

Activated Carbon from Fly Ash of Heavy Fuel Oil: Characterization and its Utilization for Removal and Determination of Chlorophenols in Water

A.Abu-Rizaiza¹, M.W. Kadi² and M.S. El-Shahawi^{2*}

¹Department of Environmental Sciences, Faculty of Meteorology, Environment and Arid Land Agriculture, King Abdulaziz University, Jeddah, Saudi Arabia.

²Department of Chemistry, Faculty of Science, King Abdulaziz University, P.O.Box 80203, Jeddah 21589, Saudi Arabia.

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Activated carbons (AC) prepared from volatile fly ash (FA) of heavy fuel oil via gasification with combined steam - CO₂ was characterized and used as a low-cost adsorbent for removal of chlorophenols (CPs) e.g. 2-chlorophenol (2-CP), 4-chlorophenol (4-CP), and 2,4,6-tetra chlorophenol (TCP) in water. At pH < 2.0, maximum CPs uptake was achieved and the average half-life time ($t_{1/2}$) of the equilibrium adsorption of CPs was in the range 0.80 ± 0.01 - 1.1 ± 0.04 h. Data suggested use of AC in packed column for separation and determination of various concentrations (0.5 - $100 \mu\text{gL}^{-1}$) of CPs in water (0.5 - 1.0 L). Complete extraction and recovery ($97.4 \pm 2.9\%$, $n=5$) of CPs were achieved at 2 mL min^{-1} flow rate. Analysis of CPs spiked onto tap- and seawater were also analyzed by AC packed column and the results were compared with the standard HPLC method at 95% confidence ($P=0.05$, $n=5$). The experimental student t test ($t_{\text{exp}} 1.81$ - 1.93) and F ($F_{\text{exp}} 1.21$ - 5.76) values were lower than the tabulated t ($t_{\text{crit.}} = 2.78$) and F (6.38), respectively. AC packed column provides remarkable selectivity, reproducibility, and cost-effectiveness towards removal and/or determination of CPs. AC adsorbent may serve positively in point-of-care use.

Keywords: Fly ash; Activated carbon; Adsorption; Chlorophenols removal; HPLC; Water.

In the last couple of decades, FA generated from heavy fuel oil has received less attention compared to coal (Pires and Querol, 2004; Alonso-Hernández *et al.*, 2011; Al-Degs *et al.*, 2014). Currently, Saudi Arabia power plants are powered by heavy fuel oil, diesel, and natural gas (Salehin *et al.*, 2015; Gómez *et al.*, 2007). The composition of FA of coal origin is characterized by high Si and Al content which make it suitable ingredient for Portland cement and starting material for geopolymers (van Jaarsveld *et al.*, 2002). A

limited number of articles have been reported on surface characterization residual FA of heavy fuel oil (Komnitsas and Zaharaki, 2007; Al-Degs *et al.*, 2014; Caoa *et al.*, 2014). Few reports on treatment of FA have been published (Bailey *et al.*, 1999; Jaarsveld *et al.*, 2002; Nazari *et al.*, 2011; Izquierdo and Querol, 2012; Tao *et al.*, 2014; Alhamed *et al.*, 2015). Both treated and untreated FA are considered solid wastes that create serious pollution problems in power plants, its surroundings and in its landfill areas (Ghouti *et al.*, 2011; Alhamed *et al.*, 2015).

In recent years, many articles have been studied the utilization of FA with two fold approaches: i) reduction of solid waste generation (Anadinin *et al.*, 2008 ; Al-Degs *et al.*, 2014;

* To whom all correspondence should be addressed.
Tel.: +9662- 0551691130; Fax: +966-12- 6952292;
E-mail: malsaeed@kau.edu.sa

Alhamed *et al.*, 2015) and ii) use of AC prepared from FA as a low cost solid phase extractor (SPE) for removal of phenols, heavy metal ions, and other pollutants in industrial wastewater samples and liquids (Kurniawan *et al.*, 2003; Izquierdo and Rubio, 2008; Petrova *et al.*, 2010; Barakat, 2011; Vigan and Neag, 2012; Ismail *et al.*, 2013; Ihsanullah *et al.*, 2015). AC is one of the most widely used solid adsorbent and it has many uses in filtration, purification, super capacitors, hydrogen storage and in catalysis because of its high surface area, well-developed internal pore structure and surface chemical functional groups at the outer and inner surfaces (Bouzerara *et al.*, 2006; Liu *et al.*, 20013; Zhu *et al.*, 2015). Utilization of FA has become a novel technology in the last few decades (Izquierdo and Rubio, 2008; Al-Ghouti, *et al.* 2011, Alhamed, *et al.*, 2015; Salehin, *et al.*, 2016).

Phenol and CPs are introduced into aquatic environment from various industries that include petrochemical industry, dyes, plastics, pesticides, drugs antioxidants, adhesives and epoxy resins and paper (Rodríguez *et al.*, 2000). US- Environmental Protection Agency (EPA) has prioritized phenols as potential toxin at trace and ultra-trace levels in water and fish due to their toxicity and other unpleasant organoleptic properties (Martínez *et al.*, 1996; Pizarro *et al.*, 2007). The permissible range set by The European Union (EU) set the permissible range for total phenols of in drinking water as 0.5 mg L^{-1} and the level of individual phenolic compound should be under 0.1 mg L^{-1} (Pizarro *et al.*, 2007; Limam *et al.*, 2010). In seawater, 2, 4-Dichlorophenol (DCP) and penta-chlorophenol (PCP) have relatively high levels up to 1500 ng L^{-1} (EPA Method 804, 1995; Basheer and Lee, 2004). In surface water, median levels of DCP, TCP and polychlorinated phenol (PCP) are 5.0, 2.0, and 50 ng L^{-1} , respectively. Such technology can provide extraction, sampling, concentration and sample introduction processes as a whole automatically at one time.

Recently, utilization of AC prepared from FA as low cost SPE as a novel technology for removal, extraction of many pollutants have received considerable interest in the last few years (Izquierdo and Rubio, 2008; Al-Ghouti, *et al.* 2011; Alhamed, *et al.*, 2015). AC is one of the widely used industrial solid adsorbents and carbonaceous materials which have developed

internal pore structure (Gomes, *et al.*, 2010). It has many important applications e.g. filtration and purification, super capacitors, drug delivery, hydrogen storage, catalysts, etc (Gokce and Aktas, 2014). These applications are related with the adsorption behavior of AC. Thus, in this context the present study reports: i) Characterization of heavy fuel oil FA generated during the heavy fuel burning process of thermal power stations in Saudi Arabia; ii) Surface characterization of AC produced from FA by gasification with the combined gas mixture of CO_2 and steam.; iii) adopting, designing and integrating the analytical utility of AC derived from FA as a SPE for removal of CPs from aquatic environment and finally; iv) developing of low cost AC packed column for chromatographic separation and/ or determination of CPs in water. The study will also helps in developing cost-effectiveness SPEs for monitoring and hampering the effects of phenols on local inhabitants.

MATERIALS AND METHODS

Sampling

Rabigh is one of the smallest towns in Saudi Arabia and has one of the lowest populations as reported by Saudi government. It lies at latitude 23° N and longitudes $400^\circ 30' \text{ E}$ along the Red Sea coast in the west central part of the Arabian Shield, Saudi Arabia. Residual FA samples of heavy fuel oil (Vacuum gas oil, Bunker "C") generated from Rabigh water desalination power station were randomly collected from three locations around the station. The samples were then air dried for 21 days and sorted to remove unwanted materials. FA samples were washed with HCl solution (1.0 mol L^{-1}) for 16-17 h at room temperature where mixed with HCl (37%v/v) solution at FA waste/HCl weight ratio of 1: 20 (m/v) in a polytetrafluoroethylene beaker. The mixture solutions were filtered and washed several times with deionized water just to remove the water-soluble impurities and the adhered particles on the surface. The samples were dried in oven at 105° C for 24 h and kept in the desiccators prior to activation. Three replicate samples were collected from the same site and analyzed separately.

Preparation of AC from FA residue

Pre treated FA samples ($>3\text{-}4 \text{ g}$) were then dipped into H_2O_2 (30%v/v) solution for

24 h to oxidize volatile organic impurities and subsequently washed with water. In an oven, the FA samples were then heated at 100 °C for 60 min to remove the moisture content. Heat treatment of the samples were carried out by the tube furnace connected to an electric heating boiler for passing combined CO₂ (grade 2.5-B) -steam at 4 psi. The absolute pressure inside the tube was always kept below 0.12 MPa (Mega Pascal) and the heating rate of the furnace was maintained at 5 °C min⁻¹ and 6 psi, respectively. The absolute pressure inside the tube was always kept below 0.12 MPa (Mega Pascal). Samples were further heated between 850-950 °C at a heating rate of 15 °C/min for 3 h at 120 mLmin⁻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 finally dried in the oven at 105 °C for 24 h. The calculated weight loss of FA samples during activation was in the range 17.57 % m/m (Table 1).

Reagents and materials

Analytical reagent grade chemicals were used.

Glassware's were washed with conc.

HNO₃ and deionized water. Phenol, 2-chlorophenol (2-CP), 4-chlorophenol (4-CP), 2,4,6-trichlorophenol (TCP) were purchased from BDH (Poole, England). Stock standard solutions (10-1000 ¼g mL⁻¹) of each phenolic compound were prepared individually at 1.0 mgL⁻¹ in water in the presence of few drops of ethanol and stored at 4 °C in dark. Working solutions (0.1-200 µg mL⁻¹) were prepared by suitable dilution weekly with water from the stock standard solution and stored at 4 °C in in amber glass bottles. Low density polyethylene (LDPE) bottles were carefully cleaned with hot detergent, soaked in 50 % HCl: HNO₃ (2.0 mol L⁻¹), subsequently washed with dilute HCl (0.5 mol L⁻¹) and finally rinsed with deionized water. Britton-Robinson (B-R) buffer (pH 2.2-10) solutions were prepared as reported (Vogel, 1966). A total of six raw FA samples were randomly collected from Rabigh (C₁, C₃, C₅, C₇, C₉, C₁₁) power plants. Vacuum gas oil (Bunker "C") on burning emits enormous amounts of obnoxious and toxic pollutants to the environment along with large amount of high C (87-92%) (36-38 tons/day) (Al-Degs *et al.*, 2014; Alhamed *et al.*, 2015).

Instrumentation

Textural properties (surface & pore size)

of the FA samples before and after activation were measured using NOVA 2200e instrument (Quntachrome) at liquid nitrogen temperature. Heat treatments were carried out by 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. A rotary van vacuum pump (Pfeiffer vacuum) was used to achieve a final pressure < 6x10⁻³ mbar and an exhaust pressure of 250-1500 mbar. Adsorption/desorption isotherms were measured in P/P^o range 0.005 to 0.99. Adsorption measurements of N₂ gas (AHG, 99.99%) as an adsorbate was measured. A particle size analyzer (Fritsch, Analysette 22 MicroTec Plus) installed with Mass Control software was used for measuring of particle size distribution of FA. A Perkin Elmer inductively coupled plasma-optical emission spectrometer (ICP- OES, Optima 4100 DC (Shelton, CT, USA) was used for analysis of V, Fe and Ni in FA samples. A Perkin Elmer spectrophotometer and high performance liquid chromatography (Agilent technologies, C₁₈, 4.6× 150 mm) and UV detector were used for recording the absorbance and HPLC analysis of phenol, 2-chlorophenol (2-CP), 4-chlorophenol (4-CP) and 2,4,6 trichlorophenol (TCP). In HPLC, methanol-H₂O was used as a mobile phase for analysis of phenols at 1.0 mL/min flow rate, 5.0 µl injector volumes, and 3.0 min run time at 270 nm. An Orion model 720 pH Meter was used for pH studies and glass columns (18cm x 15mm id) was utilized for flow experiments. A digital micropipette (Volac) was used for preparation of the solutions. Ultra pure water from Milli-Q Plus system (Millipore, Bedford, MA, USA) was utilized throughout the work.

Recommended experimental procedures

Batch experiments

Batch studies were carried out for the adsorption of phenols onto AC as follows:

In conical flasks (250 mL), accurate weights (0.2 ± 0.001g) of AC prepared by activation of FA by gasification using the combined system steam- CO₂ were equilibrated with aqueous solutions (100.0 mL, 10µg mL⁻¹). The solution pH was adjusted to the required pH (2d" pH d"10) and shaken for 8.0 h at 25±1 °C. After shaking the samples were filtered and the filtrates were subjected to the absorbance measurements and the amounts were determined from absorbance at

»_{max} vs. blank. The amount of CP adsorbed onto the AC adsorbent was calculated by difference in absorbance before and after (A_b , A_a). Following these procedures, the influence of shaking time and analyte concentration (10-50 $\mu\text{g mL}^{-1}$) on phenols uptake by combined steam- CO_2 activated AC after leaching were also studied. The adsorption percentage (% E), the amount of phenol retained at equilibrium (q_e), and the distribution ratio (D) of phenol uptake by AC adsorbent were calculated (El-Shahawi *et al.*, 2011).

Chromatographic separation of CPs by AC-packed column

HPLC analysis of CPs spiked onto in deionized water

The tested phenols were analyzed by the standard HPLC method (Limam, *et al.*, 2010) as follows: Standard solutions (5-10 $\mu\text{g mL}^{-1}$) of phenol, 2-CP, 4-CP and TCP were prepared in deionized water. Separation of phenols individually and in their standard mixtures was carried out in X- Bridge C_{18} (BEH 1.7 μm , 100 Å mm), (Waters, Acoquity UPC²) using the mobile phase 95 % CO_2 : 5 % methanol (at 1.0 mL min^{-1}), the injector volume was 5.0 μL . The system was preconditioned by passing the mobile phase through HPLC system at 1.0 mL min^{-1} flow rate for 3.0 min. Photodiode array detector at the optimum wavelength of each phenolic compound was used for data acquisition.

Chromatographic separation of CPs in water by AC packed Column

Retention and recovery of 2-CP, 4-CP and TCP individually and in their mixtures

A 0.5 L of deionized water spiked with various concentrations (0.1-10.0 $\mu\text{g mL}^{-1}$) of phenol, 2-CP, 4-CP and TCP at pH d^o 2 was percolated individually through the AC packed column at 3-5.0 mL min^{-1} flow rate *versus* reagent blank. Analysis of the effluent by the method of Limam, *et al.*, 2010 revealed complete adsorption of the tested phenols on the AC packed column. The retained phenol, 2-CP, 4-CP and TCP species were recovered with NaOH (10 mL, 0.2 mol L^{-1}). Complete recovery of the phenols was achieved as noted from the absorbance and HPLC measurement (Limam, *et al.*, 2010) after adjustment the pH of the eluate to pH d^o 2 *versus* reagent blank. On the other hand, a various mixtures (0.5-1 L) of 2-CP and TCP (1.0-10 $\mu\text{g mL}^{-1}$) were percolated through

the AC (0.5 \pm 0.02 g) packed column at pH d^o 2 at 2.0 mL min^{-1} flow rate *vs.* blank. Adsorbed CPs species were then recovered with NaOH (10 mL, 0.2 mol L^{-1}) at 2.0 mL min^{-1} flow rate and analyzed by HPLC (Limam, *et al.*, 2010) *versus* reagent blank

Analytical applications

Tap and Red seawater samples were collected from the Chemistry laboratories, King AbdulAziz University and coastal area of north Jeddah city, Saudi Arabia, respectively. The samples were filtered through 0.45 μm cellulose membrane filter prior to analysis. A 1000 mL of tap water spiked with tested 2-CP and TCP individually at concentration (0.1-10 mg mL^{-1}) was percolated through AC packed column. Complete retention and recovery was achieved as described. Data were expressed as mean \pm standard deviation (n=5). Precision was tested by subjecting five sub samples to the sequential procedures

RESULTS AND DISCUSSION

Recently, great attention has been focused on: i) The production of AC from different natural and solid waste materials to be used for removal of inorganic and organic pollutants from contaminated wastewater (Visa *et al.*, 2014; Petrova *et al.*, 2010) and ii) Modifying water treatment technologies for removal of phenol and CPs. Thus, this study is focused on preparation of AC adsorbent from fuel oil FA for utilization as low cost adsorbent for removal of trace phenol and CPs in wastewater.

Characterization of FA and AC

Applications of AC are related to its adsorption characteristics e.g. high surface area, well-developed internal pore structure and surface chemical functional groups located at the outer and inner surfaces (Gokce and Aktas, 2014). Chemical analysis of FA samples revealed considerable content of V, Fe and Ni. The most next abundant elements are Na, S, K, Si, Al in addition to other trace elements. V, Fe and Ni content in the FA samples were in the range 3625.1 \pm 21.8-5601.3 \pm 27.6; 4057.0 \pm 32.7-9913.9 \pm 23.2 and 751.2 \pm 13.7-2632.9 \pm 41.2 $\mu\text{g g}^{-1}$, respectively. The average content of V and Fe was in agreement with the data reported except for Ni (Norris, *et al.*, 2010). Ni species able to form stable complexes and/or organo-nickel compounds with the oxygenated and organo-carbon species in FA resulting in a partial

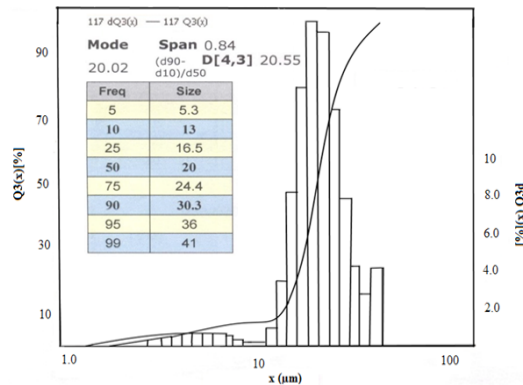


Fig. 1. Particle size distribution for FA (C₁) released from Rabigh desalination power plant

or incomplete digestion of the FA. Average C, H, N and total CHN of FA samples were in the range 87.85 ± 3.78 - 87.93 ± 5.3 ; 0.04 ± 0.003 - 0.15 ± 0.03 ; 1.49 ± 0.27 - 1.51 ± 0.27 and 89.46 ± 3.6 - 89.51 ± 2.14 , respectively. The weight loss of FA samples was 91.45 close with the FA of other heavy fuel oils (Caoa *et al.*, 2014; Alhamed *et al.*, 2015).

Particle size distribution (PSD) of FA samples is measured and representative data of C₁ (without activation) are shown in Fig. 1. Variation of the particle size with milling time and the distribution curve shift to fine size region with increase in the milling time. The curve shows that the effect of longer milling times on the particle

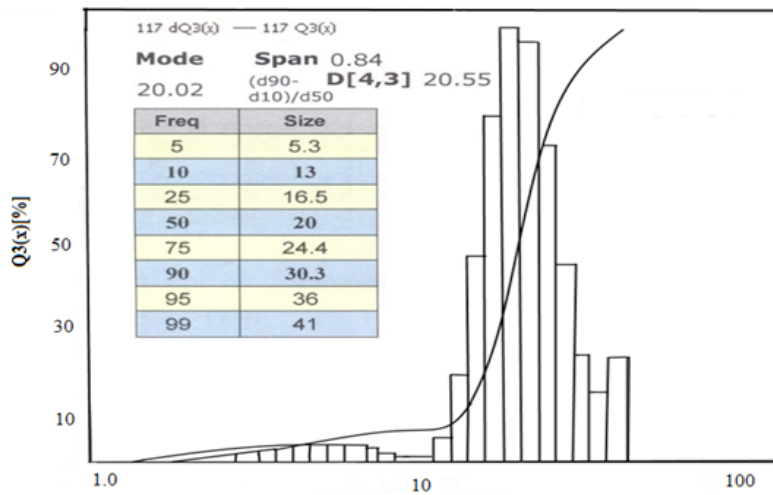


Fig. 2. N₂ Adsorption-desorption isotherm at 77 K of combined CO₂-steam activated carbon (C₂)

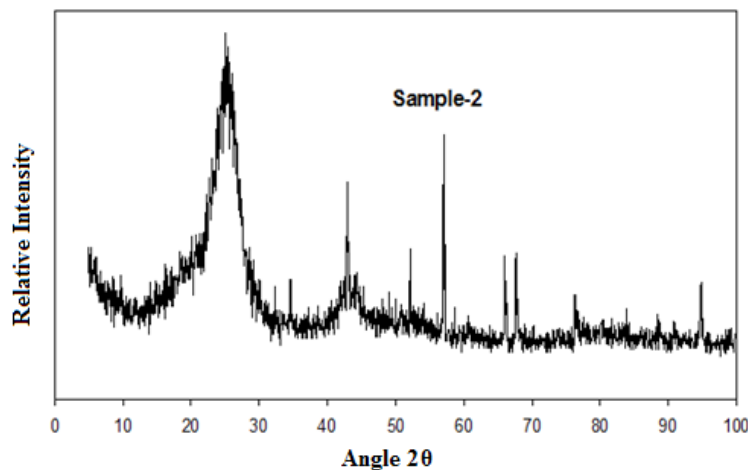


Fig. 3. X-ray diffraction pattern of FA (C₁) sample

size is significant, most likely due the hardness of the particles. Three major sizes were found in the range 1.8-16.4, 15.1-21.6 and 25.3 -30.3 μm with frequencies 10, 50 and 90, respectively. PSD is slightly trimodal and broader than other samples.

Nitrogen adsorption-desorption isotherms of the samples were recorded. Representative data for combined CO_2 -steam activated carbon (C_5) are shown in Fig. 2. Isotherms of samples revealed combination of micro porous and mesoporous

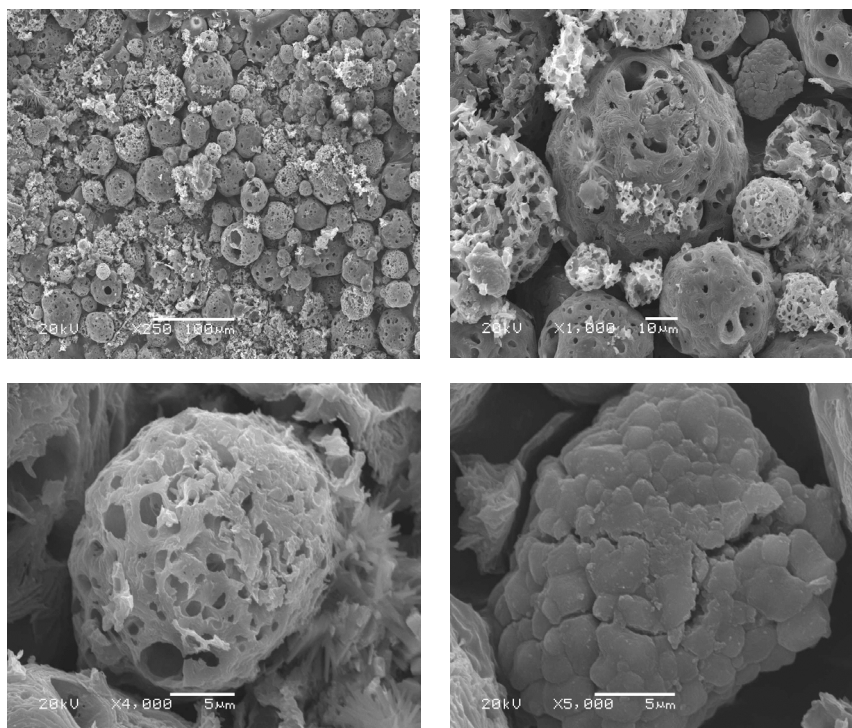


Fig. 4. SEM micrographs of FA sample (C_1) at different resolution (100, 10, 5 and 5 μm)

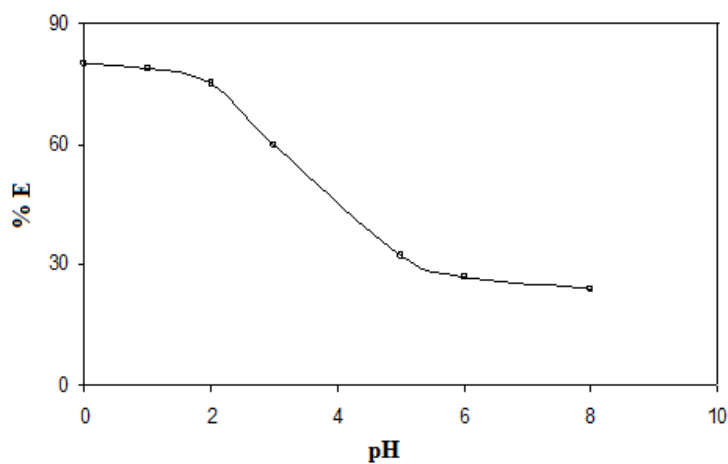


Fig. 5. Effect of pH on the adsorption percentage (%) of 2-CP from the aqueous solutions onto CO_2 -steam AC (C_5) (0.2 ± 0.002 g) at 25 ± 0.1 $^\circ\text{C}$ and $\text{pH} \leq 2$

structures. The surface area of non activated (C_1) and activated FA residues (C_2 - C_6) are summarized in Table 2. The burn of at 850 and 950 °C lies in the range 16.15-25.39 and 16.67-64.6%. The surface area of samples C_5 activated by the combined gasification of CO_2 steam system was 775.919 m^2/g , while for non activated (C_1) and activated carbons (C_2 - C_4 & C_6), the surface area was in the range 71.554 - 423.094 m^2/g , respectively.

The surface area and pore volume of non activated (C_1) and activated FA residues (C_2 - C_6) were critically measured.

The results of pore volume distribution of the investigated non activated (C_1) and activated (C_2 - C_6) samples are depicted in Table 2. Excellent value of pore volume of C_5 (0.138cc/g) was achieved compared to other samples (C_1 and C_2 - C_4 and C_6) samples (Table 2). At 850 °C, the pore volume decreased or did not develop well at

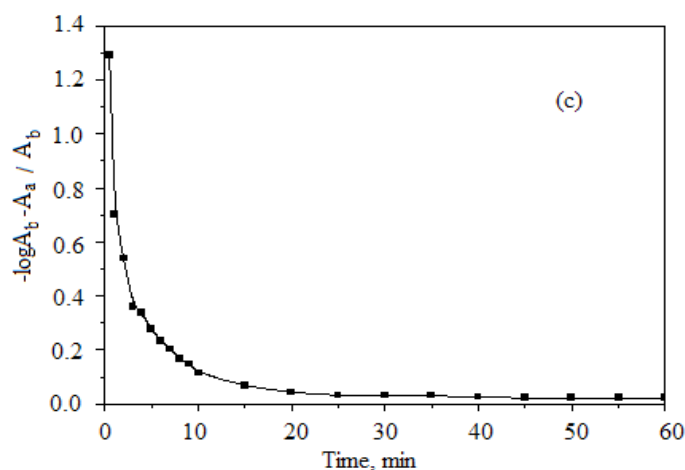


Fig. 6. Rate of 2-CP adsorption from aqueous solution onto combined CO_2 -steam AC (C_5) adsorbent (0.2 ± 0.002 g) at 25 ± 0.1 °C and $pH \leq 2$

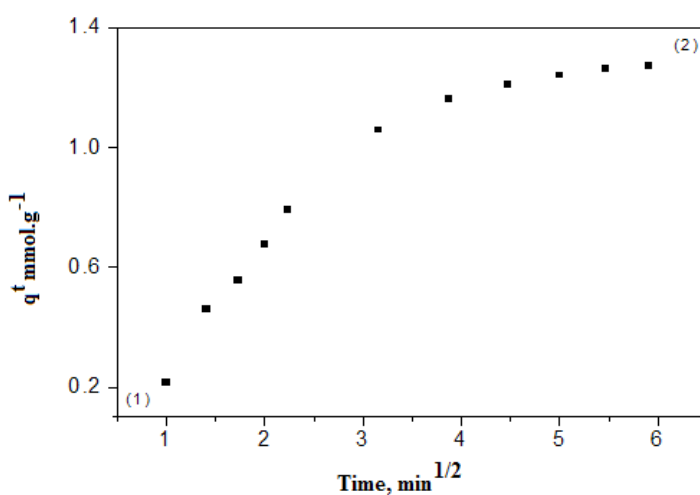


Fig. 7. Plot of the adsorbed concentration of 2-CP onto combined CO_2 -steam AC carbon (C_5) adsorbent (0.2 ± 0.002 g) at 25 ± 0.1 °C and $pH \leq 2$ vs. square root of time at $pH \sim 2$ and 25 ± 1 °C

different time intervals. Thus, activation by CO₂-steam system is the most successful approach for FA activation at 950 °C for 2 h. Thus, C₅ AC was selected in the next work for separation of CPs from water samples.

The XRD patterns of traces of FA samples were recorded at room temperature. Representative XRD for C2 is shown in Fig. 3. Similar broad peaks were noticed in all samples showing highly disordered and amorphous nature

of raw and FA samples. In all samples, calcium containing minerals e.g. CaSO₄, K₂CaCl₃ etc were found whereas anorthite (CaAl₂Si₂O₈) was the only aluminosilicate found with an FOM close to 20 in a agreement with the data reported earlier in the precipitator (Liu *et al.*, 2009.) Presence of sharp structural peaks in the XRD spectra of residual oil FA (C1 & C2) suggested that they are polycrystalline in nature

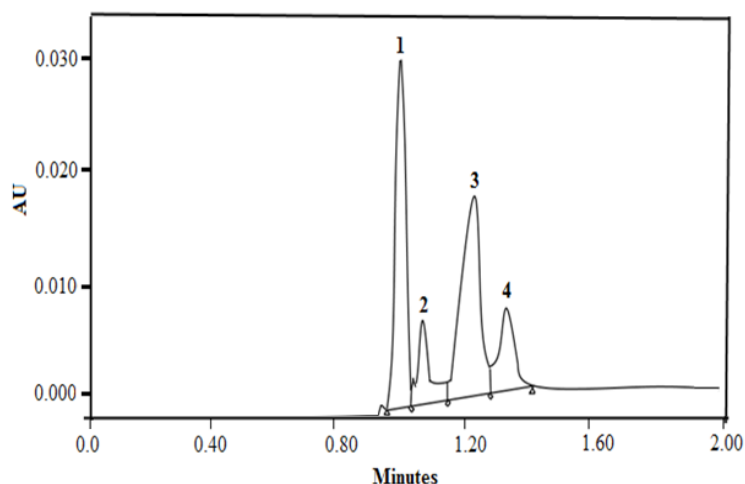


Fig. 8. HPLC chromatogram of the standard solution mixture containing 2-CP, 4-CP, TCP and phenol in water before and after percolation through AC (C₅) packed column

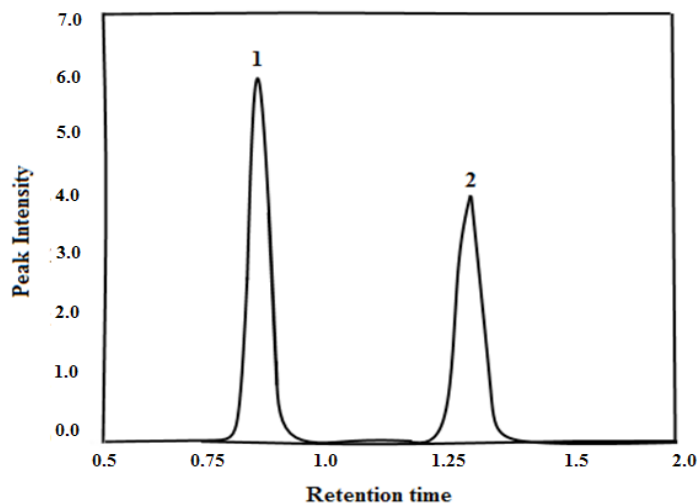


Fig. 9. HPLC chromatogram of 2-CP (a) and 4-CP (2 µg mL⁻¹) at 1.0 mL min⁻¹ flow rate for 2-CP at 25 ± 1 °C in water before and after percolation through AC (C₅) packed column

Table 1. Activation of Rabigh fly ash samples*

Sample	Activation status	Weight loss during activation (%)	Conditions
C ₁	Not activated	—	—
C ₂	Activated	25.39	Steam/850 °C / 1 hr
C ₃	Activated	64.6	Steam/950 °C / 2 hr
C ₄	Activated	16.67	CO ₂ /950 °C / 2 hr
C ₅	Activated	17.57	(CO ₂ -Steam)/950 °C / 2 hr
C ₆	Activated	16.15	(Steam + CO ₂)/850 °C / 2 hr

Table 2. Surface area and pore volume of Rabegh FA samples*

Sample	Activation status	Experimental conditions	Burn-off level(%)	Surface area (m ² /g)	Pore volume (cc/g) in (1.65-1.85 nm) pore width
C ₁	NA	—	—	110.887	0.043
C ₂	Activated	SA at 850 °C (1 hr.)	25.39	256.447	0.091
C ₃	Activated	SA at 950 °C (2 hrs.)	64.6	275.076	0.325
C ₄	Activated	CA at 950 °C (2 hrs.)	16.67	269.013	0.07
C ₅	Activated	SCA at 950 °C (2 hrs.)	17.57	775.919	0.138
C ₆	Activated	SCA at 850 °C (2 hrs.)	16.15	423.094	0.078

*NA: Not Activated; SA: Steam Activated; CA: CO₂ Activated; SCA: Combined CO₂-steam activated.

SEM images were recorded for selected FA samples (C1-C4) at different resolution (10, 20 and 100 μ m) to assign the surface microstructure. SEM images for C1 sample are shown in Fig. 4. The main composition of FA is a porous spheroid of unburned carbon with diameters within a range from 10.0 to 120 μ m larger than that of black carbon and contains small pores few μ m in sizes. The images showed many of iron spheres composed of Fe₂O₃ 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 particles are mainly spherical, porous spheroid of unburned carbon, hollow and granular in size (Fig. 4).

Batch adsorption characteristics of phenol and CPs

Considerable progress has been made on the use of FA and AC generated from heavy oil and coal FA as inexpensive and effective solid adsorbent for the removal of water pollutants (Izquierdo and Rubio, 2008; Alonso-Hernández *et*

al., 2011; Al-Degs, *et al.*, 2014; Salehin, *et al.*, 2015; Alhamed *et al.*, 2015). AC adsorbent concentrates inorganic and organic substances from different aqueous media by adsorption mechanism rather than phase distribution (Al-Ghouti *et al.*, 2011; Salehin, Alhamed *et al.*, 2015). Preliminary study on the extraction of phenol and selected CPs from aqueous solution at pH d'' 2 by combined CO₂-steam AC (C₅) revealed considerable adsorption of the analyte. Thus, in batch experiments, the adsorption profile of 2-CP and 4-CP (10 mg mL⁻¹) individually at a wide range of pH (pH 1.0-9) onto AC (0.1 \pm 0.001g) was performed after shaking at room temperature. CPs in the test aqueous solution before (A_b) and after (A_a) extraction was determined via the difference in the absorbance (A_b - A_a) at λ_{max} for each individual phenol or CP. Results for 2-CP is shown in Fig. 5. The uptake of phenols reached maximum at pH d'' 2 and decreased markedly at higher pH (Fig. 5). The adsorption was rapid and reached equilibrium in a short time, followed by a plateau. At pH d'' 2.0, the high adsorption of phenol and CPs is attributed to: i) Multi mode mechanism involving adsorption

and/ or solvent extraction mechanism; ii). Phenol and/or CPs species at pH d'' 2.0 present in neutral form (not dissociated) and finally iii). Formation of intermolecular H-bonding between the available oxy- species on the AC adsorbent and phenol or CP in the bulk aqueous solution. In aqueous solution of pH >2 , the uptake of phenolic species onto AC adsorbent decreased markedly (Fig. 5) because of deprotonation of phenols at higher pH. Phenol and CPs uptake followed the order: TCP $>$ 2-CP $>$ 4-CP $>$ phenol in agreement with their pKa 6.35, 8.55, 9.38 and 9.90, respectively. Thus, in the next experiments, the solution pH was adjusted at pH d'' 2.0.

Kinetic of phenol and CPs adsorption by AC

The effect of shaking time on phenols uptake by AC adsorbent was studied at various time

Table 3. Extraction and recovery of 2-CP and 4-CP from deionized water by AC packed column at 5 mL min^{-1} flow rate

Compound	Amount added, $\mu\text{g mL}^{-1}$	Found, $\mu\text{g mL}^{-1}$	Recovery*, %
2- CP	1	0.953 \pm 0.07	95.3 \pm 4.9
	5	4.77 \pm 0.23	95.00 \pm 4.8
	10	9.5 \pm 0.5	95.4 \pm 5.3
TCP	1	0.95 \pm 0.04	95.0 \pm 5.3
	5	4.96 \pm 0.04	99.2 \pm 0.81
	10	10.0 \pm 0.0	100 \pm 0.0

* Average (n=3) \pm relative standard deviation at 5 mL min^{-1} flow rate

intervals. The adsorption of the phenols attained equilibrium within a short shaking time followed by a plateau. A representative adsorption rate of 2-CP from the aqueous solution at pH d'' 2 is shown in Fig. 6. The half-life time ($t_{1/2}$) of equilibrium adsorption as calculated from Fig. 6 was 0.80 \pm 0.01, 1.05 \pm 0.01, 1.0 \pm 0.01 and 1.2 \pm 0.04 h for TCP, 2-CP, 4-CP and phenol, respectively.

The results of CPs uptake by AC were further subjected to Weber & Morris, 1963 model:

$$q_t = R_d (t)^{1/2} \quad \dots(1)$$

where, R_d = rate constant of intraparticle transport ($\text{mmol g}^{-1} \text{min}^{-1/2}$) and q_t is the adsorbed phenol concentration (mol.g^{-1}) at time t . Representative results for 2-CP adsorption are demonstrated in Fig. 7. The plot of q_t vs. time was linear ($R^2=0.975$) in the initial stage up to 12.25 min and deviate on time passage (Fig. 7). The plot does not pass through the origin, the kinetics of 2-CP adsorption depends on film and intra particle diffusion and the more rapid one will control the overall rate of 2-CP transport (El-Shahawi *et al*, 2011). The diffusion of 2-CP was high at the early stage and decreased on time passage. Thus, the rate of the retention step is film diffusion at the early stage of extraction. In the second stage, diffusion remains fairly constant where the pores volume of the AC adsorbent is exhausted. Thus, it can be concluded that, 2-CP uptake onto the adsorbent involves the following steps: i- bulk transport of phenol in solution, ii- film transfer of analyte within the pore volume and/or along the pore wall

Table 4. Analytical results of 2-CP and TCP spiked into tap and sea water samples by the proposed iron (0) treated PUFs packed column

Compound	Water sample	Taken, $\mu\text{g L}^{-1}$	Found, $\mu\text{g L}^{-1}$	Recovery*, %
2- CP	Tap water	1	0.945 \pm 0.06	94.5 \pm 5.8
		5	4.83 \pm 0.17	96.6 \pm 3.5
		10	9.58 \pm 0.42	95.8 \pm 4.4
	Sea water	1	0.959 \pm 0.041	95.9 \pm 4.3
		5	4.75 \pm 0.25	94.9 \pm 5.3
		10	9.5 \pm 0.5	95.3 \pm 5.3
TCP	Tap water	1	0.93 \pm 0.07	93 \pm 4.0
		5	5 \pm 0.0	100 \pm 0.0
		10	10 \pm 0.0	100 \pm 0.0
	Sea water	1	1 \pm 0.0	100 \pm 0.0
		5	5 \pm 0.0	100 \pm 0.0
		10	10 \pm 0.0	100 \pm 0.0

*Average (n=3) \pm relative standard deviation

surface by diffusion to the active adsorption sites of AC and finally iii- formation of adsorbed phenols species on the AC. Compared to other microsized adsorbents (Vigan, Neag, 2012), the proposed AC offers a short diffusion route and high surface area which results in rapid extraction dynamics and high extraction capacity.

Chromatographic separation of phenol and CPs by the proposed AC packed column

The kinetics of CPs and phenol uptake from water by AC adsorbent suggested its use in packed column for their separation from deionized water. Thus, deionized water (0.5L) containing 2-CP, 4-CP, TCP and phenol at various concentrations ($1.0-10.0\mu\text{g mL}^{-1}$) were individually percolated through AC packed column at pH d^o 2.0 vs. reagent blank. Complete retention of phenols was achieved as indicated from the absorbance and/or HPLC (Limam, *et al.*, 2010, Pizarro *et al.*, 2007) measurement in the effluent solution. The retained species were then recovered with NaOH (10 mL, 0.2mol L^{-1}) at 2.0 mL min^{-1} flow rate. The absorbance and HPLC (Limam, *et al.*, 2010) data of the eluate after adjusting the solution to pH d^o 2.0, revealed complete recovery of 2-CP ($94.0 \pm 4.9 - 95.4 \pm 5.3\%$) and 4-CP ($95.0 \pm 5.3 - 100 \pm 1.0\%$) (Table 3). These results suggested application of the AC packed column for developing HPLC method for analysis of trace concentrations ($<0.5\mu\text{g L}^{-1}$) of phenols in environmental water samples.

HPLC chromatogram of the standard solutions ($10.0\mu\text{g mL}^{-1}$) for phenol, 2-CP, 4-CP and TCP were recorded individually and their retention times were found equal 0.946, 0.994, 1.222 and 1.31 min, respectively. HPLC chromatogram of standard solution mixture of phenol, 2-CP, 4-CP, TCP at total concentration d^o $10\mu\text{g mL}^{-1}$ in deionized water was recorded at pH 2-3. Representative HPLC chromatogram of the four phenols is shown in Fig. 8. Phenol, 2-CP, 4-CP and TCP were easily identified from their retention times. The slight change in the retention times mixtures as compared to each individual may be attributed to the electrostatic interaction of their phenolic OH group and formation of inter molecular H- bonding between phenols.

HPLC chromatograms of the test solution containing 2-CP, 4-CP, TCP and phenol in water before and after percolation through AC packed column were also recorded. Good recovery

percentage (95.3-107%) of 2-CP, phenol and TCP were achieved whereas low recovery of phenol (85.1 ± 3.9) and 4-CP ($76.8 \pm 2.9\%$) was noticed. A possible explanation for the poor recovery of phenol and 4-CP in comparison to 2-CP and TCP may be due to the incorrect calculation of their HPLC peak areas and/or high adsorption affinity towards AC resulting in incomplete recovery of their species. The low lipophilicity of phenol and 4-CP decreases their penetration through the AC packed column. Thus, the HPLC chromatogram of phenol and 4-CP very sensitive to any slight change in the experimental conditions. The results suggested use of AC packed column for HPLC separation of trace concentrations ($<0.5\mu\text{g L}^{-1}$) of 2-CP and TCP in environmental water samples.

Figures of merits of the proposed AC packed column

Solution mixtures containing 2-CP and TCP at various concentrations ($0.1-10\mu\text{g/L}$) in deionized water were passed through the AC packed column at pH < 2. Complete extraction of 2-CP and TCP was achieved as indicated from the HPLC chromatograms before and after percolation through AC packed column. The adsorbed species were then recovered with NaOH (10 mL, 0.2 mol/L) at 2.0 mL min^{-1} flow rate. The plots of peak area (A) of the HPLC chromatograms vs. concentrations ($0.1-10\mu\text{g/L}$) of 2-CP and/or TCP were linear as given by the following regression equations:

$$A = 5.1 \times 10^3 C (\text{ng L}^{-1}) + 12.96, (r^2=0.9995, n=10) \quad \dots(2)$$

$$A = 4.2 \times 10^3 C (\text{ng L}^{-1}) + 11.15, (r^2=0.9985, n=10) \quad \dots(3)$$

respectively. The value of C is the CP concentration. Representative HPLC chromatogram of the recovered 2-CP and TCP ($2\mu\text{g mL}^{-1}$) in water with NaOH (1.0 mol/L) at 1.0 mL min^{-1} flow rate at $25 \pm 1^\circ\text{C}$ is shown in Fig. 9.

The values of LOD ($\text{LOD} = 3S_{y/x}/b$) and quantification ($\text{LOQ} = 10S_{y/x}/b$) (Miller and Miller, 2010) for 2-CP were found equal 0.7 and $2.7\mu\text{g L}^{-1}$ for 2-CP and 0.8 and $2.9\mu\text{g L}^{-1}$ for TCP, respectively ($V_{\text{sample}} = 0.5\text{L}$) where, $S_{y/x}$ is the standard deviation of y- residual and b is the slope of the linear plot. The enrichment factor ($F_c = V_{s,b}/V_{e,v}$) i.e. the ratio between the volume of 2-CP before preconcentration ($V_{s,b} = 1.0\text{ L}$) and the volume of eluent after recovery

($V_{e,v} = 0.01L$) was in the range 100-110, where's the sensitivity factor (the ratio of the slopes with and without preconcentration) was 33.3-35.2. The RSD for extraction and subsequent determination of standard 2-CP solution ($5 \frac{1}{4}g L^{-1}$) was $\pm 2.3 \%$ ($n = 5$). The LOD and LOQ of the developed AC packed column were satisfactorily compared with the standard HPLC methods ((Pizarro *et al.*, 2007; Limam, *et al.*, 2010) and many spectrophotometric and electroanalytical methods confirming the utility of the AC packed column. The value of LOD of the proposed AC packed column is lower than the allowable limit for CPs set by WHO in water. The proposed AC packed column good enrichment and selectivity, low LOD and easy sample preparation for analysis of CPs in water.

Method validation

The analytical utility of AC packed column was validated by preconcentration and determination of 2-CP and TCP from water at trace concentrations ($0.1 - 1.0 \mu g mL^{-1}$). Satisfactorily extraction and recovery of $1.0 \frac{1}{4}g L^{-1}$ (93.0 ± 5 to 101.8 ± 1.6) of both 2-CP and TCP in their mixture in water (1.0 L) was achieved. The results were compared with the standard HPLC methods (Limam, *et al.*, 2010; Pizarro *et al.*, 2007) for analysis of 2-CP and TCP in water. CPs. The results were further subjected to student *t* test at 95% confidence ($n=5$). No significant differences between the experimental *t* ($t_{exp} = 0.0-2.17$) and tabulated ($t_{tab} = 2.78$) values (Miller & Miller, 2010). Thus, the proposed AC packed column provides good precision for collection and subsequent analysis of CPs in water. AC packed column could be reused for more than three times without decrease in column performance, Hence, the utility of our low SPE may serve positively in point-of-care applications.

Analytical applications

The utility of AC packed column was assessed by performing the recovery tests of spiked 2-CP and/ or TCP ($1.0 - 10 \frac{1}{4}g L^{-1}$) individually and/ or in mixture onto tap- and seawater sample (0.5-1.0 L). The test solutions were first spiked with the tested 2-CP ($1.0 - 10 \frac{1}{4}g L^{-1}$); filtered with cellulose membrane filter ($0.25 \mu m$) and percolated through AC packed columns at $pH < 2.0$. The retained CPs onto the AC packed column were recovered by NaOH and finally analyzed by the proposed and standard HPLC method (Limam, *et al.*, 2010).

The results are summarized in Table 4. At 95 % confidence ($P=0.05, n=5$), the experimental student *-t* ($t_{exp} 1.81-1.93$) and *F* ($F_{exp} 1.21-5.76$) tests were lower than the tabulated *t* ($t_{crit.} = 2.78$) and *F* (6.38) values showing no significant differences between the added and found CPs (Miller, Miller, J.C. (2010).

Robustness (pH, volume of analyte and mass of AC adsorbent packed column)

The robustness test of the AC packed column was performed by measuring the extraction percentage of TCP after slight change in various pH, volume of analyte and mass of AC as described. The recovery percentage (%E) of TCP measured at various pH (pH 0.0-2.5) showed no significant differences ($\%E = E_2 - E_1$) between the recovery of the sample measured following the recommended procedures (E_1) and results after slight change of pH (E_2). Thus, AC packed column has acceptable working pH range adding further confirmation to the used adsorbent. The test was also performed by measuring the recovery percentage after slight changes in volume of the extraction media and mass of AC. Acceptable data were achieved as the differences in the percent recovery was $d \pm 5\%$.

CONCLUSIONS

This manuscript offers a snapshot of the field of utilization of FA solid waste at this critical stage. AC prepared from FA solid waste has a great potential for portability and field applicability as an effective SPE for removal, enrichment and/or subsequent HPLC determination of CPs in water samples. Fast development in the field of utilization of FA in analytical chemistry will continue in the foreseeable future bringing solutions to many of the current CPs analysis challenges. The developed method offers LOD lower than maximum allowable level (MAL) of phenols in water set by WHO and favorably compared with LOD of many spectrochemical, chromatographic and electrochemical techniques. The method could be extended to pico-mole regime via online preconcentration methods. More work is necessary to: i) predict the performance of CPs removal from real effluents; ii) perform more work on phenol adsorption from mixed pollution effluents; iii) better understand mechanism of phenol retention on various adsorbents including

AC and finally; iv) perform the feasibility study of various cost-effectiveness adsorbents at industrial scales at shorter reaction time. The results suggest a rationale techno-economic sense for an organization to a prudent environmental management program to assess the environmental impacts of global petroleum industry is of great importance (Ismail *et al.*, 2013). AC packed column could be reused for 3 times without decrease in column performance.

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