Int. J. Environ. Sci. Technol. (2014) 11:2037–2050
DOI 10.1007/s13762-013-0406-x

ORIGINAL PAPER

Impact of petroleum coke characteristics on the adsorption of the organic fractions from oil sands process-affected water

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Received: 23 August 2012 / Revised: 30 April 2013 / Accepted: 21 October 2013 / Published online: 7 November 2013

Abstract Petroleum coke (PC) is a waste by-product generated during the oil upgrading processes by the petroleum industry. The continuing accumulation of large quantities of PC requires the development of innovative strategies for the effective utilization of this carbon-rich material. In this study, PC was used for the removal of naphthenic acids (NAs) and acid-extractable fraction (AEF) from oil sands process-affected water (OSPW), generated during the oil refining process. A systematic study on the adsorption of organic fractions, vanadium leaching from PC, adsorption mechanisms, and the effect of physico-chemical characteristics of the PC on adsorption process was performed. Physico-chemical properties of PC were determined by Fourier transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy, thermogravimetric analysis (TGA), scanning electron microscopy, and Brunauer–Emmett–Teller surface area analysis. AEF and NAs removals of 60 and 75 %, respectively, were achieved at PC dose of 200 g/L after 16 h of contact. FT-IR and TGA analysis of PC suggested the physisorption of organic compounds onto the surface of PC. The calculated mean free energy of adsorption ($E < 8$ kJ/mol) also indicated the physisorption of organics to the PC surface. The hydrophobic interactions between the NAs and the PC were suggested as the dominant adsorption mechanisms. The vanadium release occurred when PC was mixed with OSPW and vanadium concentration increased with an increase in the PC dose. Speciation analysis indicated that the vanadium leached was predominantly vanadium (V) and insignificant amount of vanadium (IV) was also detected.

Keywords Adsorption · Petroleum coke · Naphthenic acids · Vanadium · Oil sands process-affected water

Introduction

With a recoverable 170.4 billion barrels of bitumen, Athabasca oil sands in Alberta, Canada, constitutes the third largest oil deposit in the world after Venezuela and Saudi Arabia (ERCB 2008; Gray et al. 2009; Watkins 2010). The increasing worldwide demand in crude oil leads to a steady increase in the amount of waste by-products generated by the petroleum industry including coke, fly ash, and water tailings (Allen 2008a, b; Majid and Kotlyar 1999; Malekshahian and Hill 2011). Petroleum coke (PC) is generated in large quantities during the oil refinery process when the ratio of H:C has to be upgraded (Speight 1998). With a 20 kg of PC typically produced per barrel of synthetic crude oil (Zubot 2010), the PC inventory in Alberta has reached 68 million

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Electronic supplementary material The online version of this article (doi:10.1007/s13762-013-0406-x) contains supplementary material, which is available to authorized users.

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tonnes in 2010 (ERCB 2011). The presence of low combustible volatiles and relatively inactive carbon forms (Friedrich et al. 1983; Parmar and Tollefson 1977) makes PC ineffective in heat generation as compared to coal. The high sulfur and heavy metals content raises significant environmental concern over its potential use as an alternative energy source. PC has been investigated as a precursor of activated carbon for the removal of organic contaminants and heavy metals from aqueous solutions (Yuan et al. 2010a; Zamora et al. 2004; 2000). However, it has been reported that the activation of PC significantly increased the vanadium concentration in the treated water as compared to water treated with the fresh PC (Zubot 2010). Therefore, the continuing accumulation and stockpiling of large quantities of PC require the development of innovative strategies for the effective utilization of this carbon-rich material on an industrial scale.

Another environmental concern in petroleum industry is the process-affected water. One of the examples of such water is the oil sands process-affected water (OSPW), generated after Clark hot water extraction of bitumen from oil sands operations. OSPW is a complex alkaline mixture of inorganic and organic compounds (Allen 2008a, b). OSPW is retained on-site, and a part of it is recycled back to the extraction process to reduce the freshwater consumption. As a result, it becomes corrosive and highly toxic due to high concentrations of salts and refractory organic compounds such as naphthenic acids (NAs) (Jones et al. 2011). The storage of OSPW has raised several environmental concerns, including the presence of trace concentrations of NAs in surface waters around the oil sands operation facilities due to their leaching from tailings ponds (Allen 2008a).

Adsorption is viewed as an effective process to remove persistent organic chemicals from wastewaters (Zubot et al. 2012). Given the complexity of environmental problems and continuous accumulation of different by-products that the petroleum industry is facing, the process shortcomings can be turned into benefits by applying one waste to treat another waste product. In this approach, PC can be used as an in situ adsorbent for the treatment of OSPW. Since PC is a residual of oil refining, it is available virtually free of charge and does not require any transportation costs. As such, the investment cost associated with the development of any other technology for OSPW treatment could be significantly reduced. Currently, at Syncrude Canada Ltd. production site in Alberta, Canada, PC, produced after fluid coking process, is mixed with OSPW at approximately 22 % (by weight) before its transport to the tailings ponds for a long-time storage (Zubot 2010). The operating pipeline acts as a “plug-flow” carbon adsorption reactor that reduces the concentration of organic fraction in OSPW during the transfer process. Water quality analyses have shown that chemical oxygen demand (COD), concentration of acid-extractable fraction (AEF), and NAs decreased after adsorption (Gamal El-Din et al. 2011; Zubot 2010). The PC-treated OSPW required less ozone doses to remove the remaining organics, and the resulted water was more biodegradable (Gamal El-Din et al. 2011). Majid and Kotlyar (1999) showed that PC reduced the concentration of total dissolved carbon from 300–600 to <50 mg/L during the removal of free phase bitumen from wastewater by agglomeration.

Leaching of vanadium from PC and its environmental impact has been investigated in several publications (Puttaswamy and Liber 2012; Puttaswamy et al. 2010; Small et al. 2012; Zubot et al. 2012). Vanadium, released from PC, was accounted as a primary cause of leachate toxicity to a freshwater invertebrate *Ceriodaphnia dubia* in a hard reconstituted water (Puttaswamy and Liber 2011). In a follow-up study, Puttaswany and Liber (2012) showed that the concentrations of nickel and vanadium released into water, which mimic anion content of OSPW, were above the chronic *C. dubia* half-maximal inhibitory concentration (IC_{50}) or median lethal dose (LC_{50}). However, OSPW treated with PC did not show any toxicity toward *Vibrio fischeri* and rainbow trout as compared to fresh OSPW (Zubot et al. 2012).

The promising results with respect to the removal of organic compounds and reduced toxicity of OSPW after PC treatment require further evaluation of the PC for the removal of organic compounds in terms of adsorption mechanism, adsorbent properties, and vanadium speciation. The objectives of the present study were to: (1) investigate the effect of the contact time and PC concentration on the removals of AEF and NAs from OSPW without any pre-treatment; (2) determine the mechanisms of NAs adsorption on PC; (3) study the effect of physico-chemical properties of PC on the adsorption of NAs; and (4) investigate the vanadium leaching from PC and its speciation during the adsorption process. To achieve these objectives, adsorption studies were performed by mixing the PC and OSPW in various proportions and for different contact times. The experimental data were fitted to different adsorption isotherms to determine the adsorption capacity and elucidate the mechanism of NAs adsorption. The physical and chemical characteristics of the adsorbent were evaluated by using Fourier transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA), scanning electron microscopy (SEM), and Brunauer–Emmett–Teller (BET) surface area analysis. This work was conducted at the University of Alberta, Canada, and was completed in November 2011.

Materials and methods

Sampling

OSPW was collected in January 2010 from the West In-Pit (WIP) recycle tailings pond at Syncrude Canada Ltd., Alberta, Canada. The barrels were transported to the University of Alberta, Edmonton, Canada, and stored at 4 °C. OSPW characteristics are shown in Table 1. OSPW was used as-received without any pre-treatment and all adsorption experiments were conducted at room temperature (20–23 °C).

Adsorbents

PC was also provided by Syncrude Canada Ltd. The samples were sieved by a No. 40 (0.422 mm) mesh to separate the larger-sized clumps. Granular activated carbon (GAC, JA04) was supplied by Jacobi Carbons (Jacobi Carbons Inc., Columbus, OH, USA), and powdered activated carbon (PAC, WPX-Z) was purchased from Calgon Carbon (Calgon Carbon Corporation, Pittsburgh, PA, USA).

Preliminary adsorption experiments

This set of experiments was aimed at evaluating the effects of adsorbent concentrations and contact times on the overall adsorption of organic compounds from OSPW. Adsorption studies were performed in a batch mode in 500-mL stoppered conical flasks. Specific pre-weighed amounts of PC, GAC, or PAC were mixed with OSPW to result in 50, 100, 200, 300, and 400 g/L concentrations. The control samples were prepared without the addition of adsorbents. The flasks were placed on an incubator shaker (New Brunswick Scientific, Enfield, CT, USA) and shaken at 270 rpm. After predetermined contact times (1, 3, 6, and 12 h), the mixtures were filtered through 0.45 μm Nylon filters (SUPELCO, Bellefonte, PA, USA). Untreated and treated OSPWs were analyzed in terms of AEF concentration, COD, pH, and alkalinity. The two-tailed *t* test at 95 % confidence interval was used to determine the statistically significance of the results.

Table 1 Characterization of as-received OSPW (average of $n = 3$ replicates)

Parameter	Value
pH	8.4 ± 0.2
Alkalinity (mg/L as $CaCO_3$)	694 ± 19
COD (mg/L)	233 ± 12
NAs (mg/L)	60.3 ± 3
AEF (mg/L)	81 ± 7
Vanadium (μg/L)	13.1 ± 0.7

Equilibrium time experiments for PC

The aim of this set of experiments was to determine the contact time needed for the concentration of AEF in the liquid phase to reach equilibrium with the PC. Based on the COD and AEF removals during the preliminary adsorption experiments with PC and because of the dense slurry formed upon mixing 300 and 400 g/L of PC with OSPW, 200 g/L concentration of PC was chosen to perform the equilibrium time experiments. The experiments were conducted for the contact times of 2, 4, 6, 8, 10, 12, 14, 16, 18, 20, 25, 30, 35, and 40 h by following the same procedure described in the preliminary adsorption experiments section. Untreated and treated OSPWs were analyzed in terms of AEF removal.

Adsorption isotherms

In this set of experiments, the specific pre-weighed amounts of PC, GAC, or PAC were added to OSPW to result in a series of mixtures with the adsorbent concentrations in the range of 0–200 g/L for PC and 0–20 g/L for PAC or GAC. The isotherms of adsorption experiments were conducted in the same manner described in the preliminary adsorption experiments section for 16 h and 12 h for PC and GAC/PAC, respectively. The experimental data were fitted to the *Langmuir*, *Freundlich*, and *Dubinin-Radushkevich* isotherm equations as explained in detail in the Electronic Supplementary Material (ESM).

End points for NAs analysis and physico-chemical characterization of adsorbents

Because of the high cost and complexity associated with the NAs analysis, the NAs removal was measured for 200 g/L of PC after 16 h of treatment and for 50 g/L of PAC/GAC after 12 h of treatment. These conditions were also used for the physico-chemical characterization of adsorbents.

Vanadium leaching and speciation experiments with PC

In adsorption experiments aimed at evaluating vanadium speciation in the treated OSPW, 2.5 mM ethylenediaminetetraacetic acid disodium salt dehydrate (Na_2EDTA) (Sigma-Aldrich, Oakville, Ontario, Canada) was added first to untreated OSPW or Milli-Q water (Millipore, Molsheim, France) to form a stable complex with vanadium (IV) and (V) to prevent speciation change (Li et al. 2009). The adsorption experiments were performed in a similar manner as described in the preliminary adsorption experiments section. The filtrate was diluted using a 2.5 mM Na_2EDTA to a concentration that fell within the calibration range. Vanadium speciation was performed by using a PerkinElmer high-performance liquid chromatography–inductively coupled plasma–mass spectrometer (HPLC-ICP-MS) instrument (HPLC, PE Instruments, Shelton, CT, USA and ICP-MS, PE Sciex, Concord, ON, Canada) by following the method described by Li et al. (2009). A Tukey test in combination with ANOVA at 95 % confidence interval was used for the analysis of the obtained data.

Water quality analysis

Milli-Q water from Synergy® UV instrument (Millipore, Molsheim, France) was used throughout the study. COD, pH, and alkalinity were determined according to the standard methods (Greenberg 1992). A solid addition method was used to determine the pH of the zero surface charge (PZC) of the adsorbent. The AEF concentrations in OSPW before and after adsorption were measured using a FT-IR instrument (PerkinElmer Spectrum, 100 FT-IR Spectrometer, Waltham, USA), following the methodology explained in details elsewhere (Jivraj et al. 1996; Pourrezaei et al. 2011).

Vanadium speciation

Vanadium speciation was performed on a HPLC-ICP-MS (HPLC, PE Instruments, Shelton, CT, USA, and ICP-MS, PE Sciex, Concord, ON, Canada) using the method developed by Li et al. (2009). A PerkinElmer Series 200 HPLC system equipped with an autosampler was connected to a PerkinElmer Elan 6100 DRC^{plus} ICP-MS using a 38-cm-long piece of Peek tubing (1/16" OD, 0.007" I.D.) (Supelco, Bellefonte, PA, USA). The sample injection volume was 50 L. The mobile phase flow rate was 1 mL/min. The column was a SAX PRP-X100 column (50 mm × 4.1 mm × 5 µm) (Hamilton, Reno, NV, USA). A Tukey test in combination with ANOVA at 95 % confidence interval was used to determine whether the obtained results for various PC concentrations were statistically different.

Surface functional groups

A Bio-rad diffuse reflectance FT-IR spectrophotometer (FTS 6000, Philadelphia, PA, USA) was used to identify the functional groups on the surface of the studied adsorbents. The adsorbents were dried at 110 °C overnight in the oven, mixed with potassium bromide (KBr) (FT-IR grade, Sigma-Aldrich, Oakville, ON, Canada) at a 5 % by weight ratio, and grounded to result in a fine powder. Pure KBr was used to collect the background spectra. The spectra were recorded with 128 scans and 4 cm^{-1} spectral resolution.

Surface area analysis

The surface area was determined from the nitrogen adsorption/desorption isotherms performed at 350 °C using a surface analyzer (IQ2MP, Quantachrome, FL, USA). Prior to analysis, samples were degassed at 300 °C for 5 h. The specific surface area was calculated by the Brunauer–Emmett–Teller (BET) equation at the relative pressure range of 0.01–0.07. The V–t model was used to calculate the micropore volume. A density functional theory (DFT) model for slit pores was used to obtain the pore size distribution.

Thermogravimetric analysis (TGA)

TGA was performed by a thermal analyzer system (TGA/DSC 1, Mettler Toledo, Mississauga, ON, Canada) under the 50 standard cubic centimeters per minute N_2 flow at a heating rate of 10 °C/min. The experiments started at 30 °C and finished at 1,000 °C. The temperature was increased to 120 °C and 400 °C maintaining for 60 min at each temperature to completely remove moisture and NAs, respectively. Afterward, the temperature was raised to 1,000 °C.

Scanning electron microscopy (SEM)

SEM (Hitachi SEM S-2500, Tokyo, Japan) was used to study the morphology of the adsorbents. The sample particles were first dried at room temperature and then scattered onto the stub pasted with a thin layer of silicon before it was examined with the SEM instrument.

X-ray Photoelectron spectroscopy analysis (XPS)

The XPS measurements were performed on the AXIS 165 spectrometer (Kratos Analytical, Manchester, UK). The base pressure in the analytical chamber was less than 3×10^{-8} Pa. A monochromatic Al Kα source ($h\nu = 1486.6$ eV) was used at a power of 210 W. The analysis spot was 400 × 700 μm. The resolution of the instrument is 0.55 eV for Ag 3d and 0.70 eV for Au 4f peaks. The survey scans were collected for binding energies spanning from 0 to 1,100 eV with an analyzer pass energy of 160 eV and a step of 0.4 eV. For the high-resolution spectra, the pass energy was 20 eV with a step of 0.1 eV. An electron flood gun was used to compensate for sample charging. Vision-2 instrument software was used to process the data. All spectra were calibrated for the C 1 s binding energy position at 284.8 eV. Compositions were calculated from the survey spectra using the major elemental peaks and sensitivity factors provided by the NIST database.

Point of zero charge (PZC)

A solid addition method was used to determine the pH of the zero surface charge on the adsorbent. Fifty milliliters solutions of 0.1 N NaCl, adjusted to the desired pH, was transferred to a series of 125-mL stoppered flasks. The initial pH of the solutions was adjusted between 2 and 12 by adding 0.1 N HCl or 0.1 N NaOH and recorded as the initial pH (pH_0) of the solutions. Then 1 g of PC was added to each flask and capped immediately. The suspensions were shaken by the incubator shaker for 48 h to reach equilibrium. After the designated time, the final pH (pH_f) of the supernatant was recorded. The difference between the final and initial pH values ($\Delta pH = pH_f - pH_0$) was plotted against the pH_0. The point of intersection of the curve at which $\Delta pH = 0$ corresponds to the pH_{PZC}.

Analysis of NAs

Two milliliter of the samples was centrifuged for 10 min at 10,000 rpm. Following centrifugation, 500 μL of the supernatant was placed in a 2-mL glass vial with 450 μL of methanol (Fisher Scientific, Ottawa, ON, Canada), and 50 μL of an internal standard (tetradecanoic acid-1-^{13}C) (Sigma-Aldrich, Oakville, ON, Canada) solution was added to result in a concentration of 200 ng/mL in each sample. A Waters Acquity UPLC® System (Milford, MA, USA) was employed for efficient and rapid chromatographic separation of the NAs and oxidized products. Detection was performed with a high-resolution Synapt G2 HDMS mass spectrometer equipped with an electrospray ionization source operating in negative ion mode. The system was controlled using MassLynx® ver. 4.1. Tuning and calibration were performed using standard solutions of leucine enkephalin and sodium formate, respectively, provided by Waters Corporation (Milford, MA, USA). TargetLynx® ver. 4.1 was used for data analysis of the target compounds, and the relative ratio of the chromatographic peak area of each analyte to that of the internal standard was calculated for subsequent analysis. Chromatographic separations were run on a Waters UPLC Phenyl BEH column (1.7 μm, 150 mm × 1 mm,) using a mobile phase of: A, 10 mM ammonium acetate solution prepared in Optima-grade water and B, 10 mM ammonium acetate in 50 % methanol 50 % acetonitrile, both Optima-grade. Gradient elution was as follows: 1 % B for the first 2 min, then ramped to 60 % B by 3 min, to 70 % B by 7 min, to 95 % B by 13 min, followed by a hold until 14 min, and finally returned to 1 % B, followed by a further 5.8-min re-equilibration time. The flow was constant at 100 μL/min, and column temperature was kept at 50 °C, while samples were maintained at 4 °C.

Results and discussion

pH and total alkalinity

The adsorbents used in this study showed different effects on the pH and alkalinity of the samples after adsorptive treatments (Table 2). The PC insignificantly increased the pH of the treated OSPW, whereas the alkalinity decreased by 1–27 %. The latter could be related to the dissolution of metal oxides present in the PC and their subsequent reaction with bicarbonate ions present in OSPW (Zubot

Table 2 pH and alkalinity of OSPW before and after 12 h of adsorption

Concentration (g/L)	pH			Alkalinity (mg/L as $CaCO_3$)		
	PC	GAC	PAC	PC	GAC	PAC
0	8.4 ± 0.1	8.5 ± 0.1	8.6 ± 0.1	704 ± 4	704 ± 4	704 ± 4
50	8.5 ± 0.1	9.6 ± 0.1	8.8 ± 0.1	688 ± 4	818 ± 5	696 ± 4
100	8.5 ± 0.1	9.9 ± 0.1	9.1 ± 0.1	664 ± 6	912 ± 5	692 ± 11
200	8.5 ± 0.1	10.4 ± 0.1	8.9 ± 0.1	637 ± 4	1,004 ± 6	–
300	8.4 ± 0.1	10.4 ± 0.1	9.0 ± 0.1	595 ± 1	1,042 ± 5	717 ± 24
400	8.6 ± 0.1	10.4 ± 0.1	8.9 ± 0.1	544 ± 3	1,092 ± 5	720 ± 4

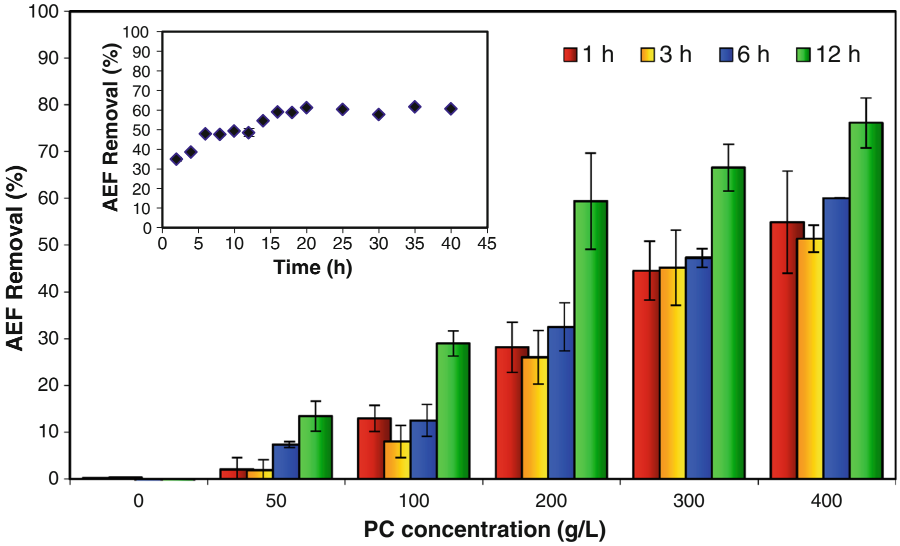


Fig. 1 AEF removal as a function of PC concentration and contact time. An inset shows the AEF removal as a function of contact time at 200 g/L PC

2010). Increasing the concentration of PAC did not change the pH and alkalinity of the treated OSPW, whereas increasing the GAC concentration resulted in increments in pH and alkalinity after treatment. This is likely due to the higher amount of OH groups present on the GAC surface (discussed later in XPS analysis section). The effect of contact time on the pH and alkalinity was negligible for PC, PAC, and GAC.

COD and AEF concentrations

An increase in PC concentration resulted in an increase in the COD removal from OSPW (Fig. ESM-1 in ESM). No statistically significant difference in the COD removal was observed at 1, 3, and 6 h of contact time; however, when contact time approached 12 h, the COD removal increased for all the studied PC concentrations. The COD removal at 12-h contact time for 200 g/L PC was significantly higher as compared to 50 and 100 g/L, but no statistically significant difference was observed among 200, 300, and 400 g/L PC at 12 h. At PC concentrations above 200 g/L, very dense slurries were formed resulting in improper contact between the PC and OSPW. This may explain no statistically significant difference in the COD removal for the PC concentrations above 200 g/L. AEF removal followed the same trend as the COD removal, reaching 60 % reduction at 200 g/L PC after 12 h of contact (Fig. 1). The higher COD and AEF removals at higher PC concentrations are likely arisen from the higher available surface area at higher PC concentrations (Khan et al. 2011; Sharma et al. 2011). Based on the COD and AEF results, 200 g/L of PC was chosen in further equilibrium time studies.

Table 3 Calculated isotherm parameters for acid-extractable fraction (AEF) adsorption

Parameters*	PC	GAC	PAC
Langmuir			
q_m (mg/g)	1.02	50.5	71.0
K_{ads} (L/mg)	0.01	0.02	0.02
R_L	0.67	0.39	0.52
r^2	0.95	0.98	0.84
Freundlich			
K (mg/g)(L/mg)$^{1/n}$	0.01	1.01	0.23
n	1.22	1.21	1.85
r^2	0.95	0.96	0.92
Dubinin-Radushkevich			
q_m (mg/g)	0.28	12.43	107
β (mol^2/J^2)	7×10^{-5}	5×10^{-6}	3×10^{-5}
E (kJ/mol)	0.01	0.35	0.13
r^2	0.85	0.83	0.97

* q_m is the maximum adsorption capacity; K_{ads} and K indicate the adsorption affinity of the adsorbate for the Langmuir and Freundlich isotherms, respectively; R_L is the separation factor; n is the adsorption intensity; β is the adsorption energy constant; E is the adsorption free energy; and r^2 is the coefficient of determination

The application of GAC and PAC to OSPW treatment led to COD and AEF removals of >93 %, regardless of the contact times and adsorbent concentrations. Higher removal in the case of activated carbons is likely arisen from the significantly higher surface area of the commercial activated carbons as compared to PC (discussed later in Surface area analysis section). Therefore, the lowest concentrations of 50 g/L of GAC and PAC at 12-h contact time were chosen for physico-chemical analysis of adsorbents and NAs analysis.

Equilibrium time studies

AEF removal (Fig. 1) increased gradually from 2 to 16 h and reached a plateau after 16 h of contact. The linear and plateau portions of the curve corresponded to the diffusion of AEF to surface layers and pores, respectively (Goel et al. 2005). The observed effect was indicative of the rapid adsorption of AEF on the easily accessible adsorption sites at the beginning of experiment, followed by limited diffusion of the adsorbate molecules into the mesopores (Yuan et al. 2010b). Based on the results, 16 h was chosen as the equilibrium contact time for further physico-chemical analysis of PC and NAs analysis.

Adsorption isotherms

The calculated parameters for the *Langmuir*, *Freundlich*, and *Dubinin-Radushkevich* isotherms for AEF adsorption are shown in Table 3. Plots of the isotherms can be found in Fig. 2. Both *Langmuir* and *Freundlich* isotherms showed high correlation coefficients for PC and GAC. For PAC, *Freundlich* isotherm showed higher correlation coefficient as compared to that obtained using the *Langmuir* isotherm. The maximum adsorption capacity (q_m) for the PC to adsorb AEF from OSPW was calculated as 1.0 mg/g by fitting the experimental data to the *Langmuir* isotherm. This value, compared to 51 and 71 mg/g for GAC and PAC, respectively, indicated that larger mass of PC is required for the removal of the AEF from OSPW. The adsorption capacity also decreased with the increase in PC concentration, suggesting that some of the available sites remained unsaturated (Khan et al. 2011; Sharma and Forster 1993). The values of the separation factor (R_L) in the range of 0–1 suggested the favorable adsorption of AEF from OSPW. In addition, the calculated mean free energy of adsorption ($E < 8$ kJ/mol) suggested that the AEF was physically adsorbed to the surface of the adsorbents.

Removal of NAs

Figure 3 shows the distribution of the NAs compounds present in OSPW as a function of the carbon number (n) and the number of the rings ($-Z/2$) before and after

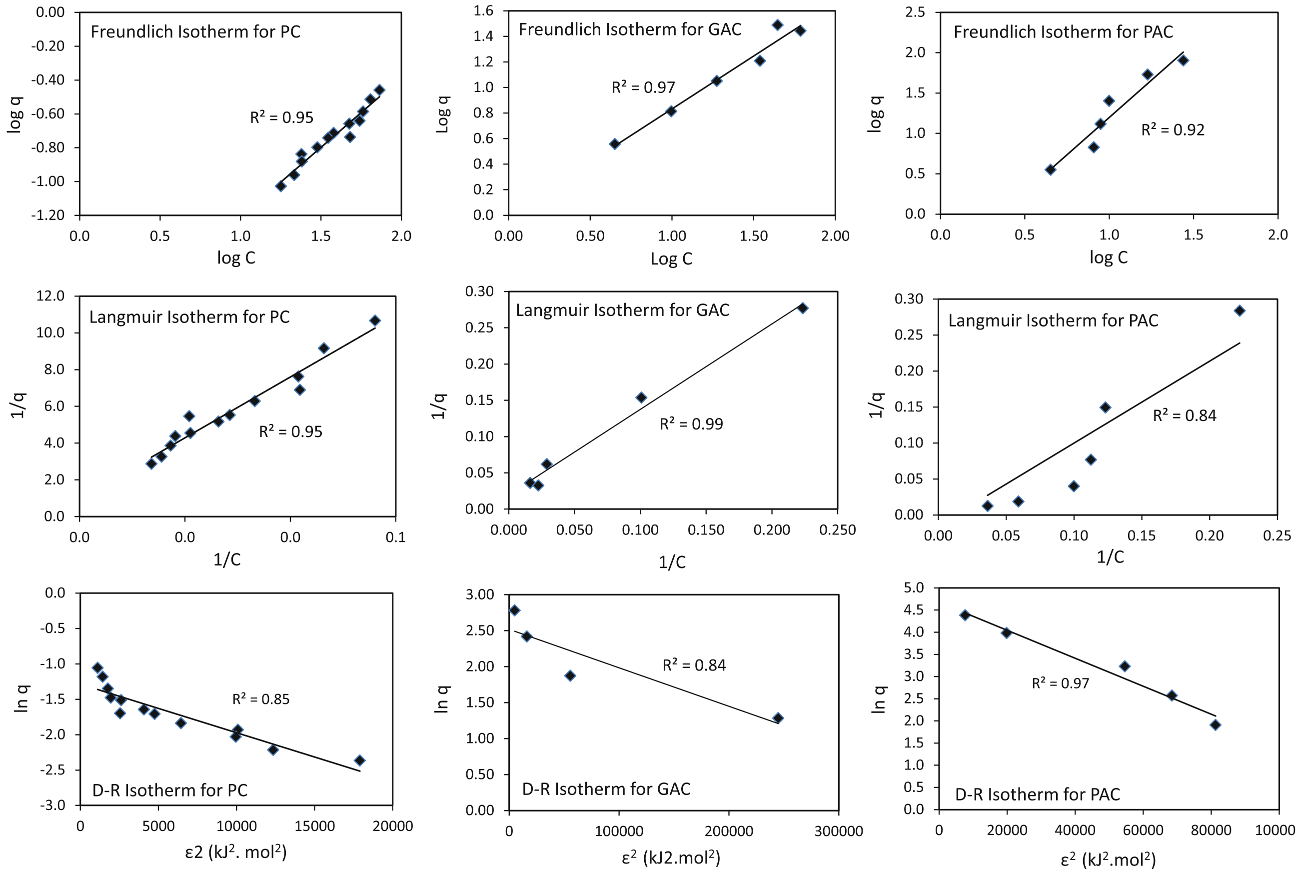


Fig. 2 *Freundlich*, *Langmuir*, and *Dubinin-Radushkevich* (D-R) isotherm plots for PC, GAC, and PAC

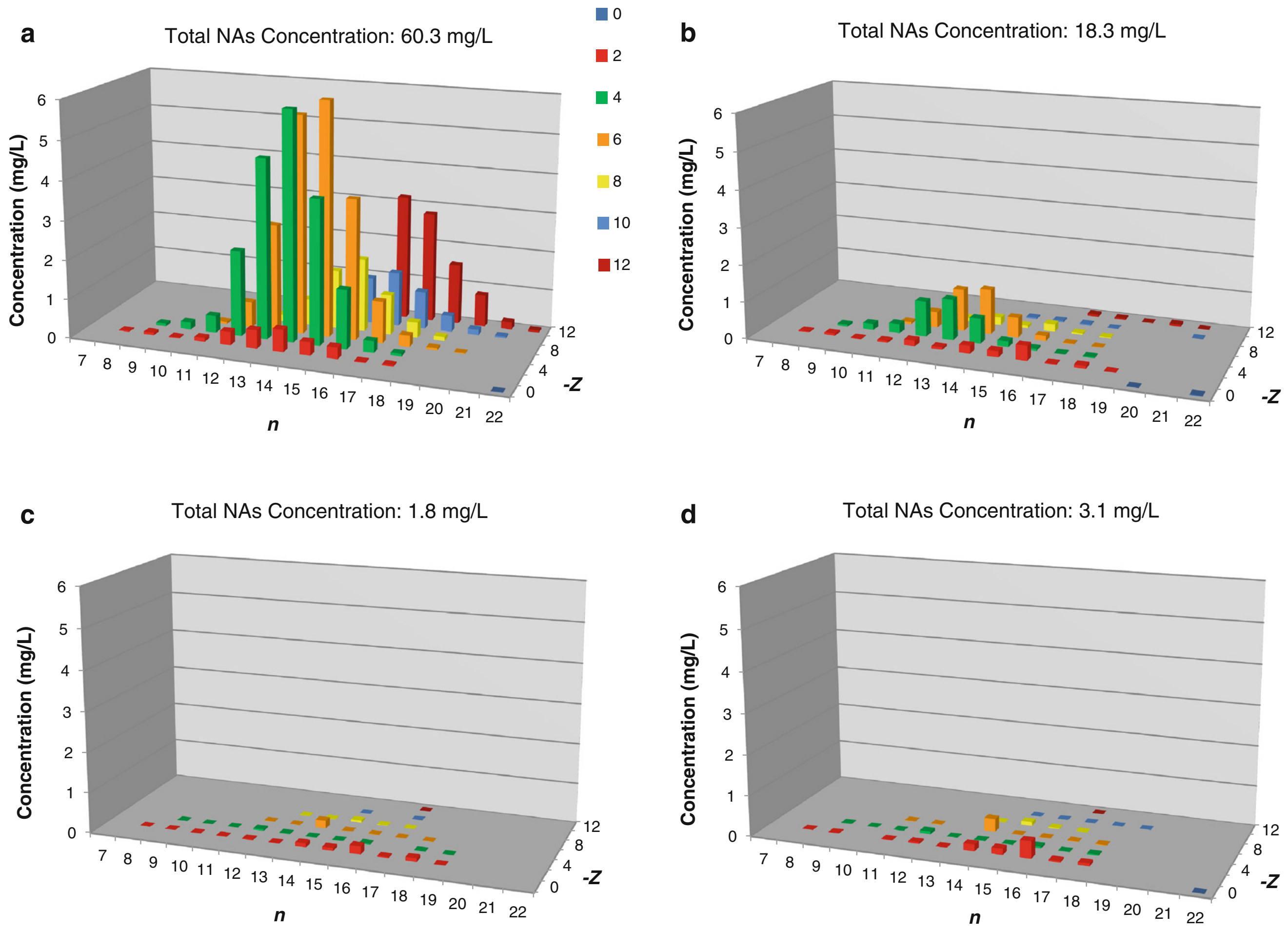


Fig. 3 Distribution of the NAs compounds for **a** fresh OSPW, **b** OSPW treated with PC at 200 g/L for 16 h, **c** OSPW treated with GAC at 50 g/L for 12 h, and **d** OSPW treated with PAC at 50 g/L for 12 h

treatments with PC, GAC, and PAC. The total NAs removals following PC, GAC, and PAC treatment were 75, 97, and 95 %, respectively. The results of the control samples showed that there was no change in the concentration of the NAs as a result of experimental procedure. The NAs found in OSPW were in the carbon range of 8–22 within 1–6 numbers of rings, indicating that there were no acyclic NAs compounds present. Consistently with previous results (Jones et al. 2011; Rowland et al. 2011), monocyclic NAs were the least predominant species among all the *Z* groups; whereas, bicyclic and tricyclic acids within the carbon range of 12–16 were the most abundant compounds. For the PC (Fig. 3b), the NAs were predominantly removed in the carbon range of 14–17 (81–100 %), 15–20 (86–100 %), 15–19 (93–100 %), 15–21 (94–100 %), and 17–22 (96–100 %) for the $-Z = 4$, 6, 8, 10, and 12 group of compounds, respectively. This implies that the adsorption of NAs onto PC increased with the increase in both *n* and $-Z$ numbers, with *n* having greater effect on the adsorption as compared to $-Z$. The NAs removal followed a similar trend for GAC and PAC (Fig. 3c, d). For the GAC and PAC

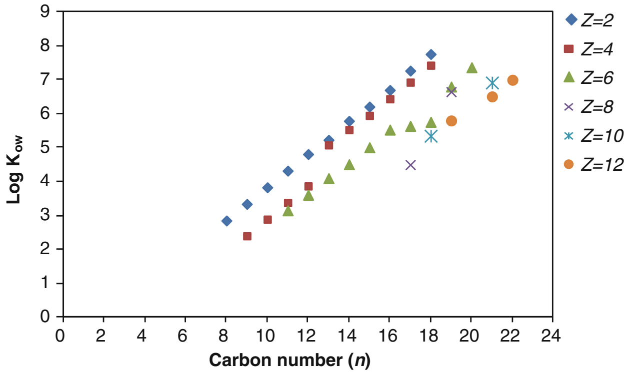


Fig. 4 Log K_{ow} values for individual NAs as a function of carbon number (*n*) and number of the rings (*Z*). Log K_{ow} values were obtained from ChemSpider chemical database

treatments, the NAs removals exceeded 88 % for all individual NAs.

Increase in the molecular mass of NAs renders the compounds less soluble and more hydrophobic, which, in turn, increase their affinity for the adsorption on the surface of the adsorbents (Bansal and Goyal 2005). Octanol/water distribution coefficient (expressed as log K_{ow}) for the NAs is shown in Fig. 4 as a function of n and $-Z$. Increasing n within each $-Z$ group of compounds resulted in the increase in the log K_{ow}, which is consistent with the increase in the removal efficiency of the individual NAs by n. This confirms the higher tendency of NAs with the higher number of the carbons to adsorb onto the surface of the adsorbents (Gotovac et al. 2007).

Identification of surface functional groups by FT-IR

FT-IR analysis is an important characterization method for the investigation of the changes in the surface properties of the adsorbents (Alhamed and Bamufleh 2009; Juan and Ke-Qiang 2009; Rennert et al. 2007). The FT-IR absorption spectra of the fresh and saturated PC at 200 g/L and 16-h contact time are shown in Fig. 5a. The absorption peaks at 1,680, 1,583, and 874 cm^{-1} were characteristics of carbonyl stretching vibrations, N–H bending vibration of primary amines, and C–H bending vibrations of benzenes, respectively (Juan and Ke-Qiang 2009; Pradhan and Sandle 1999; Shen et al. 2008). The broad absorption band in the region of 3,400–2,500 cm^{-1} was related to the stretching vibration of O–H groups (Jiang et al. 2008; Njoku and Hameed 2011; Pradhan and Sandle 1999). The FT-IR spectra of GAC and PAC (Fig. 5b) also showed the presence of the carbonyl (1,682 cm^{-1}), C=C bond of aromatic rings (1,477 cm^{-1}), and hydroxyl functional group (2,400–2,700 cm^{-1}), respectively (Jiang et al. 2008; Njoku and Hameed 2011; Pradhan and Sandle 1999).

Spectra of the fresh and saturated adsorbents showed peaks with similar positions for each identified functional groups, indicating that there was no change in the chemical bonding before and after adsorption. This observation suggests physisorption of organic compounds on the surface of adsorbents (Gotovac et al. 2007; Leng and Pinto 1997; Njoku and Hameed 2011).

XPS analysis

XPS analysis was performed in order to identify and quantify the functional groups on the surface of the fresh PC, GAC, and PAC (Figs. ESM-2, 3, and 4). As shown in Table ESM-1, carbon comprised the highest atomic concentration (89.08, 89.43, and 93.63 % for PC, GAC, and PAC, respectively) in all tested adsorbents. The atomic concentration of oxygen was 6.6, 8.0, and 4.6 % for PC, GAC, and PAC, respectively. The N and S contents of the GAC and PAC were lower as compared to those found in PC (Table ESM-1).

The results of the peak deconvolution of C_{1s}, O_{1s}, N_{1s}, and S_{2p} could be found in the ESM. The percentage of the oxygen-containing functional groups of PC, GAC, and PAC estimated from the area of the deconvoluted C_{1s} and O_{1s} peaks is shown in Table ESM-2. Fraction of hydroxyl functional groups on GAC is higher than that of PC and PAC, which is consistent with the basic surface characteristic of the GAC ($pH_{pzc} = 11.9$; Table 4). This may account for the pH increase in the treated OSPW upon its

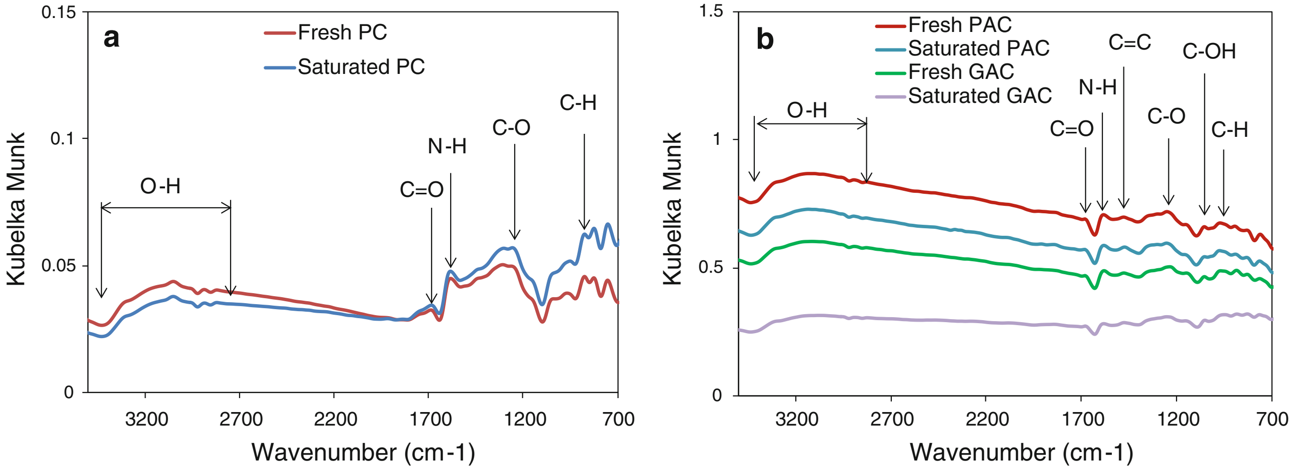
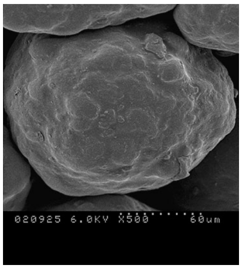
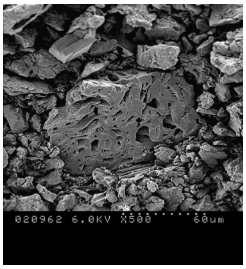
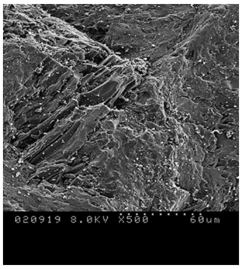


Fig. 5 FT-IR spectra of the (a) fresh and saturated PC, (b) fresh and saturated GAC and PAC

Table 4 Characterization of PC, PAC and GAC

Parameter	PC	PAC	GAC
Size distribution of the pores (nm)	2.3–36	0.5–36	0.5–36
pH of the zero surface charge (pH_{pzc})	6.5	9.3	11.9
BET surface area (m^2/g)	7.7	800	912
SEM image			

contact with GAC. PC contained higher percentage of carbonyl functional groups as compared to GAC and PAC.

Surface area analysis and SEM images

Surface area is an important factor that affects the adsorption capacity of the adsorbents. BET surface area of PC was calculated as 7.7 m^2/g (Table 4). The low surface area of PC as compared to 912 and 800 m^2/g for GAC and PAC, respectively, implies that PC has lower porosity as compared to the highly porous structure of the GAC and PAC (Ahn et al. 2005; Alhamed and Bamufleh 2009; Carter et al. 2011; Ding et al. 2008; Lu and Sorial 2004). The pore size distribution curves of PC, GAC, and PAC are shown in Fig. ESM-5. Size distribution of the pores in PC was in the mesoporous range (2.3–36 nm) with the highest peaks centered at 2.8 and 3.2 nm (Fig. ESM-5a). No micropores (<2.0 nm) or macropores (>50 nm) were detected on the surface of the PC, suggesting that mesopores play a significant role in the adsorption of organic compounds from OSPW. Size distribution of the pores for GAC and PAC (Figs. ESM-5b and 5c) was in the range of 0.5–36 nm, with the highest peaks centered in the range of 0.6–1.4 nm among the micropores. SEM images of the PC (Table 4) also showed the spherical non-porous structure of adsorbent; whereas, PAC and GAC showed highly porous structures, which contributed to high surface area and adsorption capacity of these adsorbents.

Adsorption mechanism

Organic compounds with high molecular weights and molecular sizes similar to the pore diameters may block the pores and reduce the available adsorption sites (de Ridder et al. 2011; Kilduff et al. 1998; Matsui et al. 2002; Moore et al. 2010; Newcombe and Drikas 1997; Pelekani and Snoeyink 1999). However, NAs with low molecular weights (160–500 g/mol) would easily diffuse into the micro- and mesopores (Moore et al. 2010; Yuan et al. 2010b), and there would be no limitation for their diffusion into the pores based on their size.

The pH_{pzc} for the PC was found to be 6.5 ± 0.3 (Fig. ESM-7a). NAs have a pK_a in the range of 5–6 (Perez-Estrada et al. 2011), which implies that over the operating pH of this study (~8.4), they exist in the dissociated form. As a result, the surfaces of the PC and NAs are both negatively charged. Therefore, electrostatic repulsion forces may reduce the adsorption capacity of PC for NAs (Ayranci et al. 2005; Faria et al. 2008). On the other hand, the metal ions present in OSPW may neutralize the negative charge of NAs and thus decrease the repulsion between the NAs and PC (Pan and Xing 2008). Additionally, based on XPS results, N–H functional groups on the surface of the PC may facilitate formation of hydrogen bonds between the PC and hydroxyl groups of NAs. However, low nitrogen content of the PC suggests that H-bonding does not significantly contribute to the adsorption. NAs with higher molecular weights may contain aromatic rings or double bonds which may increase the adsorption affinity of these compounds through the π–π interactions to the graphitelike surface of the adsorbents (Kavanagh et al. 2009; Lin and Xing 2008; Rowland et al. 2011; Zhu and Pignatello 2005). Given that NAs are highly hydrophobic compounds, the hydrophobic interactions between the NAs and the surface of PC are suggested as a dominant adsorption mechanism.

At the operating pH of this study, surface of the GAC ($pH_{pzc} = 11.9$) and PAC ($pH_{pzc} = 9.3$) (Figs. ESM-7b and

7c) is positively charged, which is favorable for the adsorption of NAs through the electrostatic attractive forces (Ayranci et al. 2005). Besides, the high surface area and microporosity of these adsorbents suggest that the adsorption occurred through the micropore filling mechanism. In addition, no change in the peak positions in the FT-IR spectra and desorption profile of the samples in TGA analysis (Fig. ESM-6) of PC before and after adsorption suggests that the physisorption of the organic compounds mainly depends on the porosity of the adsorbent rather than the surface functionality (Leng and Pinto 1997; Njoku and Hameed 2011). This is in accordance with the high adsorption capacity of GAC and PAC and low adsorption capacity of PC.

Vanadium leaching

Leaching of vanadium from PC is a complex process, which is expected to depend on water matrix. As shown in Fig. 6, the amount of vanadium leached from PC increased with the increase in PC concentration from 50 to 400 g/L for both OSPW and Milli-Q water. This is consistent with Galvin et al. (2012), who observed the increase in the concentration of a range of metals leached from different recycled aggregates with the increase in the amount of the added material. While studying the leaching of copper, zinc, and lead from the cement-based wasted materials, Li et al. (2001) showed that metal concentrations increased with increasing solid to liquid ratio, reached equilibrium, and remained constant afterward. Under the experimental conditions applied in this study, the equilibrium between the solid phase and liquid phase vanadium was not achieved, suggesting that more leaching could occur if higher PC concentration is used for the removal of organic compounds from OSPW. Depending on the PC concentration, the percentage of leached vanadium was in the range of 8.7–17.0 and 9.1–11.5 % for OSPW and Milli-Q water, respectively (Table ESM-3). The leaching of vanadium (V) increases with increasing pH (Wehrli and Stumm 1989). Puttaswamy and Liber (2011) showed that as pH increased, more vanadium leached from PC into hard reconstituted water (688 μg/L at pH 5.5 and 2,205 μg/L at pH 9.5 for a PC to water v/v ratio of 1:4). Therefore, the increase in vanadium mobility with the pH increase may account for the higher amount of vanadium leached from OSPW at pH 8.4 ± 0.2 as compared to that leached from Milli-Q water at pH 4.6 ± 0.2. While studying the effect of inorganic anions on vanadium leaching from PC in water which contained sulfur, chloride, and bicarbonate ions, Puttaswamy and Liber (2012) showed that bicarbonate ions increased the release of vanadium from PC. Since the concentration of bicarbonate ions in OSPW is very high (775–950 mg/L) (Allen 2008a), this may also promote leaching of vanadium from PC upon its contact with OSPW. In addition, the organic fraction of OSPW contains large variety of compounds which could stabilize vanadium in the aqueous phase and increase its equilibrium concentration as compared to Milli-Q water. Although the percentage of the released vanadium did not exceed 20 % of the vanadium present in PC for all studied PC concentrations, its concentrations exceeded the background vanadium concentrations reported for natural waters (0.5–300 μg/L) (Crans et al. 1998; Li et al. 2009) in both OSPW and Milli-Q water.

The vanadium leached from PC was predominantly vanadium (V) for both OSPW and Milli-Q water, although vanadium (IV) was also detected (Fig. 6). However, given that vanadium (IV) is unstable at circumneutral pH, it is expected that it would be oxidized into vanadium (V) upon its release into OSPW. Consistently with the vanadium speciation as a function of pH, the fraction of vanadium (IV) was larger in Milli-Q water as compared to OSPW at all studied PC concentrations.

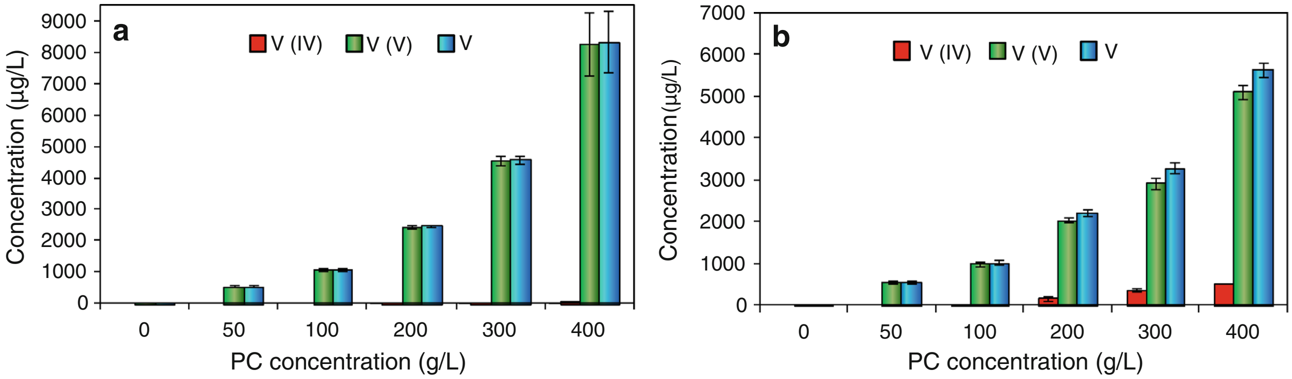


Fig. 6 Concentration of vanadium (IV), vanadium (V), and vanadium leached from PC into (a) OSPW and (b) Milli-Q water after 12 h of contact

Conclusion

The results of this study demonstrated that two waste by-products generated by petroleum industry, PC and process-affected water, can be successfully coupled together in the adsorption process in order to remove persistent organic contaminants from liquid stream. This, in turn, could reduce the adverse impacts of the petroleum industry on the environment. A significant advantage of this process is that while the concentration of toxic compounds is reduced, the amount of dry waste does not increase. A huge amount of PC is continuously produced worldwide. Currently, PC is stockpiled in huge quantities on-site of the refinery plants. PC is virtually cheap, and its direct application as an adsorbent does not require large investments. The ability of PC to adsorb organic contaminants in conjunction with the manner petroleum industry produce, transport, and store the PC present a unique opportunity to treat generated process-affected waters for large-scale applications. PC also has a potential in commercial wastewater applications provided that the activation process is optimized with respect to increasing surface area and minimizing leaching of trace metals.

Electronic Supplementary Material

Adsorption isotherms, XPS analysis, TGA analysis, and related tables and figures are provided in the Electronic Supplementary Material.

Acknowledgments The authors acknowledge the financial supports provided by the research grants from Alberta Innovates-Energy and Environment Solutions (Gamal El-Din and Le), Syncrude Canada Ltd. (Gamal El-Din), Helmholtz-Alberta Initiative (HAI) (Gamal El-Din), NSERC research grant for the research tools and instruments (Gamal El-Din), and NSERC Industrial Research Chair in Oil Sands Tailings Water Treatment (Dr. Gamal El-Din). Dr. Le was supported by the Canadian Water Network and NSERC. The authors acknowledge the Alberta Centre for Surface Engineering and Science at the University of Alberta for XPS analysis. Finally, thanks go to technicians in the Department of Civil and Environmental Engineering and Ms. Xiufen Lu for her help with the HPLC-ICP-MS analysis.

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