

Enhancing the removal of hazardous pollutants from coke making wastewater by dosing activated carbon to a pilot-scale activated sludge process

Application of activated carbon for coke making wastewater treatment.

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ABSTRACT

BACKGROUND

Powdered activated carbon (PAC) was investigated for its ability to remove 6 polycyclic aromatic hydrocarbons (Σ 6PAHs) (fluoranthene, benzo[b+J]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, benzo[g,h,i]perylene), trace metals and colour from coke making wastewater when dosed to a pilot-plant activated sludge process (ASP). The ASP had a volume of 0.68 m³ and was operated to simulate the full-scale ASP treating coke wastewater from a steel works. Operational conditions included a flow rate of 0.78 m³/day, a hydraulic retention time of 21 hours, a sludge retention time of 38 days and a temperature of 27°C. The ASP was operated for a control period before PAC was dosed directly into the aeration cell at a dose of 400 mg/L.

RESULTS

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Powdered activated carbon addition resulted in a 20% increase in removal efficiency of the Σ 6PAHs. Removal efficiency of trace metals was variable, but increased for nickel, chromium and cadmium by 22.6%, 20.5% and 12.4%, respectively. Improvement in colour removal efficiency was marginal at 5%.

CONCLUSION

PAC addition allowed the improvement of treatment efficiencies in the ASP process at relatively low capital and operational costs, which may assist in reaching tighter effluent emission limits set for the industry.

KEYWORDS

Activated carbon Polycyclic aromatic hydrocarbons Trace metals Activated sludge process Coke wastewater

INTRODUCTION

Coke making wastewaters originate from the quenching of hot coke masses and washing of ammonia stills as well as the cooling and washing of coke oven gases ¹. Coke making wastewater contains numerous compounds capable of causing toxic effects in the environment including ammonia (NH_4^+), thiocyanate (SCN^-), cyanide (CN^-), phenols, polycyclic aromatic hydrocarbons (PAHs) and trace metals ²⁻⁸. Characteristics of coke making wastewater vary between production plants in response to both the composition of the coals used and differences in plant operation ³. Ammonia concentrations have been reported from as low as 123 mg/L ⁹ up to 4500 mg/L ¹⁰. Thiocyanate was reported by Gould ¹⁰ in the range of 130 to 860 mg/L with values of ca. 200 mg/L being reported at other

treatment plants ^{9,11}. Phenol concentrations also vary between plants from as low as 60 mg/L ¹¹ to 1900 mg/L ¹⁰ with average values of ca. 250 mg/L ^{10,12}. Typically chemical oxygen demand (COD) averages at 2300 mg/L ¹⁰⁻¹² whilst biological oxygen demand (BOD) shows large degrees of variation from 683 mg/L ¹² to 2800 mg/L ¹⁰.

As a result of increasing concern over pollutant emissions to the aquatic environment emission limits for industrial wastewater have become increasingly stringent. New emission limits were introduced in 2016 for coke making wastewaters under the Industrial Emissions Directive (IED) ¹³. Six PAHs (Σ 6PAHs: fluoranthene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene and benzo[g,h,i]perylene) and some metals have been identified in the best available technology (BAT) reference document for the production of iron and steel ¹³ but there is little information available on their concentrations in coke making wastewater. Zhang et al. ¹⁴ reported Σ 18PAHs of 5470 ± 907 μ g/L and 4.7 ± 0.4 μ g/L in untreated and treated wastewater, respectively. Recently Σ 6PAHs were reported for treated effluent from a UK steel making wastewater with average concentrations of 36.3 μ g/L and a range of 8.5 - 99.4 μ g/L ⁸. Burmistrz and Burmistrz ¹⁵ reported EPA Σ 16PAHs in untreated coke wastewater varying between 255 - 312 μ g/L and 0.94 - 4.46 μ g/L in treated effluent. Chen et al. ⁸ also reported trace metal emission factors for cadmium (Cd), lead (Pb), nickel (Ni), chromium (Cr), iron (Fe), copper (Cu), zinc (Zn) and arsenic (As) of 0.04, 4.7, 6.0, 11.7, 1003, 1.1, 410 and 4.6 mg/tonne of coke, respectively.

A number of trace metals and PAHs frequently occurring in coke making effluents have been listed as priority substances ¹⁶ (Table I) under the Water Framework Directive (WFD) ¹⁷. The new achievable emission limits introduced for coke making wastewaters based on emissions

associated with the BAT¹³ consist of <220 mg/L COD, <20 mg/L BOD₅, <4 mg/L SCN⁻, <0.1 mg/L easily released cyanide ion (CN⁻), <50 µg/L Σ6PAHs and <15-50 mg/L for the sum of ammonia-nitrogen, nitrate-nitrogen and nitrite-nitrogen. In particular, the high variability of PAH concentrations in coke making effluent reported by Chen et al.⁸ means consistently achieving the emission limit may be problematic and consequently there is a need to improve pollutant removal efficiencies.

Table I: Priority Hazardous Substances (PHS), Priority Substances (PS) and Specific Pollutants (SP) associated with coke wastewaters.

The treatment of coke making wastewater typically takes place through biological treatment using activated sludge processes (ASP), although, many treatment plants also use initial pre-treatment methods e.g. steam stripping and chemical coagulation^{6,18}. Different treatment plants can also use different combinations of anoxic, anaerobic and aerobic treatment cells in order to reduce target pollutants.

The use of activated carbon (AC) has received considerable attention for a number of decades for the removal of pollutants found in both industrial¹⁹⁻²⁶ and domestic wastewaters²⁷⁻³¹ and may allow improved treatment efficiencies of coke making wastewater. Activated carbon can be applied as a pre-treatment method, dosed directly into the treatment process or applied as a post-treatment method^{32,33}. It can also be in either a granular (GAC) or powdered (PAC) form. Due to its larger pore size GAC is more suitable for heavy molecular weight pollutants³⁴. When added into the ASP, it acts as an absorbent whilst also providing a surface for microorganisms to grow in a biofilm^{19,35}. This allows pollutants to be absorbed and then

diffused out gradually, allowing increased contact times between the microorganisms and pollutant, which enhances the removal of less easily degradable compounds which may require a higher residence time³⁵.

Activated carbon has been successfully applied to PAHs and trace metal removal in a variety of industrial as well as domestic wastewaters using a range of AC types and operational configurations^{19-21,36-38}. Removals of 96.9 - 99.7% of Σ 36PAHs have been demonstrated in a batch mode pilot-scale biologically activated carbon system treating wastewaters containing petroleum products³⁹. Furthermore, the benefit of addition of AC to coke making wastewaters has been demonstrated in a laboratory-scale continuous flow reactor. A dose rate of 300 mg/L and a hydraulic retention time (HRT) of 20 h resulted in a 26% increase in COD removal and more stable cyanide removal²⁶. More recently a batch study using activated coke (carbonaceous material activated by steam and similar to AC but with a lower surface area) demonstrated improved removals of COD (91.6%) and colour (90%) at a dose rate of 200 g/L⁴⁰.

The majority of research focussing on PAH and trace metal removal with AC has been completed in batch systems. Goel et al.²² identified the limitations of applying those results to real treatment applications, explaining that in batch tests adsorption continues until an equilibrium is established but in a continuous treatment system this equilibrium is never achieved, resulting in significantly different efficiencies. Therefore, the objective of this study was to address the current gap in knowledge on the ability of AC to improve removal efficiencies of PAHs and trace metals from coke making wastewater in a continuous process at a significant scale (0.68 m³) pilot-plant. Results from this study can also offer insight on

the treatability of other types of wastewaters that contain PAHs and or trace metals through an ASP with AC addition.

EXPERIMENTAL

Wastewater and activated sludge seed

Coke making wastewater and return activated sludge (for seeding the pilot-plant) were sourced from a UK, full-scale, industrial wastewater treatment plant (WWTP) that processed coke making wastewater. The full-scale WWTP included an inlet reservoir and an activated sludge process with 4 aeration tanks, followed by 2 clarifiers. Each aeration tank had a volume of 570 m³ and received wastewater at a flow rate of 680 m³/day allowing for a HRT of 21 hours and a sludge retention time (SRT) of 38 days. Return activated sludge was recirculated from the clarifier to the aeration cell.

Pilot-plant

In order to investigate the ability of PAC to treat coke making wastewater, an ASP pilot-plant was established following the configuration shown in Figure I. The pilot-plant followed the same configuration as the full-scale treatment plant running at an equivalent HRT and SRT of 21 hours and 38 days, respectively. The wastewater entered the aerobic cell at 0.78 m³/day with an overflow into the clarifier. The settled sludge was recirculated at a flow rate of 1.6 m³/day and waste sludge removed manually at a rate of 6 L/day. The temperature and dissolved oxygen was maintained at ca. 27°C and 2 - 4 mg/L respectively, the same conditions as the full-scale plant. The pH within the system averaged at 6.8.

Figure I: Schematic representation of the activated sludge pilot-plant with PAC addition.

The pilot-plant was operated for a control period, equivalent to 14 times the HRT, with samples collected 3 times per week for PAH, trace metal, suspended solids and colour analysis. After the control period the pilot-plant was dosed with 400 mg/L of PAC directly into the aeration cell in batch mode 3 times per week. The PAC used was, a commercial product, produced from lignite and characterised by a grain size (D_{50}) of 24 μm , a bulk density of 0.44 g/cm^3 , a specific surface area of $300 \pm 30 \text{ m}^2/\text{g}$ and a 0.5% moisture content. The PAC dose rate was based on a previous application by Chao et al.²⁶ of 300 mg/L, being increased to reflect the slightly higher average total phenol and thiocyanate levels in the studied coke making wastewater (Table II). Samples were taken for PAH, trace metal, suspended solids and colour analysis 3 times per week. Removal efficiencies of total phenol and SCN^- were monitored throughout to ensure no negative impacts occurred due to PAC addition as the degradation of these compounds is an essential requirement for the successful treatment of coke making wastewater.

Analysis

Total phenol

Total phenol analyses were completed by adding Folin Ciocalteu reagent and sodium carbonate (20% w/v) to filtered samples (1.25 μm filter) and quantified by measurement in a spectrophotometer at wavelength of 760 nm (20 mm cell) (Cecil CE 1011)⁴¹.

Thiocyanate

Samples were filtered (1.25 μm filter) and the SCN^- concentration measured using a Galley photometric system (Thermo Scientific, United States) that was calibrated using potassium

thiocyanate (0-500 mg/l) (based on The Institute of Gas Engineers analytical method for thiocyanate)⁴².

Colour

Samples were filtered through a 0.45 μ m filter and the residual colour was then analysed using a Jenway 6300 spectrophotometer (Staffordshire, UK) at a wavelength of 470 nm⁴³.

Suspended solids (SS)

Suspended solids were analysed according to standard methods⁴⁴. A 100 ml sample was filtered (1.25 μ m filter) and dried at 105 \pm 5°C for 1 hour. Filter papers were then weighed and dried until a constant weight was achieved.

PAHs

Samples were collected and stored at 2 - 8°C. Analysis was based on ISO 11338-2⁴⁵. Samples were filtered (Whatman GF/C 70 mm diameter) to separate the particulate matter from the liquid phase. The particulate matter was dried for 12 h in a fume cupboard and subsequently extracted by accelerated solvent extraction with dichloromethane at 2000 psi and 150°C using a Dionex ASE 200 (Runcorn, UK). Filters were placed into the cells where they were filled with dichloromethane. The solvent containing the organics was then flushed out under a nitrogen stream. The dichloromethane extract was then concentrated, solvent exchanged with methanol, added to the liquid phase and then extracted using an AutoTrace solid phase extractor (Caliper Life Sciences). The PAH SPE extraction cartridges (750 mg/3 ml) were conditioned with methanol and water. The samples were loaded and PAHs were retained on the cartridge which was rinsed with methanol and water (20/80 v/v) and dried under a stream of nitrogen. The PAH fraction was then eluted using tetrahydrofuran and hexane. The extract was then solvent exchanged with hexane and analysed using GC-MS

(Agilent 6890 Gas Chromatograph coupled to a Agilent 5973 MSD Mass Spectrometer). A capillary column (Agilent DB-5MS) was used with a constant flow rate operating under temperatures between 50°C and 310°C at specified rates and intervals over a 55 minute timescale. The Σ 6PAHs quantified were fluoranthene, benzo[b+j]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene and benzo[g,h,i]perylene.

Trace metals

Samples were analysed for total metals, aluminium (Al), vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), arsenic (As), cadmium (Cd) and lead (Pb) based on ISO method 17294-1⁴⁶. For the analysis of total metal concentrations, 3 ml of nitric acid were added to 27 ml of sample and placed on a hotplate for 2 h at 90°C. Each sample was then digested using a CEM Microwave Assisted Reaction System (MARS) using XP-1500 Plus High-Pressure Digestion vessels. Samples were then analysed using an Agilent 7500cx ICP/MS (Stockport, UK) with an Octopole Reaction System in order to overcome interferences (Agilent Technologies).

Statistical analysis

Due to the high degree of natural variation in PAH concentrations measured in the wastewater feeding the pilot-plant both PAH and trace metal data was analysed statistically using an f-test, to ensure that the data fitted within a normal range of variance. PAH data was analysed using a paired T-Test at a 90% confidence level. Trace metal data was analysed using a paired T-Test with 95% confidence level.

RESULTS AND DISCUSSION

Wastewater characterisation

On average the full-scale coke making wastewater contained 221 mg/L of total phenol and 195 mg/L of thiocyanate (SCN^-) (Table II). Trace metal concentrations ranged from 0.13 $\mu\text{g/L}$ Cd to 3612 $\mu\text{g/L}$ Fe. Therefore, Fe constituted the majority of the total trace metals measured at 4216 $\mu\text{g/L}$ (Table II). The $\Sigma 6\text{PAHs}$ presented typical total concentrations of 179 $\mu\text{g/L}$. Individual PAHs varied from 13.6 $\mu\text{g/L}$ (benzo[g,h,i]perylene) to 64.4 $\mu\text{g/L}$ (fluoranthene). The new emission limit for the $\Sigma 6\text{PAHs}$ to achieve following treatment is 50 $\mu\text{g/L}$, hence effective treatment of PAHs in the treatment facility is crucial to achieve the required limit¹³.

Table II: Typical characteristics of coke making wastewater before and after treatment in the ASP pilot- plant during control operational conditions (without PAC treatment) and their associated treatment efficiencies.

Comparison of treatment efficiencies of the pilot-plant and full-scale treatment works during the control period (without PAC dosing)

During the control period the ASP achieved total phenol and SCN^- removal efficiencies comparable to the full-scale treatment works. Effluent SCN^- averaged at 0.7 mg/L leading to an average removal efficiency for SCN^- was 99%. Removal efficiencies remained stable despite fluctuations in inlet feed concentrations allowing compliance with the 4 mg/L emission limit (Figure II). Total phenol removal reached 97%, which was in the same order of magnitude as the full-scale treatment removal efficiency of 99% (Figure II). Such results confirmed that the pilot-plant was operating effectively. Removal efficiencies of total phenol and SCN^- were maintained during the addition of PAC demonstrating that PAC did not impact the removal of the biodegradable pollutants SCN^- and total phenol (Figure II).

Similarly, Chao et al. ²⁶ reported removal of total phenol to <1 mg/L and therefore observed no improvement in total phenol removal at dose rates of 200 -1000 mg/L. Although both SCN^- and total phenol were efficiently degraded by the well adapted biomass under control conditions it was equally important that no negative impacts were observed as emissions of both SCN^- and total phenol are regulated under the IED.

Figure II: a - Removal efficiency of total phenol and SCN^- during the control ASP and ASP dosed with 400 mg/L PAC. • SCN^- without PAC, ○ SCN^- with 400 mg/L PAC, ■ Total phenol without PAC, □ total phenol with 400 mg/L PAC. b - Suspended solid concentrations in outlet during the control ASP and ASP dosed with 400 mg/L PAC. ■ Suspended solids without PAC, □ suspended solids with 400 mg/L PAC. c- Colour removal efficiency during the control ASP and ASP dosed with 400 mg/L PAC. ■ Colour removal efficiency without PAC, □ colour removal efficiency with 400 mg/L PAC.

Impact of PAC addition on suspended solids (SS) and colour removal

The SS removal showed a small increase from 20 mg/L to 24 mg/L, before and after PAC dosing, respectively. Despite this, the standard deviation of the SS measurement after PAC dosing (SD) decreased from 11 to 7 mg/L, suggesting a small improvement on sludge settling characteristics. The use of AC in ASP processes has been reported to promote rapid settling and enhance sludge dewatering, which are added benefits of the AC dosing ³². Addition of PAC resulted in a 5% improvement in colour removal, which was lower than other values previously reported. The use of PAC in the treatment of steel mill coke effluent at a dose of 300 mg/L resulted in a 50% removal of colour ²⁶. Zhang et al. ⁴⁰ reported a 90% colour

removal when treating coking wastewater with activated coke, however, this was at a much larger dosing rate of 200 g/L and under batch rather than continuous operational conditions.

Impact of PAC addition on trace metals removal

Addition of PAC to the ASP led to variable removals of trace metals (Table III). Cadmium, a Priority Hazardous Substance (PHS), showed improved removal with average efficiency, increasing from 45.4% to 57.8%, after PAC dosing. Cadmium removal was also more stable with the removal efficiency standard deviation decreasing from 16% to 11%. Trace metal removal has been strongly associated with the pH of a solution due its role in influencing the ion charge and associated characteristics⁴⁸. The pH in this study was not at the optimum for Cd removal averaging at 6.8. During batch tests with GAC Leyva-Ramos et al.⁴⁹ reported a twelve fold increase in adsorption and associated removal of Cd(II) with a pH change of 3 to 8.

Table III: Average treatment efficiencies for the removal of trace metals, in the continuous activated sludge pilot- plant with and without PAC, showing a significant increase in the removal of Ni using T-test statistical analysis.

Figure III: Removal of nickel • Inlet no AC, ○ inlet 400 mg/L AC. ■ Outlet no AC, □ outlet 400 mg/L AC, showing increased stability of outlet Ni concentrations.

The largest improvement in trace metals removal was observed for Ni. Addition of PAC to the ASP process led to a significant improvement in Ni with an increase in average removal

efficiency of 22.6%. As with Cd, the average removal efficiency became more stable with the standard deviation being observed to fall from 12.3% to 7.7% (Table III). Through batch tests with AC, Karnib et al.³⁷ found that Ni showed the greatest removal efficiency in comparison to Pb, Zn and Cd for each of the tested metal concentrations of 30 - 200 µg/L. PAC was also identified as the best absorbent for Ni in batch tests due to its higher surface area (710 m²/g) compared to other tested AC products which were characterised by lower surface areas (420-485 m²/g)⁵⁰. The PAC selected in this investigation had a lower surface area than the PAC products tested by Rao et al.⁵⁰, however, it managed to achieve higher removal rates at lower dose rates. Rao et al.⁵⁰ also reported an optimum pH of 8 for maximum Ni removal (56% with 1000 mg/L PAC). As stated earlier the studied ASP process, with a pH of 6.8, was operating below the reported optimum of 8 but despite this a dose rate of 400 mg/L was capable of a removal efficiency of 69.5%. Powdered activated carbon addition resulted in a 20.5% improvement in Cr removal. As in the case of Ni and Cd, the observed removal efficiency standard deviation decreased from 40.7% to 14.0%, after PAC dosing.

The average removal efficiency of Zn increased by just 2% leading to no significant difference. Zn removal has been shown to be dependent on individual treatment process conditions (pH and temperature) and the type of AC³⁸. For some AC products temperature has little impact on adsorption whilst for others temperature increases also increased removal³⁸. At 27°C, the temperature in the studied ASP process, should have encouraged Zn removal, however, only small improvements were seen suggesting that the PAC selected in the current application may lack the acidic adsorption sites necessary for Zn adsorption.

Although improvements were seen in the removal of some trace metals after PAC dosing, this was not observed for all metals investigated. Trace metal removals for Al, Mn, Fe, Co, Cu, As and Pb were shown to decline (Table III). The presence of a mixture of trace metals in the wastewater may be responsible for some removal efficiencies being lower than those reported in literature. Many investigations consider the ability of AC to improve the removal of a single trace metal. When numerous trace metals are present, their ability to compete for available active sites impacts the observed removal efficiencies. Petrov et al.⁵¹ reported that the presence of Cu^{2+} , Pb^{2+} , Zn^{2+} and Cd^{2+} in equal quantities resulted in decreased adsorptions of each. This was due to the preferential adsorption of Cd^{2+} over the other metal ions ($\text{Cd}^{2+} > \text{Zn}^{2+} > \text{Pb}^{2+} > \text{Cu}^{2+}$). Netzer and Hughes⁵² reported the impact of different contact time requirements of different metals, with those requiring less contact time demonstrating higher removals. Lead removal efficiencies, for example, decreased in the presence of other metals such as Cu and Co. Low removal efficiencies of As in control conditions (12.6%) and the further decline in efficiency when PAC was dosed (0.5%) may be the result of such factors.

Impact of PAC addition on PAHs removal

$\Sigma 6\text{PAHs}$ entered the pilot-plant at $213 \pm 71 \mu\text{g/L}$ (Figure IV). Improvements in removal efficiencies were significant for fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene and benzo[g,h,i]perylene resulting in a significant improvement in the removal of the average $\Sigma 6\text{PAHs}$ (58.2% to 77.8%) (Table IV). Stability in the treatment of the $\Sigma 6\text{PAHs}$ was also improved with a reduction of ca. 50% in the standard deviation (Table IV). Overall the concentration of $\Sigma 6\text{PAHs}$ fell from an average of $54 \pm 21 \mu\text{g/L}$ under control conditions to $34 \pm 11 \mu\text{g/L}$ after combined ASP and PAC addition (Table IV). Outlet concentrations were

therefore in compliance with the new emission limit of $<50 \mu\text{g/L } \Sigma 6\text{PAHs}$ ¹³, demonstrating the benefit of adding PAC to ASP.

Figure IV: Removal of $\Sigma 6\text{PAHs}$. • Inlet no AC, ○ inlet 400 mg/L AC. ■ Outlet no AC, □ outlet 400 mg/L AC.

Table IV: Average removal efficiency for PAHs with and without AC dosing in the continuous activated sludge pilot plant. Improvements in removal efficiency were significant and standard deviations were reduced by 50%.

High molecular weight PAHs are known for increased persistence in the environment being characterised by high n-Octanol/water partition coefficients ($\log K_{ow}$)^{35,53}. Of the PAHs investigated $\log K_{ow}$ values range from 5.12 - 7.66 demonstrating their lipophilic nature and the likelihood of the PAHs to adsorb^{54,55}. As AC contains macro as well as micro-pores it is particularly suitable for the sorption of PAHs including those of high molecular weights³⁴. If the PAH mixture contains varying sizes there will therefore be an increased removal efficiency for smaller PAH molecules, especially in PAC, due to a higher number of micropores which are suitable for their sorption. The AC product used in this investigation was in powdered form. Consequently, micropores would outnumber macropores which could result in lower removal efficiencies of high molecular weight PAHs⁵⁶. Both indeno[1,2,3-cd]pyrene and benzo[g,h,i]perylene have a high molecular weight of 276 g/mol and therefore improved removal of these more resistant PAHs is of notable importance. Despite PAC being characterised by fewer macropores improved removal efficiencies were seen for both

indeno[1,2,3-cd]pyrene and benzo[g,h,i]perylene (28% and 30% respectively). Research into the effect of multiple PAH compounds occurring simultaneously suggests that the adsorption of PAHs will be influenced by the molecular weight of the compound ⁵⁶. This is a limiting factor in the current investigation.

Removal of PAHs was associated with adsorption due to their lipophilic nature and associated poor biodegradability ¹⁵. Furthermore, biofilm formation would be limited as a result of the high levels of aeration applied in aeration cell and resulting shear ⁵⁷. Additionally, any further benefit of PAC in relation to biofilm formation would be limited as a result of the high SRT of 38 days present under normal operational conditions and a long-term adaptation period required for biofilm formation which was not accounted for in this investigation ¹⁹. Longer-term investigations are required to investigate whether biofilm formation would result in biological degradation rather than adsorption alone.

Economic feasibility of PAC addition to the ASP process

In order to assess the economic feasibility of PAC addition to the ASP, for the removal of PAHs and trace metals from coke making wastewater, the capital expenditure (CAPEX) and operational expenditure (OPEX) were calculated (Table V). Costs were calculated for a full-scale ASP, following the configuration of the tested pilot-plant, based on an assumed plant with a capacity of 2000 m³/day. A dose rate of 400 mg/L was selected due to the aforementioned comparison with the previous application by Chao et al. ²⁶, however, the selected dose rate has an important impact on observed removal efficiencies. Lü et al. ⁵⁸ reported that adsorption of phenol on lignite increased up to 500 mg/L and then remained stable. Similarly, Amuda et al. ²¹ showed that Zn adsorption increased up until the point at which the adsorption peak is reached which was impacted by both the adsorbent type (as a

result of the specific surface area) and the adsorbent dose. The economic costs are therefore specific to a dose rate of 400 mg/L and would therefore change in response to required dose rate optimisation.

The CAPEX costs consisted of the initial manual PAC dose required to reach a concentration of 400 mg/L in the aeration cell. Hence, an initial 800 kg of PAC would be required representing a cost of £760 (£0.38 per m³ wastewater). The OPEX costs consisted of the cost of PAC addition required to maintain a dose rate of 400 mg/L. The amount of PAC lost via sludge wasting was therefore calculated. Suspended solids in the wasted sludge were 15,000 mg/L with PAC accounting for 4% of the suspended solids. Assuming sludge was wasted at 5 L/m³ of treated effluent, this would lead to a total suspended solids loss of 54,750 kg/yr resulting in an annual loss of PAC of 2190 kg/yr, costing £2081/yr. Therefore, loss of PAC through suspended solids represents a cost of £2.85 per 1000 m³ of wastewater or less than £0.01 per m³ of wastewater. The excess sludge was returned to the full-scale coke making process, hence no costs of sludge disposal were predicted in this study.

Table V: CAPEX and OPEX cost analysis of PAC dosing to full-scale ASP.

The costs associated with the addition of PAC were then compared to the CAPEX and OPEX costs of alternative techniques available to improve removals of PAHs and trace metals in wastewater. Tiravanti et al.⁵⁹ demonstrated the economic feasibility of ion exchange processes for Cd removal from tannery wastewater. Costs were estimated at ca. £1.85 per m³ of wastewater. This represented an improvement on the conventional physiochemical treatment method which cost ca. £2.43 per m³. Heavy metal removal can be achieved through

the application of coagulation followed by sand filtration. Høibye et al. ⁶⁰ considered the economic viability of sand filtration taking a holistic approach to the cost calculation. This considered both the potential and prevented environmental costs of the application, leading to an expense of £0.04 per m³. Costs were also compared to the treatment of textile wastewater, which is considered a complex effluent ⁶¹ as is the case with coke making wastewater. Typical treatment often uses a combination of biological, physical and chemical treatment methods, with costs being reported as £0.28 per m³. When combined with electrochemical treatment, operating costs were reduced to £0.21 per m³ ⁶¹. Additionally, the cost of PAC addition was compared to the use of membranes and ozone (Table VI). Reports into the economics of these techniques focus on the treatment of domestic wastewater. Pollutants requiring treatment in domestic wastewater are typically 10 - 100 times lower than concentrations observed in coke making wastewater whilst the consent limits are typically higher than those required by the IED for coke making wastewater and therefore this requires consideration when comparing treatment costs. Furthermore, reported costs can vary significantly for the use of membranes due to the varying pre-treatment costs which can be extensive ⁶².

Table VI: Economic feasibility of PAC addition to the ASP in comparison to other treatment methods.

PAC addition therefore offers an economically favourable option to achieve improvements in pollutant removal. Capital expenditure is minimal when PAC is dosed directly into the ASP process as it removes the requirement for plant modifications such as the installation of adsorption columns and pumps. The economic advantage of direct addition to an ASP was

also reported by Flynn and Stadnik⁶³ who reported savings of ca. £4.5 million in CAPEX costs and a £3.2 million saving in OPEX costs compared to GAC columns. Operational costs are also cheaper than other removal strategies such as sand filtration and ion exchange processes. Treatment processes used for domestic wastewater such as ozonation and membrane filtration have high CAPEX and OPEX costs. As industrial wastewaters, such as coke making wastewater, are characterised by higher pollutant concentrations the use of ozonation and membranes is associated with further economic costs and therefore PAC offers an economically viable treatment method for coke making wastewaters.

CONCLUSION

The ASP pilot-plant performed similarly to the full-scale treatment works regarding total phenol and SCN^- with removal efficiencies at 99%, and 97%, respectively, demonstrating effective treatment. Powdered activated carbon dosing to ASP increased the removal efficiency of a range of trace metals and PAHs associated with coke making wastewater. In the case of Ni the removal increased by 22.6% whilst the $\Sigma 6\text{PAH}$ removal efficiency increased by ca. 20%. Overall the $\Sigma 6\text{PAHs}$ concentration was reduced to 34 $\mu\text{g/L}$, allowing compliance with the new emission limit of $<50 \mu\text{g/L}$ $\Sigma 6\text{PAHs}$ at relatively low capital and operational costs, which may assist in reaching tighter effluent emission limits set for the steel industry. Other wastewaters containing PAH and trace metal, from industries such as agrochemical, pharmaceutical, petrochemical, coal gasification, coke processing, insecticide, hydrocarbon and produced wastewaters amongst others, may benefit from PAC addition in a future of increasingly stringent emission limits. Overall, PAC addition was associated with a CAPEX cost of £0.38 per m^3 and an OPEX cost of $<£0.01$ per m^3 , offering an economically viable method to remove pollutants from coke making wastewater.

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Table I: Priority Hazardous Substances (PHS), Priority Substances (PS) and Specific Pollutants (SP) associated with coke wastewaters.

Priority Hazardous Substances	Anthracene Cadmium Benzo[a]pyrene Benzo[b]fluoranthene + Benzo[k]fluoranthene
Priority Substances	Fluoranthene Lead Naphthalene Nickel
Specific Pollutants	Iron Arsenic Chromium Zinc

Table II: Typical characteristics of coke making wastewater before and after treatment in the ASP pilot plant during control operational conditions (without PAC treatment) and their associated treatment efficiencies.

	Inlet	SD	Outlet	SD	Treatment efficiency (%)
Phenols (total) (mg/L)	219	15	6.3	0.4	97
Thiocyanate (mg/L)	195	24	0.6	0.2	100
Total trace metals ($\mu\text{g/L}$) *	4216	568	2878	220	35
Total of 6 PAHs ($\mu\text{g/L}$) **	179	35	53.6	21	58
Suspended Solids (mg/L)	23	8	20	3	-
Colour (Absorbance 470 n)	0.32	0.03	0.31	0.01	2.04

* Sum of Al, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Cd and Pb.

** Sum of PAHs identified in BREF as associated with coke making- fluoranthene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene and benzo[g,h,i]perylene.

Table III: Average treatment efficiencies for the removal of trace metals, in the continuous activated sludge pilot plant with and without PAC, showing a significant increase in the removal of Ni using T-test statistical analysis.

	No activated lignite		400 mg/L activated lignite		T-test	
	Av. removal (%)	SD	Av. removal (%)	SD	P-value	Significant (95%)?
Al	41.6	10.2	24.3	17.0	0.07	N
Cr	16.7	40.7	37.2	14.0	0.33	N
Mn	37.1	5.4	35.9	9.0	0.80	N
Fe	29.8	6.0	24.7	5.9	0.16	N
Co	18.4	1.6	12.5	8.8	0.10	N
Ni	46.9	12.3	69.5	7.7	0.00	Y
Cu	65.5	6.2	61.5	9.2	0.42	N
Zn	65.7	5.2	69.1	8.1	0.43	N
As	12.6	6.3	0.5	17.9	0.10	N
Cd	45.4	16.0	57.8	11.0	0.18	N
Pb	57.4	13.6	56.0	22.7	0.90	N

Table IV: Average removal efficiency for PAHs with and without AC dosing in the continuous activated sludge pilot plant. Improvements in removal efficiency were significant and standard deviations were reduced by 50%.

	MW (g/mol)	Removal efficiency (%)			
		Without AC		400 mg/L AC	
		Mean	SD	Mean	SD
Fluoranthene	202	93.9	3.10	96.6	1.68
Benzo [b + j] fluoranthene	252	53.4	28.1	74.2	12.9
Benzo [k] fluoranthene	252	62.9	22.7	79.0	10.7
Benzo [a] pyrene	252	59.1	26.9	79.3	11.8
Indeno [1,2,3-cd] pyrene	276	42.0	34.7	70.0	18.9
Benzo [g,h,i] perylene	276	38.1	32.1	67.7	18.9
ΣPAHs		58.2	24.4	77.8	12.2

Table V: CAPEX and OPEX cost analysis of PAC dosing to full-scale ASP.

ASP plant configuration:	
Plant capacity (m ³ /day)	2000
Suspended solids in wasted sludge (mg/L)	15,000
Sludge wasted (L/day)	10,000
PAC dose rate (mg/L)	400
Costs and dosing associated with PAC addition:	
Cost of PAC per kg (£) ⁶⁴	0.95
Initial PAC dose required (kg)	800
Cost of PAC per m ³ of wastewater (£)	0.38
CAPEX (initial dose) (£)	760
PAC lost via sludge wasting (kg/yr)	2190
Cost of PAC loss per 1000m ³ wastewater (£)	2.85
OPEX cost (PAC required for maintenance) (£/yr)	2081

Table VI: Economic feasibility of PAC addition to the ASP in comparison to other treatment methods.

Technology	Type of wastewater	CAPEX (per m ³) (£)	OPEX (per m ³) (£)	Reference
PAC	Coke making	0.38	<0.01	This study
Ozone	Mixed*	583 - 972	0.17	⁶²
Membrane	Domestic**	810 - 1620	0.22 - 1.33	⁶²

* removal of benzene, toluene, ethylbenzene and xylenes (BTEX) and methyl tertiary butyl ether (MTBE)
 ** removal of pathogens and priority substances with turbidity removal and taste and odor control

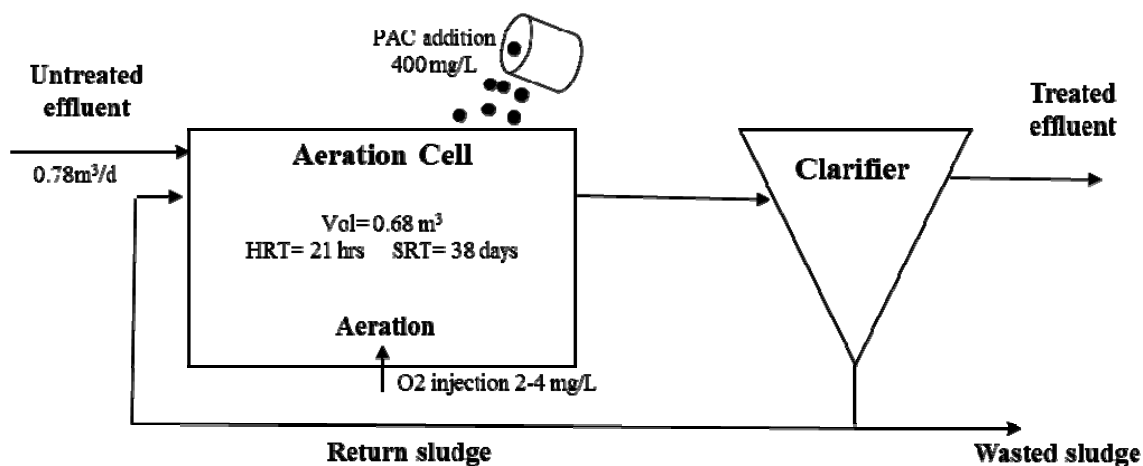


Figure I: Schematic representation of the activated sludge pilot-plant with PAC addition.

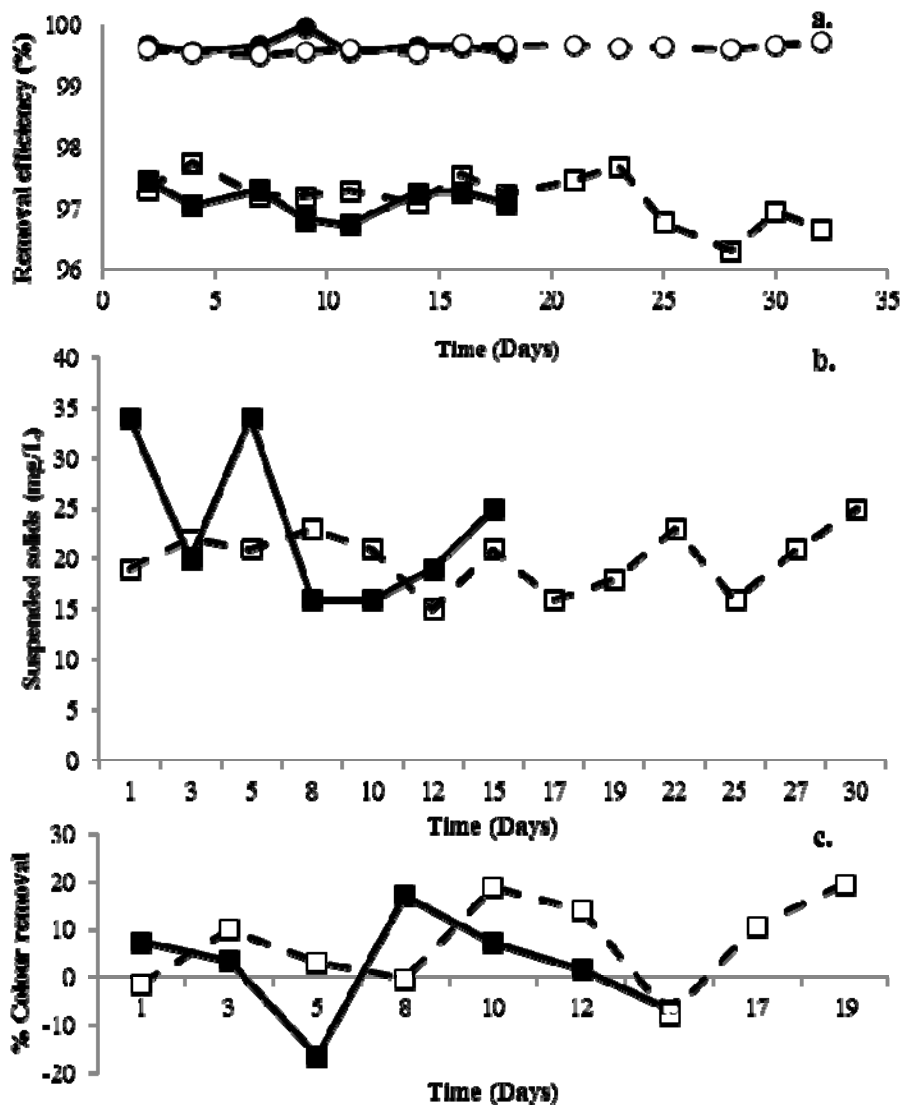


Figure II: a- Removal efficiency of phenol and SCN^- during the control ASP and ASP dosed with 400 mg/L PAC. ● SCN^- without PAC, ○ SCN^- with 400 mg/L PAC, ■ Phenol without PAC, □ phenol with 400 mg/L PAC. b- Suspended solid concentrations in outlet during the control ASP and ASP dosed with 400 mg/L PAC. ■ Suspended solids without PAC, □ suspended solids with 400 mg/L PAC. c- Colour removal efficiency during the control ASP and ASP dosed with 400 mg/L PAC. ■ Colour removal efficiency without PAC, □ colour removal efficiency with 400 mg/L PAC.

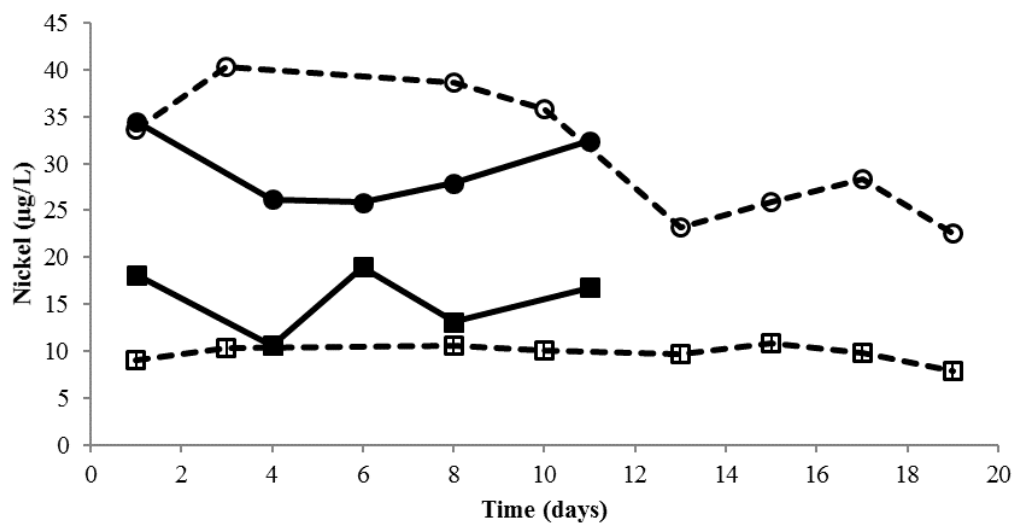


Figure III: Removal of nickel ● Inlet no AC, ○ inlet 400 mg/L AC. ■ Outlet no AC, □ outlet 400 mg/L AC, showing increased stability of outlet Ni concentrations. Standard deviation of method typically 2.5.

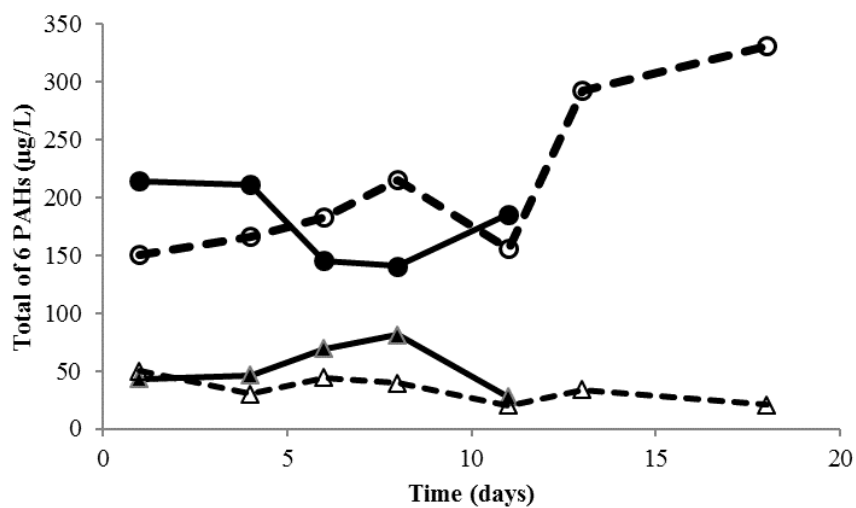


Figure IV: Removal of $\Sigma 6$ PAHs. ● Inlet no AC, ○ inlet 400 mg/L AC. ■ Outlet no AC, □ outlet 400 mg/L AC. Standard deviation of method typically equal to 0.15.