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Adsorption of Phenol and Chromium (VI) Pollutants in Wastewater using Exfoliated Graphite

Shepherd M. Tichapondwa[a,*], Siyabulela Tshemese[a], Washington Mhike[b]

[a]Department of Chemical Engineering, University of Pretoria, Pretoria 0002, South Africa
[b]Department of Chemical, Metallurgical and Materials Engineering, Polymer Technology Division, Tshwane University of Technology, Pretoria 0183, South Africa
shepherd.tichapondwa@up.ac.za

Phenol and Cr(VI) are two of the most common organic and heavy metal-based pollutants found in industrial effluents. Both pollutants pose considerable health risks if left untreated. Activated carbon adsorption is generally used for the physical removal of these types of pollutants during wastewater treatment. This work investigates the use of thermally exfoliated graphite as an alternative adsorbent material for the removal of phenol and Cr(VI) in wastewater. The well-developed surface pore structure and high adsorption capacities reported in literature make this material an ideal candidate for investigation. The effectiveness of the exfoliation process was characterised using x-ray diffraction whilst the particle morphology, surface structure and adsorption surface area were determined using scanning electron microscopy and Brunauer-Emmett-Teller (BET) specific surface area measurements. Upon expansion, the particle morphology of expandable graphite changed from flakes to worm-like, accordion structures. This change was accompanied by an increase in BET surface area from 2.4 to 22.4 g/m^2. Batch experiments using simulated wastewater revealed that expandable graphite had negligible adsorption affinity towards both pollutants. However, exfoliated graphite had adsorption capacities of 0.73 mg/g and 0.55 mg/g for Cr(VI) and phenol. The equilibrium adsorption isotherms for both pollutants were best described by the Langmuir adsorption model and had adsorption constants of 0.84 and 0.32 L/mg for the two pollutants. The adsorption capacities obtained were much lower than those reported for the same pollutants when using activated carbon as an adsorbent. This is most likely due to the high BET surface areas recorded for activated carbon. Additional modification of the exfoliated graphite is required before satisfactory adsorption capacities can be achieved for large-scale wastewater treatment applications.

1. Introduction

Most wastewater treatment plants receive influent from both domestic and industrial sources. This results in the water containing a wide range of pollutants with varying concentrations. Typical examples of such pollutants include organic pollutants like phenol or inorganic heavy metals such as chromium (Cr) (Tshuto et al. 2017). In nature chromium is mostly found in the trivalent [Cr (III)] state, however the more mobile Cr (VI) is discharged in wastewater from various industrial processes such as mineral processing operations, electroplating, leather tanning and pigment production (Igboamalu and Chirwa, 2016). Cr (VI) is a carcinogenic and mutagenic pollutant which is highly toxic to most living organisms even at concentrations as low as 0.05 mg/L (Yang et al., 2013). When exposed to humans in high concentrations, it can also lead to liver damage, internal haemorrhage and respiratory disorders (Tchounwou et al., 2014). Phenol and its derivatives are widely used as raw materials in many industries such as petrochemicals, chemical and pharmaceutical. The effluent from these industries tends to contain high concentrations of phenol. Other sources phenol in wastewater include natural degradation products of insecticides and dyes, coking operations, as well as decomposition of plant matter. Phenol is a priority pollutant, which may result in serious health risks to humans, animals, and aquatic life if left untreated (Villegas et al., 2016). The toxicity range for both humans and aquatic life ranges from 9 to 25 mg/L (Kulkarni and Kaware, 2013), the potential health hazards can be both acute and chronic. Long-term exposure to humans leads to irregular breathing, muscle weakness, coma and respiratory arrest while chronic exposure results in anorexia, diarrhoea and dark coloration of urine (Dieguez-Santana et al., 2016). The highlighted effects of both

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Cr (VI) and phenol to humans and aquatic life make it imperative that they be removed from wastewater before it is discharged to natural water bodies.

While the organic biodegradable contaminants can be treated with relative ease using conventional biological wastewater treatment processes, the same cannot be said for phenol and Cr (VI) contaminants. A wide range of phase separation-based treatment technologies such as adsorption, reverse osmosis and liquid-liquid extraction are applied in controlling these pollutants. Adsorption is a particularly attractive technique, as it is simple, efficient, economically viable and environmentally benign (Zhong, 2017). Activated carbon adsorption is a widely used and effective process for the removal of toxic and non-biodegradable organics from water. Granular activated carbon adsorption has been widely adopted in both portable and wastewater treatment plants. However, after exhaustion the activated carbon must either be discarded or regenerated off-site. Graphite intercalation compounds (GICs) commonly referred to as expandable graphite have been explored as an alternative approach to adsorption with electrochemical regeneration (Hussain et al., 2013). These adsorbents are non-porous and have high electrical conductivity, which enables simple, cheap and quick anodic regeneration. This approach not only removes the contaminant from the water by adsorption, but also destroys the contaminant through anodic oxidation (Hussain et al., 2013). Exfoliated graphite consists of a well-developed pore structure which enhances its adsorption properties. Its environmentally benign properties make it an ideal adsorbent in wastewater treatment. Although exfoliated graphite has been studied for a wide range of water treatment applications (Li et al., 2013), to the best of our knowledge the simultaneous adsorption of phenol and Cr(VI) has not been reported. The current study details the physical properties of the expandable and thermally exfoliated graphite. It also reports the adsorption capacity of thermally exfoliated graphite towards phenol and Cr(VI) as individual pollutants. These results are the baseline of the proceeding simultaneous adsorption studies.

2. Materials and methods

2.1 Expandable graphite exfoliation and characterization

Expandable graphite grade ES250 B5 supplied by Qingdao Kropfmeuhl Graphite (China) was used in this investigation. It had a reported exfoliation onset temperature of 220 °C, however, for effective exfoliation it was exposed to 600°C for 5 min in a Thermo-power electric furnace (Mhike and Focke, 2013). The Brunauer-Emmett-Teller (BET) specific surface area and apparent density of the exfoliated graphite were used to gauge the exfoliation efficiency of the expandable graphite. The specific surface areas of the exfoliated graphite were determined using a Micrometrics TriStar BET (USA) in liquid N_2 at 77 K. Apparent density of the exfoliated graphite was determined using a graduated cylinder and an accurate balance. True densities of the various graphite forms were determined using a AccuPyc II 1340 helium gas pycnometer, Micrometrics (USA). The particle morphologies of both the expandable and exfoliated graphite were studied using both a JEOL JSM 5800LV scanning electron microscope (low resolution) (USA) and an ultrahigh resolution field emission scanning electron microscope (HR FEGSEM Zeiss Ultra Plus 55, Germany). The particle size distribution was determined using a Mastersizer Hydrosizer 3000 (Malvern Instruments, Malvern, UK). The crystal structure and ordering in the graphite forms was observed using X-ray diffraction. This was recorded using a Bruker D8 Advance powder diffractometer fitted with a Lynx eye detector (Germany). Natural graphite supplied by BEP Bestobell (South Africa) was used as a standard to establish the degree of exfoliation in the expanded graphite.

2.2 Phenol and Cr(VI) adsorption studies

Simulated wastewater was prepared using potassium chromate (Merck, Germany) and phenol (Saarchem, South Africa). The initial tests conducted determined the optimum exfoliated graphite loading required for both pollutants. 30 mg/L solutions of Cr(VI) and phenol were prepared and placed into 1 L beakers. Suitable amounts of exfoliated graphite were then added to obtain exfoliated graphite loadings in the 5 to 30 g/L range. The exfoliated graphite – wastewater slurry was stirred continuously for 24 h before being analysed for the residual concentration of pollutant after filtration. Based on the results obtained from the exfoliated graphite loading experiments, the proceeding tests sought to determine the maximum adsorption capacity of the exfoliated graphite for the individual pollutants. The equilibrium isotherms were determined by varying the model pollutant concentration from 10 to 100 mg/L while keeping the exfoliated graphite mass constant as determined in the first experiments. The test procedure used was similar that used in the first set of experiments. The adsorption capacity was then calculated using the relationship shown in Eq(1).

$$q_e = \frac{V(C_o - C_e)}{M} \quad (1)$$

q_e is the adsorbed pollutant concentration (mg/g), V is the volume of solution (L), M is the mass of exfoliated graphite used (g), C_o and C_e are the initial concentration and equilibrium concentrations of the pollutant (mg/L).

The chromium was analysed using the 3500-Cr B colorimetric method described by Federation and Association (2005). A sample volume of 0.1 mL is first acidified with 1 N H_2SO_4 before reacting it with 1,5-diphenyl carbazide to produce a purple colour. The resultant samples were then analysed using a WPA, LIGHT Wave, Labotech UV-vis spectrophotometer (South Africa) at a 540 nm wavelength. The phenol concentration was measured using a TOC-V wp Shimadzu Total Organic Carbon analyser fitted with a ASI-V auto sampler (Japan). In both phenol and Cr(VI) analysis, standard solutions were used to obtain the calibration curves, which were used to determine the concentration of the samples.

3. Results and discussion

3.1 Graphite characterization

The physical properties of the expandable and exfoliated graphite are shown in Table 1. The expandable graphite had a fairly broad size range with a d_{50} particle size of ca. 381 µm. Due to the reduced density of the exfoliated graphite it was not possible to determine the particle size distribution. The BET surface area of the exfoliated graphite was 6.8 times greater than the starting material. Figure 1 presents the SEM micrographs of the graphite samples. While the expandable graphite consists of flakes, the exfoliated graphite had a worm-like, accordion structure composed of stacks of graphene held together along the c-axis. The nano-platelets which make-up the structure are easily distinguishable. The expandable graphite is reported increase in volume by as much as 700%. This is likely due to the large volume of gas released during the exfoliation event (Focke et al., 2014).

Table 1: Physical properties of expandable and exfoliated graphite

	Particle size, µm			BET surface Area (m^2g^{-1})	Density (gcm^{-3})
Form	d_{10}	d_{50}	d_{90}		
Expandable	144	381	642	2.40 ±	2.08 ± 0.00
Exfoliated	-	-	-	22.4 ± 2.8	0.64 ± 0.03

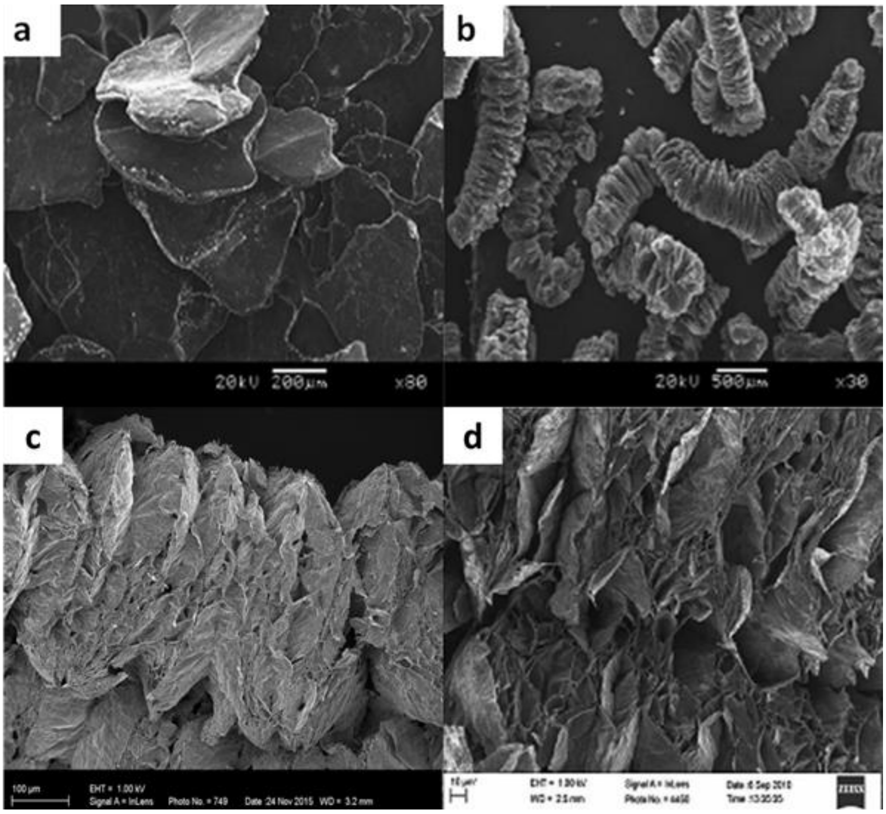

Figure 1: SEM micrographs of (a) expandable graphite (x80), (b)(x30) and (c)(x150) exfoliated graphite, (d) high resolution exfoliated graphite (x1000). The magnification is shown in the brackets (x magnification)

Figure 2 shows XRD diffraction patterns of the expandable and exfoliated ES250 graphite. Natural graphite is included as a reference. The d-spacing of natural graphite was 0.335 nm. Expandable graphite ES 250 B5 exhibited two d-spacings at 2θ positions of 30.01 ° and 30.79 °. The peak position at 2θ 30.79 ° appears as a shoulder to the main peak at 30.01 ° and its d-spacing of 0.337 corresponds to that of natural graphite. The main peak for the exfoliated graphite occurred at the 2θ position 30.01 ° had an increased d-spacing compared to that of natural graphite, showing evidence of intercalation. The fact that this peak was overlapping with that of pristine graphite shows that the expandable graphite was a high stage compound (Nakajima et al., 1988).

3.2 Adsorption studies

Figure 3 shows the effect of exfoliated graphite loading on the adsorption of phenol and Cr (VI) model pollutant solutions with an initial concentration of 30 mg/L. These tests were conducted in order to determine the optimum adsorbent loading for use in the adsorption isotherm studies. The maximum reduction was achieved using a 30 g/L exfoliated graphite loading for both pollutants. A 71.5% removal of Cr (VI) was obtained compared to 51.5% reduction in phenol concentration. Although it was clear that the concentration decreased with an increase in adsorbent loading, no further increase in adsorbent loading was possible as the resultant slurry became too viscous, making it difficult to mix. Expandable graphite at a 30g/L loading was used as a control and showed negligible adsorption capacity towards both model pollutants. No further adsorption tests were conducted using this graphite form.

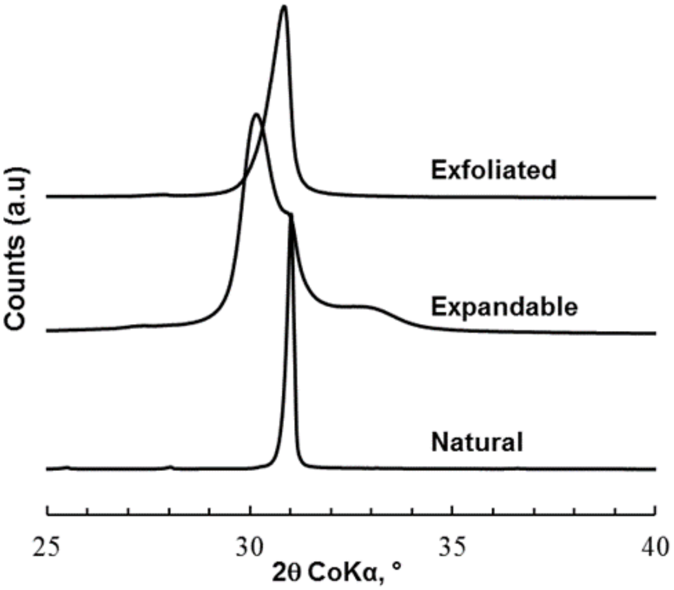

Figure 2: XRD patterns of the natural, expandable and exfoliated graphites

The equilibrium adsorption isotherms of the exfoliated graphite for the two model pollutants are reported in Figure 4. Exfoliated graphite showed a higher affinity towards Cr (VI) compared to phenol. Maximum adsorption capacities of ca. 0.73 mg/g and 0.55 mg/g were recorded for Cr(VI) and phenol. It is speculated that the higher adsorption capacity towards Cr (VI) is due to a combination of physical adsorption and hydrogen bonding between oxygen-containing surface functional groups and the Cr (VI) ion (Focke et al., 2014). Phenol adsorption results from the physical interaction between the phenol and the macropores and non-polar surface sites of the exfoliated graphite (Wang et al., 2014). The adsorption behaviour was best described by the Langmuir isothermal adsorption model (Chen et al, 2011). The estimated maximum adsorption capacities for Cr(VI) and phenol were 0.74 and 0.57 mg/g, whilst the adsorption equilibrium constants were 0.84 and 0.32 L/mg. The adsorption capacities obtained were significantly lower than those reported for activated carbon (36 mg/g Cr(VI) (Emmiya et al, 2018) and 149 mg/g phenol (Hameed and Rahman, 2008) which is the most widely used adsorbent in commercial applications. The discrepancy was attributed to the higher BET surface area attained for the activated carbon. This implies that exfoliation alone is not sufficient to attain commercially viable adsorption capacities and further surface treatment techniques are required in order to obtain higher adsorption capacities.

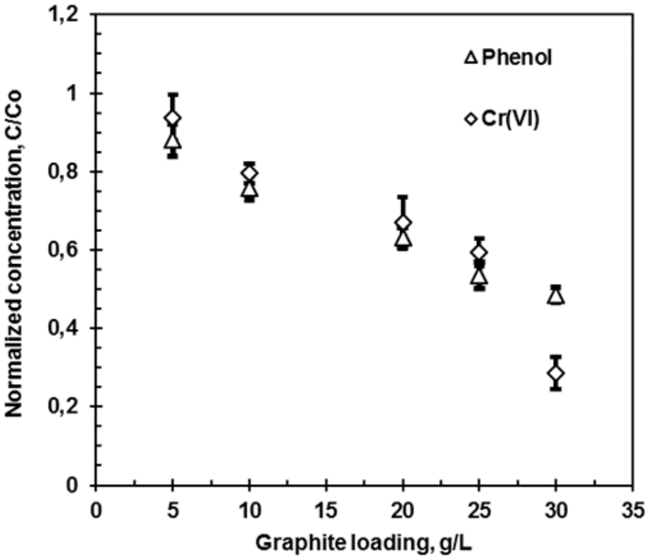

Figure 3: Effect of exfoliated graphite loading on the adsorption of phenol and Cr (VI) model pollutants with an initial concentration of 30 mg/L

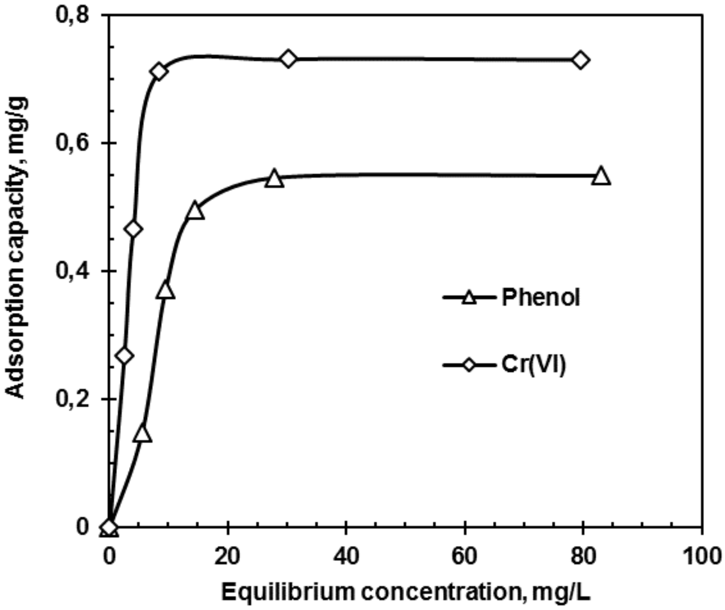

Figure 4: Equilibrium isotherm for the adsorption of phenol and Cr (VI) on exfoliated graphite

4. Conclusions

Commercial expandable graphite was exfoliated using a high temperature shock method and the resultant material was characterized. X-ray diffraction showed a clear shift from an intercalated structure to a more graphitic structure similar to natural graphite. The thermal expansion resulted in an increase in BET surface area and development of a porous surface morphology in the exfoliated graphite. This change in physical properties resulted in an increase in adsorption capacity from virtually no adsorption recorded using expandable graphite to 0.55 mg/g and 0.73 mg/g for phenol and Cr (VI) being observed for exfoliated graphite. The equilibrium adsorption isotherms for both pollutants were best described by the Langmuir adsorption model. The adsorption capacities attained using exfoliated graphite adsorption were much lower than those reported for activated carbon. This suggests that further modification of the exfoliated graphite might be required before it can be considered for commercial applications.

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