Removal of Chromium (VI) from Aqueous Solution Using Exfoliated Graphite/Polyaniline Composite

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Exfoliated graphite/polyaniline (EG/PANI) composites were successfully prepared via *in situ* polymerization of aniline monomer in the presence of exfoliated graphite. The PANI precipitated into the interlayer space of the graphite flake significantly improving physiochemical properties of EG. The particle morphology and interaction of the EG and PANI was determined using the scanning electron microscopy (SEM). The SEM images clearly showed the formation of PANI and EG/PANI composite with PANI greatly covering the EG flake. The presence of polyaniline and its major functional groups were confirmed using Fourier Transform Infrared Spectroscopy (FTIR) between 3,500 – 3,000 cm^{-1} and 1,500 - 500 cm^{-1}. A 68 % change in Brunauer- Emmett-Teller (BET) surface area was observed in the 0.35 g PANI/g EG after the in situ polymerization of the PANI. The effectiveness of the composite adsorbent on the removal of Cr (VI) from aqueous solutions was evaluated by evaluating the effects of parameters such as EG to PANI ratio and initial concentration. The optimum composite loading was found to be 0.35 g PANI/g EG and removed more than 99 % of Cr (VI) from an initial concentration of 100 ppm was removed at 20 g/L loading within 4 h. The Freundlich adsorption isotherm model best described the adsorption of Cr (VI) with a regression coefficient, r^2 of 0.99 showing the heterogeneous adsorption at the surface of the composite. The maximum capacity of the composite was 38.20 mg/g.

1. Introduction

Heavy metal contamination poses serious threat to environment. Amongst heavy metals, the hexavalent chromium, Cr (VI) is one of the most carcinogenic and mutagenic (Chen et al., 2014). Various adsorbents have been used to remove Cr (VI) from aqueous solutions including activated carbon, clays and polymer-based adsorbents (Wang et al., 2014). These polymer-based adsorbents are mainly conductive polymers such as polypyrrole, polyethylenamine and polyaniline (PANI) which can be very effective in simultaneously reducing Cr (VI) to Cr (III) and adsorbing both these species. They act as electron donors for the Cr (VI) reduction while providing adsorption sites (Jiang et al., 2018). Polyaniline (PANI) nanofibers and their composites have received enormous attention recently in wastewater treatment especially for heavy metal removal. They poses outstanding controllable electrical conductivity, ion exchange properties, environmental stability and easy and inexpensive preparation method (Najim and Salim, 2017). PANI nanofibers have also been reported to have high affinity for metal ions and high efficiency to reduce toxic pollutants (Long et al., 2011). Generally PANI powders are recommended over PANI films due to rough surface, large surface area and easy bulk production (Jiang et al., 2018). The conventional method of removing Cr (VI) from aqueous solutions is based on the reduction of Cr (VI) to Cr (III) followed by precipitation (Olad and Nabavi, 2007). Gheju and Balcu (2011) successfully removed most of Cr (VI) using this method however the major drawbacks of this method include the production of large amount of toxic sludge, high costs and low efficiency at low concentration (Ansari, 2006). Adsorption remains the most simple, well studied and efficient method preferred by most researchers. Based on the recommendations from our previous work (Tichapondwa et al., 2018) on the adsorption of Cr (VI) with exfoliated graphite, further surface modification to improve the adsorption capacity of exfoliated graphite was

deemed necessary. As such, a composite adsorbent comprising of exfoliated graphite and polyaniline (EG/PANI) was synthesized and investigated for its effectiveness in the removal of Cr (VI) from aqueous solution in the present study. The selection of PANI was motivated by its ability to be synthesized in various ways such as in situ polymerization in the presence of other adsorbents (Konwer et al., 2011) and excellent ability to adsorb metal ions such as Cr (VI) (Najim and Salim, 2017) in addition to its unique properties mentioned above. Numerous studies have been conducted on the synthesis and application of EG/PANI composites in various applications such as super capacitors. However, their application as a possible adsorbent for heavy metal remediation has not been reported to the best of our knowledge. The present study seeks to determine the adsorption properties of the composite towards Cr (VI) taking advantage of the tenability of the functional groups on the PANI during synthesis.

2. Materials and methods

2.1 Materials

The expandable graphite grade ES250 B5 was supplied by Qingdao Kropfmeuhl Graphite from China. Potassium chromate and ammonium peroxydisulfate were supplied by (Merck, Germany), Aniline, acetone, 1.5-diphenylcarbazide and 98 % sulphuric acid were purchased from Sigma-Aldrich. The hydrochloric acid was supplied by Glass-world, South Africa. The surface morphology of EG, PANI, EG/PANI composite was obtained using ultrahigh resolution field emission scanning electron microscope (FEG SEM Zeiss Ultra Plus) with an in lens detector at a voltage of 1 kV to maximize resolution of surface detail. To determine various functional groups on the adsorbents surface the Perkin-Elmer Paragon 1,000 Fourier-Transform Infrared Spectroscopy was used. All FTIR spectra were recorded at a resolution of 2 cm^{-1} for 30 scans from 4,000 to 400 cm^{-1}. The surface area was measured with a Micrometrics Tristar II Brunauer-Emmett-Teller (BET) using N_2 at 77.35 K . All the samples were measured in triplicate and the average values were reported. The nature and purity of the phases in the adsorbent materials were determined through X-ray diffraction (XRD) measurements using a Bruker D8 Advanced solid powder diffraction fitted with Lynx eye detector.

2.2 Synthesis of EG/PANI composite

For effective exfoliation the expandable graphite was exposed to 600 °C for at least 5 min in a Thermo-power electric furnace. 0.2 M of aniline liquid was oxidized with 0.25 M of ammonium peroxydisulfate (APS) in aqueous medium to produce PANI. The EG/PANI composites were prepared via an *in situ* polymerization of aniline monomer in the presence of EG. Aniline and APS solutions were prepared in 250 mL volumetric flasks while maintaining a stoichiometric APS/Aniline ratio of 1.25 as recommended by (Stejskal and Gilbert, 2002) and pre-cooled to room temperature (24 - 26 °C). This was to minimize the presence of residual aniline and to obtain the best yield. These were mixed in a beaker containing a respective mass of EG that will give the final mass ratios of EG/PANI in the range (0.18, 0.35, 0.43, 0.65 g PANI/g EG) and stirred vigorously for 2 h. The mixture was left at rest for 24 h after which the precipitate was collected on a filter and washed with three portions of 0.2 M HCl and similarly with acetone. A collected composite was air dried for a few hours before leaving it in an oven at 50 °C for 24 h.

2.3 Batch adsorption studies

Potassium chromate was dissolved in deionized water to give 1,000 ppm stock solution of Cr (VI). Batch tests were conducted to investigate the efficiency of the composite on the removal of Cr (VI) as a function of initial concentration (150 - 350 mg/L). These tests were carried out with 150 mL of Cr (VI) solution using a 1 g of the optimum composite. To determine the optimum composite, the mass ratios of EG/PANI were tested under constant conditions of loading and initial concentration. Preliminary kinetic tests demonstrated that adsorption equilibrium of Cr (VI) on EG/PANI composite was achieved within 4 h as such an equilibrium time of 4 h was adopted for further tests. After reaching equilibrium, the mixture was filtered and the concentration of Cr (VI) in the filtrate was analyzed using a colorimetric method which involved treating the Cr (VI) solution with a color chelating complexing agent as described in our previous study. Resulting samples were then analyzed using WPA, LIGHT Wave, Labotech UV-Vis spectrometer at a wavelength of 540 nm. Prior to running the experiments, a calibration curve with a high correlation coefficient (0.992) was created using Cr (VI) solutions in a concentration range that maintained linearity as per the Beer-Lambert law. Cr (VI) percentage removal was calculated as given in Eq(1):

$$\%Removal = \frac{C_i - C_e}{C_i} \times 100 \tag{1}$$

3. Results and discussions

3.1 Characterization of materials

Surface morphology of EG, PANI and the resultant EG/PANI composite was studied under the SEM with the results shown in Figure 1. The surface of EG in Figure 1(a) showed the typical worm-like structure that is associated with EG. A bulky homogeneous network of aggregated PANI particles is shown in Figure 1(b). The PANI surface was higly porous and the synthesis method adopted yielded PANI nanofibers. Similar observations were found by (Wang et al., 2014) who evaluated the effects of protonic acid. Aggregation of PANI particles was observed for the PANI particles prepared in the strong HCl acid. Even though the present samples were not protonated, washing the product multiple times with the HCl solution could have led to the observed aggregation. The EG/PANI (0.35 g PANI/ g EG) composite is shown in Figure 1(c). This composite material shows PANI particles attached to the surface of the EG sheets. This suggests that PANI precipitated on the EG surface, that is, polymerization occurred on the EG sheets (Du et al., 2004). Figure 1(d) shows the optimum composite after contact with 150 ppm Cr (VI).The EG structure in the composite was destroyed and flattened out even though the PANI particles remained attached the composite surface.
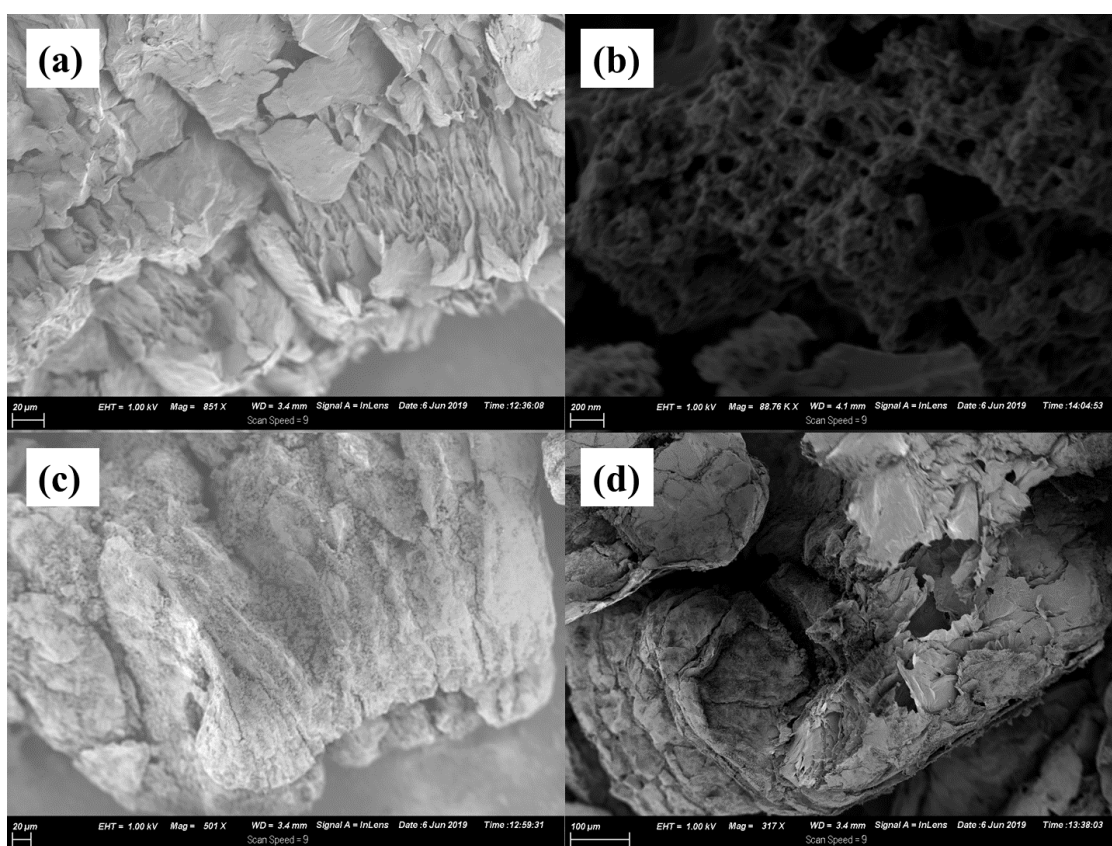

Figure 1: The SEM images of a) EG b) PANI c) EG/PANI (0.35 g PANI/ g EG) and d) EG/PANI (0.35 g PANI/ g EG) after contact with Cr (VI)

The BET surface area of EG/PANI composite was found to be 3.73 m^2/g with the pore size centered at 7.80 nm as shown in Table 1. There was a significant drop in the BET surface area of the composite adsorbent as compared to its constituent materials. It was postulated that as the PANI polymerized on the EG surface, it blinded some of the adsorption sites on the EG base material.

Table 1: BET surface area and pore size of EG, PANI and the optimum composite

Sample	Pore size (nm)	BET Surface area (m^2/g)
EG	-	10.29 ± 0.62
0.35 g PANI/ g EG	7.80	3.73 ± 0.45
PANI	5.72	11.67 ± 1.23

An FTIR spectrum is a useful tool commonly used to identify functional groups that are attached to a certain surface, for adsorption purposes these can also play a role in the adsoption of metal ions (Gupta and Balomajumder, 2015). The FTIR and XRD specta of the EG, PANI and EG/PANI composite is depicted in Figure 2. In Figure 2(a), the FTIR spectra for PANI and EG/PANI composite showed similar characteristic bands between 3,500 – 3,000 cm^{-1} and 1,500 - 500 cm^{-1}. This presence of the characteristic absorption peaks of PANI in the FTIR spectrum of the composite indicates successful polymerization of aniline on the EG surface. The peaks between 1,500 - 500 cm^{-1} were also observed by (Trchová et al., 2006) for the PANI (emeraldine salt) which suggests that the backbone of the PANI produced in this study was the emeraldine salt. Wang et al. (2014) concluded that the peaks around 1,145 cm^{-1} which were also observed in this study were characteristic of the C=N stretching in the quinoid. One can easily observe the broad peak at about 3,500 – 3,000 cm^{-1} which corresponds to the N-H bond associated with PANI. This is also prevalent in the composite suggesting the presence of amine groups on the graphite surface. A straight line was observed in the FTIR spectrum of the EG which suggests plain graphite sheets with no functional groups attached.
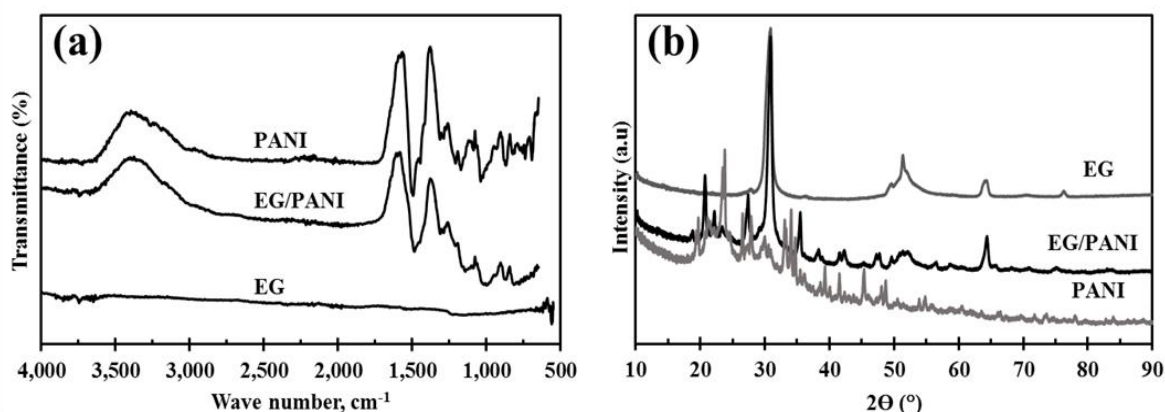

Figure 2: The FTIR spectra (a) and X-ray diffraction curves (b) of EG, PANI and the EG/PANI composite

An XRD analysis was used to examine the structure of EG, PANI and EG/PANI. Figure 2(b) presents the XRD spectra of EG, PANI and EG/PANI composite. It can be observed that the XRD pattern of the composite are similar to both the XRD pattern of EG and PANI. A sharp well developed peak can be observed for the XRD spectra of EG at $2\theta = 30$ °. This is followed by other minor peaks at $2\theta = 51$ ° and $2\theta = 65$ °. The broad peak at $2\theta = 30$ ° agrees fully with our finding on our previous study (Tichapondwa et al., 2018). A PANI spectra shows various peaks at $2\theta = 8$ °, $2\theta = 20$ - 25 ° and $2\theta = 35$ °. These PANI peaks that diffracted at an angle of $2\theta = 20$ - 25 ° are in complete agreement with the peaks found by (Mostafaei and Zolriasatein, 2012).

3.2 Adsorption studies

Figure 3 shows the effect of varying PANI/EG mass ratios in the adsorbent on the removal of Cr (VI). The optimum composite ratio was determined to be 0.35 g PANI per g EG any further increase in PANI content did not result in any significant rise in pollutant removal. A high %removal of Cr (VI), 99.15 % was attributed to both the interactions of Cr (VI) with the amine group and the pores in the composite. This suggests that most of the adsorption activity occurred mainly due to the presence of PANI with the chloride ion exchanged for chromate ion (Najim and Salim, 2017).

The experimental data for the adsorption of Cr (VI) at a normal pH of 7 in Cr (VI) concentration range of (150 - 350 mg/L) were fitted to the two typical equilibrium adsorption isotherms namely Langmuir and Freundlich models to evaluate the adsorption of Cr (VI) on the EG/PANI. These are reported in Figure 4 with their accompanying model parameters listed in Table 2. These model parameters were determined using a non-linear regression method using the solver function in excel 2013.

Based on the correlation coefficient (r^2) value, the adsorption process was best described by the Freundlich model with an estimated adsorption capacity (q_e) of 38.20 mg/g and the Freundlich intensity factor (1/n) of 0.2554. According to (Kang et al., 2020) a 1/n value less than 1 indicates effective adsorption, chemisorption process and favourable adsorption. High values of both K_F and n indicate an easy uptake of Cr (VI) ions and further suggests that the Cr (VI) concentration on the composite surface will increase as long as there is an increase in the concentration of the liquid solution (Wong et al., 2004). It is speculated that the assumed heterogeneity in the model corresponds with the heterogeneous nature of the composite. The Langmuir

isotherm model assumes a monolayer and homogeneous adsorption process which would be physically impossible considering the heterogeneous nature of this composite.
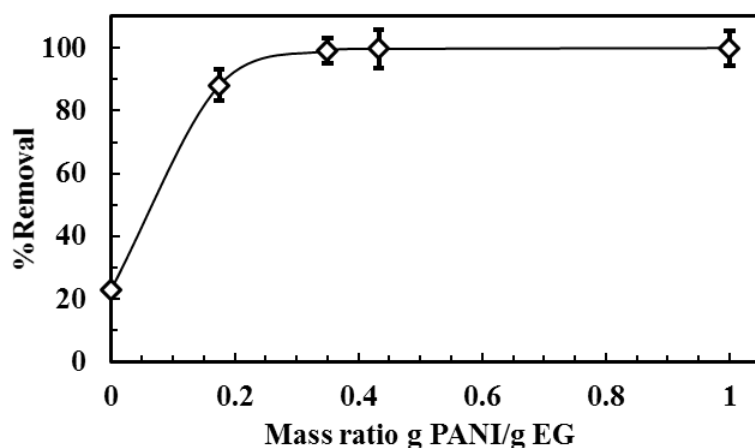

Figure 3: The amount of EG to PANI vs the percentage of Cr (VI) removed

Table 2: Parameters from adsorption isotherm modelling

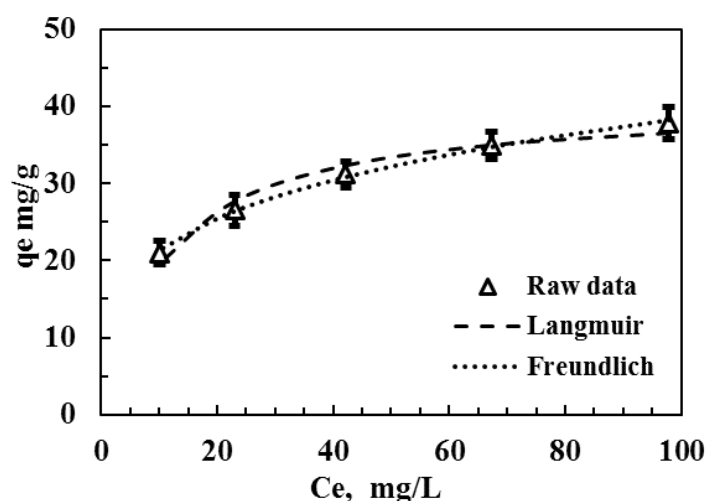| Langmuir			Freundlich		
Qo (mg/g)	K_L (L/mg)	R^2 (1)	K_F (L/g)	1/n	R^2 (1)
40.550	0.09354	0.9662	11.849	0.2554	0.9973

Figure 4: Non-linear equilibrium data modelling for the adsorption of Cr VI) on the EG/PANI composite

4. Conclusions

Exfoliated graphite/polyaniline (EG/PANI) composites were successfully prepared via an *in situ* polymerization of aniline and this material was characterized. SEM images clearly showed the PANI particles precipitated on the EG surface. This resulted in a porous material with a reduced surface area however this did not affect the adsorption of Cr (VI). The FTIR confirmed the presence of amine group on the composite material which played a critical role in the adsorption of Cr (VI). 0.35 g PANI/ g EG was found to be the optimum mass ratio with the ability to remove more than 99 % of the initial Cr (VI) concentration. The Freundlich isotherm best described the adsorption process with a maximum adsorption capacity of 38.20 mg/g as compared to the monolayer and homogeneous Langmuir isotherm. The heterogeneous nature of the composite corresponds with the heterogeneous nature of the EG/PANI composite.

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