterization of FA and AC

Chemical analysis of FA samples revealed considerable amount of V, Fe and Ni. On the other hand, Na, S, K, Si, Al in addition to other trace elements are the next abundant elements. The average content of V, Fe and Ni content lies in the range 3625.1 ±21.8; 4057.0±32.7 and 751.2 ±13.7 µg/ g, respectively. The content of Fe and V is comparable with the data reported except for Ni[42]. Digestion of FA containing Ni requires enough time resulting in an incomplete digestion of FA and it is also too tedious. Moreover, Ni able to form organo Ni compounds with the oxygenated

and organocarbon species forming stable complex species of Ni in the FA samples. C, H, N, total CHN contents and weight loss of FA samples were in the range 87.93± 5.3; 0.15± 0.03; 1.51± 0.27, 89.51± 2.14% and 91.45%, respectively. These values are in agreement with FA of other heavy fuel oil[24, 59]. The major particle sizes of FA were in the range 1.8-16.4 µm with 50 frequencies in comparable with FA generated from heavy fuel power plants[58, 59]. XRD patterns (Fig. 1) of FA at room temperature revealed similar broad peaks which are highly disordered and amorphous[58, 59]. Anorthite ($CaAl_2Si_2O_8$) was the only aluminosilicate found with a FOM close to 20 whereas calcium containing minerals e.g. $CaSO_4$, $KCaCl_3$ were noticed[58]. On the other hand, the composition of FA was porous spheroid of unburned carbon with diameters within a range from 10.0 to 120 mm larger than that of black carbon and contains pores few mm in sizes.
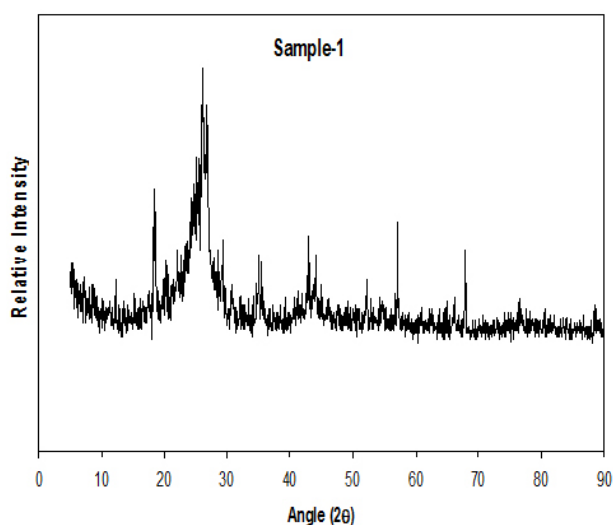

Fig. 1: X-ray diffraction pattern of FA sample.

SEM images (Fig. 2) of FA (sample C_3) showed many of iron spheres most likely composed of Fe_2O_3 mixed with amorphous alumino-silicate. Calcium associated with S and/ or P in distinct particles was also noticed not with amorphous alumino-silicate. Small pores may have formed during the combustion process of heavy oil FA. The morphology of FA particles is mainly spherical, porous spheroid of unburned carbon.These particles are porous, hollow and granular in size. The burn of FA at 850 and 950 ^{0}C lies in the range 16.15-25.39 and 16.67-64.6%, respectively.

Major particle size distributions (PSD) of AC were in the range 1.8-16. µm with frequencies 90, respectively. The surface area and pore volume of AC were 775.9 m2/g and 0.138 cc/g, respectively were reported earlier[59]. The calculated pore volume (0.138cc/g) of the AC represents the most successful approach for activation of FA at 950 ^{0}C for 2 h. The pore volume decreased or did not develop quite well at temperature of 850 ^{0}C for different time intervals. The data suggest further modification of AC by ion pairing reagent like procaine hydrochloride (PQ+.Cl-) for use as a SPE for removal of chromium(VI) from water. SEM images (Fig. 3) of AC before and after modification with PQ+.Cl give evidence to the more porous nature of the template carbons. In the AC and modified AC little porosity is also seen with their respective fraction of mesoporisity.
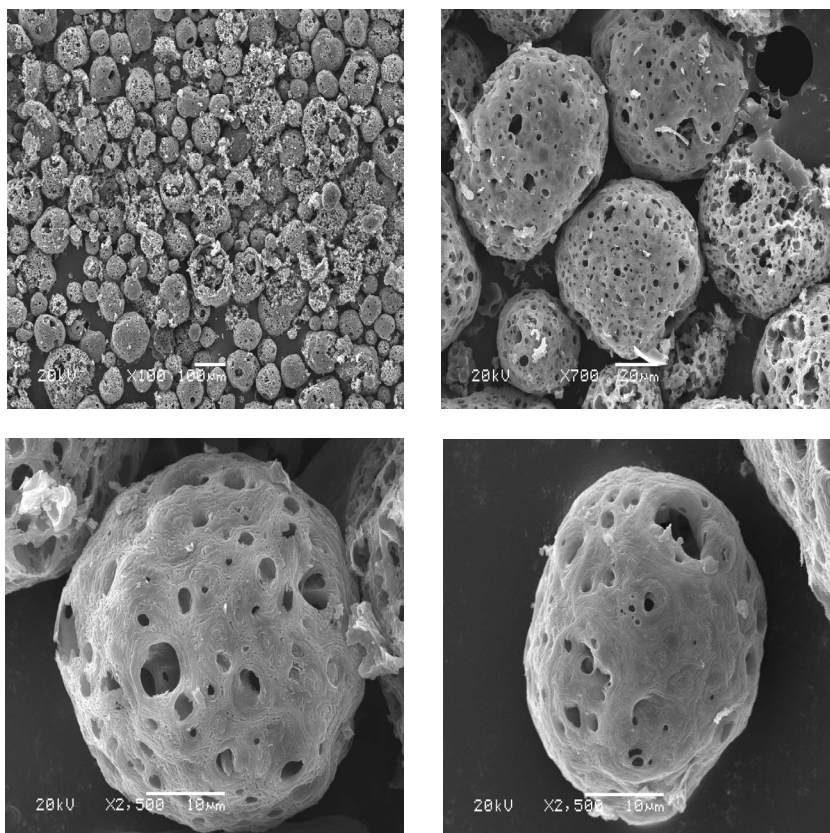
Fig. 2: SEM micrographs of FA (C$_3$) at different resolutions 100, 20, 10 and 5 µm.
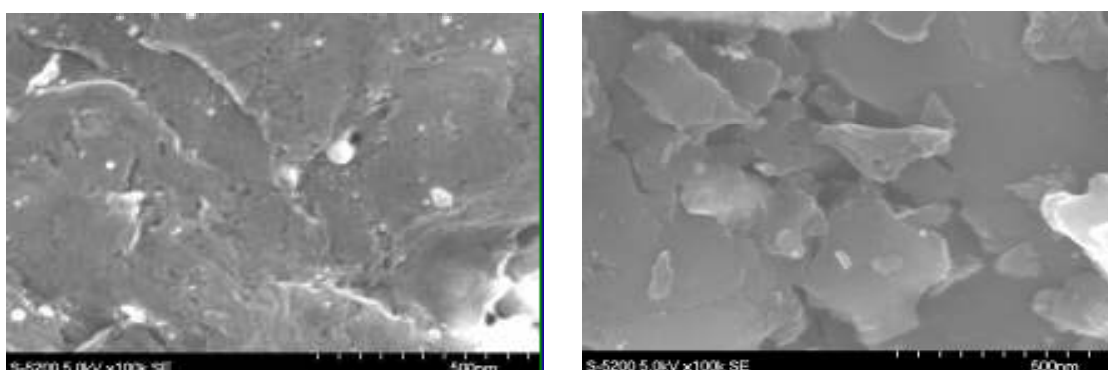
**Fig. 3: SEM images of AC before (A) and after modification (B) with procaine hydrochloride.**

Sorption Characteristics of Chromium(VI) onto Modified AC

Chromium (VI) species in HCl (1.mol L^{-1}) present as halochromate (CrO$_3$Cl$^-$) and it can be extracted into SPE by complex ion associate formation as reported earlier[46, 47]. Thus, preliminary batch experiments on chromium(VI) uptake from aqueous HCl media by PQ$^+$.Cl modified AC were critically performed. Considerable adsorption of chromium(VI) by the PQ$^+$.Cl$^-$ modified AC adsorbent was achieved. Sorbed chromium(VI) was found to depend on extraction media pH. Thus, the use of PQ$^+$.Cl$^-$ modified AC for the extraction of chromium(VI) at different pH was critically studied out.

The adsorption of chromium(VI) at two different concentrations (5, 7.5 µg/mL) from aqueous solution (100mL, 10µg mL^{-1}) at different pH by PQ$^+$.Cl$^-$ modified AC was examined over a wide range of pH after 1 h shaking period. Maximum % E and the D of chromium(VI) from the aqueous solution was achieved at pH ~ zero and lowered at higher pH of the solution pH. Thus, the influence of mineral acid e.g. HCl, HNO$_3$ and H$_2$SO$_4$ at 1.0 mol/L concentration on chromium(VI) uptake was studied. Of which, only HCl showed satisfactory extraction of chromium(VI) onto AC adsorbent. The formation of chlorochromate [CrClO$_3$]$^-$ anion which is able to form complex ion associate on/in PQ$^+$.Cl$^-$ modified AC may account for the observed trend.

HCl concentration and the formation of [CrClO^3]$^-$ anion play a crucial role on chromium(VI) uptake. Thus, the effect of various concentrations (1-5 mol L^{-1}) of HCl on chromium(VI) sorption by the used adsorbent was studied (Fig. 4). On raising HCl concentration up to 2.0 molL^{-1} , chromium (VI) retention increased and remained constant up to 3.0 mol L^{-1}. Hydrolysis, instability or the incomplete formation of the produced [PQ$^+$.CrClO$_3$]$^-$ AC ion associate on/in the adsorbent may account for the observed decrease in chromium(VI) extraction. Thus, in the next experiments, the concentration of HCl was adopted at 2 mol L^{-1}as a suitable extraction medium.
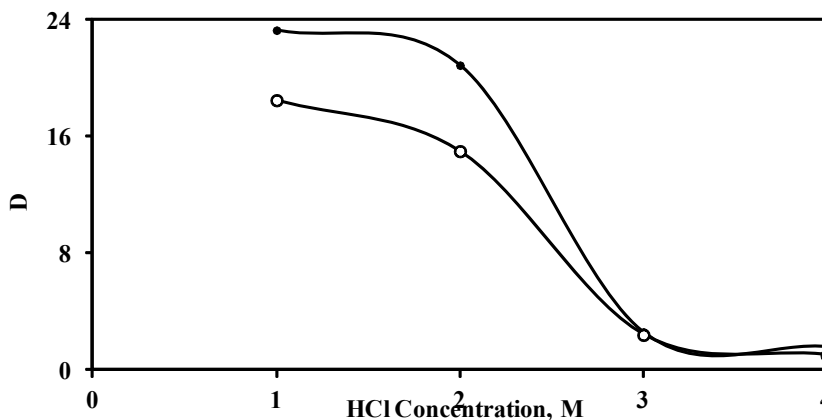

Fig. 4: Influence of HCl on chromium (VI) (5, 7.5 µg/mL) uptake onto modified AC at 25±1 ˚C.

Based on the achieved results at pH and HC and the data reported[46], a "weak base ion exchange" of the ion associate [CrO$_3$Cl$^-$. PQ$^+$] is proposed. For analyte uptake by the modified AC. Based on the results of pH, mineral acids, HCl and the surface characteristics of the AC a dual – mode of chromium(VI separation as [PQ$^+$.CrO$_3$Cl$^-$] ion associate via a "weak base anion exchanger" and an added component for "surface adsorption" is most likely proposed mechanism.

The most common specie at HCl ≤ 3.0 mol L^{-1} is hydrogen chromate oxoanion (HCrO$_4$–)[46, 47] which in HCl media converted to chlorochromate anions [CrO$_3$Cl$^-$] as follows:

$$HCrO_4^- + H^+ + Cl^- \quad [CrO_3Cl^-]_{aq} + H_2O \qquad ...(1)$$
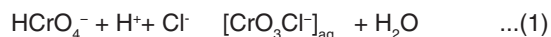
The bulky anion [CrO$_3$Cl]$^-$ is retained in/on the modified AC as follows:

$$[CrO_3Cl^-]aq + [PQ^+.Cl]^-_{AC} \quad [PQ^+.CrO_3Cl^-]_{AC} + Cl^-_{aq} \qquad ...(2)$$
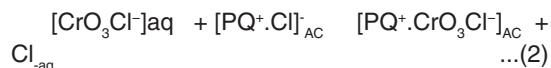
The solvent polarity on chromium (IV) extraction by the modified AC was also studied at various proportions of ethanol (1-10 %v/v). Chromium(VI) uptake increased linearly on adding ethanol up to 5% (v/v) and remained constant. The change in media polarity makes the binding sites of the AC sorbent around chromium (VI) more hydrophilic

and diminishing the need of water for solvating molecules. Thus, the analyte uptake decreased in/on the used adsorbent[47].

The effect of Triton-X 100, tetraethyl ammonium chloride or sodium dodecyl sulphate (SDS) on chromium (VI) adsorption was tested. In the presence of tetraethylammonium chloride up to 0.1% (w/v), chromium(VI) sorption increased and leveled off at higher concentrations of surfactant. The change in the viscosity of the environment of the around the complex anion associate $[CrO_3Cl]^-$ is most likely account for the observed trend[46, 47]. The solution viscosity enhances aggregation of the associate thus, reducing the diffusion rate of chromium(VI).

Kinetics of Chromium(VI) Adsorption by Modified AC

Chromium (VI) adsorption from aqueous HCl media (≤ 3.0 Mol L^{-1}) onto the modified AC was found fast and reached equilibrium within short time (~20 min). Thus, Weber-Morris equation[61] is proposed:

$$Qt = Rd\,(t)^{1/2} \qquad \qquad ...(3)$$

The amount of chromium(VI) adsorbed on the modified AC was plotted versus square root of time (min), where R_d = the rate constant of intraparticle transport in mg g^{-1} min$^{-1/2}$.
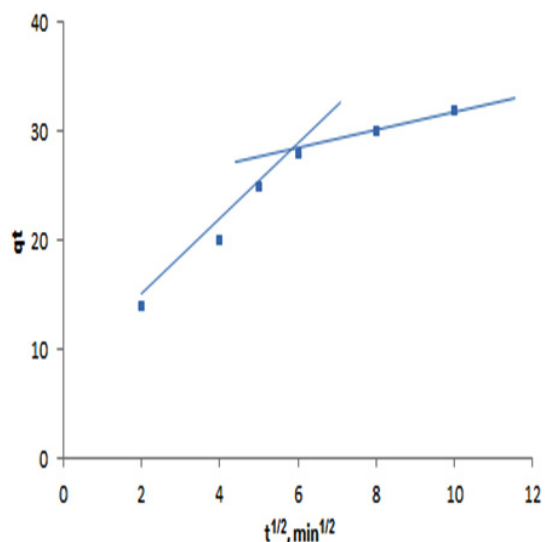
Fig. 5: Sorbed chromium(VI) concentration from aqueous HCl solution (50 mL) at pH zero and 25±0.1ºC onto PQ⁺.Cl⁻ modified AC (0.2±0.01g) as a function of square root of time.

The diffusion rate was rapid in the initial stage and slightly decreased on passage of time. The plot of qt versus time was linear (Fig. 5, $R^2 = 0.986$) in the initial stage for chromium (VI) retention onto adsorbent up to 10 ± 1 min and deviate on increasing time of shaking. The diffusion rate was high and decreased on time passage indicating that the rate of adsorption is film diffusion at the early stage of extraction[49]. The values of R_d determined from the two slopes of the plot were found 2.796 ± 1.01 and 0.793 ± 0.02 with $r^2 = 0.989$ and 0.992, respectively. The existence of different pore size is most likely account for the change in the slope[60, 61].

Chromium(VI) sorption was further subjected to the linear form of Lagergren model for pseudo – first order is expressed as follows[60]:

$$\log (q_e - q_t) = \log q_e - K_{Lager}/2.303\ t \qquad ...(4)$$

where, q_e is the amount of Cr (VI) sorbed at equilibrium per unit mass of sorbent (μ moles g^{-1}); K_{Lager} = first order overall rate constant for the sorption process per min and t is the time in min. The values of K_{Lager} and q_e computed from the slopes and intercepts of the linear plots of log ($q_e - q_t$) versus t at various analyte concentrations (20, 40, and 60 µg mL^{-1}) were in the range 0.028 - 0.030 min^{-1} and 9.03 - 23.3 mg g^{-1}, respectively with correlation coefficients ($R^2 = 0.91$-0.94) (Table 1). Because of the large difference between the calculated and experimental values of q_e, this model is not often used for the estimation of q_e[60]. Thus, the Cr (VI) adsorption onto the modified AC at 25 ± 1 ºC was subjected to the second order kinetic model[61, 62]:

$$t/qt = 1/h + (1/qe)t \qquad \qquad ...(5)$$

where, $h = k_2 q_e^2$ = the initial sorption rate. Under such circumstances, The plots of t/qt versus t at various concentrations (20, 40, and 60 µg mL^{-1}) gave linear relationship as demonstrated in Fig. 6. The second-order rate constant, k_2, equilibrium capacity, q_e, and the correlation coefficient (R^2) for the initial Cr (VI) concentrations are given in Table.1. R^2 values were in the range 0.98-0.99, thus the analyte uptake by the proposed SPE followed second order rate equation.

Table 1: Calculated kinetic parameters for pseudo first-order and second-order kinetic models for the adsorption of Cr (VI) onto PQ⁺.Cl⁻ modified as an adsorbent

S. No	Cr (mgL⁻¹)	qe (mg g⁻¹) experimental	First-order kinetic model			second-order kinetic model		
			K_1(min⁻¹)	q_e	R^2	$K_2 \times 10^3$	q_e	R^2
1	20	13.92	0.028	9.03	0.91	7.66	13.7	0.98
2	40	32	0.028	17.9	0.96	1.88	33	0.98
3	60	20.1	0.030	23.3	0.94	0.88	24	0.99
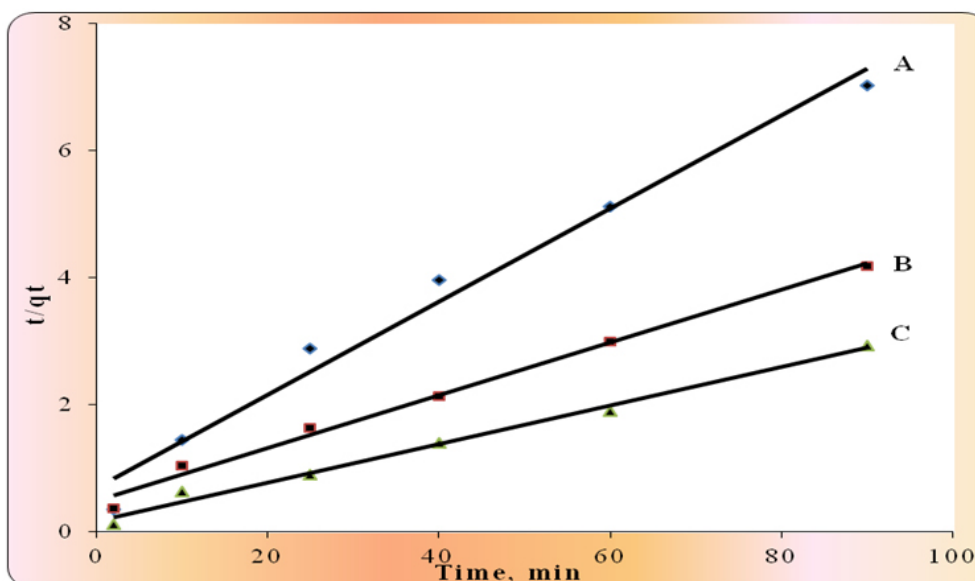
Fig. 6: Second-order plot for the retention of Cr (VI) using modified AC for the initial adsorbent concentrations of A: 20; B: 40; and C: 60 µg mL⁻¹.

Separation of Chromium(VI) by PQ⁺.Cl⁻-AC Packed Columns

The sorption profile and the kinetics of chromium(VI) by the proposed modified AC suggested the use of the modified AC adsorbent in packed column for chromatographic separation of chromium(VI). Known concentrations (0.5-20 µg mL⁻¹, 0.1 L) of chromium(VI) were passed through modified AC packed column at 2 mL/min flow rate at optimized conditions. ICP-OES analysis of Cr in the effluent revealed complete sorption of chromium(VI). Sorbed chromium(VI) species were finally quantitatively stripped (106.0±2- 110 ±3%) with NaOH (Table 2). The proposed modified AC packed column was also used for recovery of chromium(III) after its oxidation to chromium(VI)[46]. Known concentration (0.5-20 µg mL⁻¹) of chromium(III) after oxidation were passed through the modified AC packed column. The retained chromium(VI) species were stripped from the AC packed column and an acceptable apparent recovery percentage (90.0 ±6-96.0±0.6) of chromium(III) was achieved (Table 2). Incomplete oxidation of chromium(III) may account for the decrease in the recovery percentage. Total determination of chromium(III & VI) ions in their mixtures were also performed and analyzed following the optimized conditions for chromium(III) ions. The signal intensity represents a measure of total chromium(III & VI) species in the mixture and a recovery percentage in the range 92 (±3.9)-104.3 (±4.4) % was achieved.

Table 2: Analytical results for chromium(III & VI) in deionized water sample

Added, μg mL⁻¹		Found, μgmL⁻¹		Recovery*, %	
Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)
0.5	0.5	0.45 ±0.03	0.53±0.01	90.0 ±6	106.0±2
10	10	9.6 ±0.09	10.7±0.07	96±0.9	107±0.7
20	20	19.2 ±0.12	21.6 ±0.5	96.0±0.6	110 ±3

* Average of three measurements ±standard deviation (n=3).

Analytical Applications

The analytical utility of the proposed AC packed column was tested by the recovery study of a total concentration of chromium(III) and/or chromium(VI) species ≤ 50μg/ L (0.5L) spiked to tap and wastewater. Various concentrations of chromium(III) and/or (VI) were spiked into tap- and wastewater samples and analyzed following the optimized procedures for chromium(III). Complete adsorption of chromium was achieved as indicated from ICP-OES analysis of chromium in the effluent. Sorbed chromium species were recovered with NaOH (10 ml, 1 mol/L) and analyzed by ICP-OES. The results are demonstrated in Table 3. Apparent recovery percentage (94.6±6.3-102.0± 8.5 %) of chromium confirming the analytical utility of the proposed AC packed column for complete removal and/or determination of chromium species in environmental water samples.

Table 3: Determination of total chromium(VI) in distilled and tap water by the developed PQ⁺.Cl⁻ treated AC *

Sample	Cr(VI), μg L⁻¹		
	Added	Found	Recovery, %
Wastewater	100	102.6± 8.50	102.0± 8.5
Tap water	500	480.4±2.9	96.0 ± 0.58
Tap water	100	94.6±6.3	94.6±6.3

* Average ± standard deviation (n=5).

Conclusion

The manuscript provides a snapshot of the field of FA utilization. Modified AC has a great poten-tial as an effective SPE for removal, enrichment and/or total determination in environmental water samples. Utilization of FA in analytical chemistry for speciation of chromium(III & VI) species and other heavy metal ions represents challenges. The proposed PQ⁺Cl⁻. AC column offers LOD lower than maximum permissible levl (MAL) of chromium(VI) in water set by WHO and favorably com-pared with LOD of many spectrochemical and chromatographic techniques. AC adsorbent is worthwhile alternative SPE to the commercial active carbon. The used AC packed column could also be extended for trace enrichment of Cr and other toxic metals in water samples by on-line collection from large sample volumes of water. AC packed column could be reused for 3-4 times with-out decrease in its performance.

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