

Preparation and Characterization of nZnO/Fly Ash Composite

O. S. Ayanda^{*}, O. S. Fatoki^{**}, F. A. Adekola^{***} and B. J. Ximba^{****}

^{*}Department of Chemistry, Faculty of Applied Sciences, Cape Peninsula University of Technology, P.O. Box 1906, Bellville, South Africa, osayanda@gmail.com

^{**}Faculty of Applied Sciences, Cape Peninsula University of Technology, P.O. Box 652, Cape Town, South Africa, fatokio@cput.ac.za

^{***}Department of Chemistry, University of Ilorin, P.M.B 1515, Ilorin, Nigeria, faadekola@yahoo.fr

^{****}Department of Chemistry, Faculty of Applied Sciences, Cape Peninsula University of Technology, P.O. Box 1906, Bellville, South Africa, ximbab@cput.ac.za

ABSTRACT

Composite material involving fly ash and nZnO was prepared by dispersion technique. The nature, morphology and the properties of the precursors and the composite were determined and compared by scanning electron microscopy, surface area determination by BET, and x-ray diffraction. The ash and carbon contents, particle size, pH and point of zero charge of the materials were also investigated. Experimental results showed that the surfaces of fly ash and nZnO are positively charged and will be favourable to the adsorption of anionic complexes and heavy metals while the surface of nZnO/fly ash is negatively charged and will be suitable for the adsorption of cationic complexes. Moreover, the composition of fly ash and nZnO contributed to the development of intergranular voids and crevices with high surface and micropore areas that will enhance the adsorption of pollutants from wastewaters.

Keywords: fly ash, nano metal oxides, nZnO/fly ash, composite material, SEM, FTIR, XRD, BET.

1 INTRODUCTION

Fly ash is a by-product of the combustion of pulverized coal in electric power generating plants. It consists of fine, powdery particles that are spherical in shape, and mostly glassy in nature. At present, fly ash is used in the cement and concrete building industry, but is still largely disposed in landfills and in the filling of dams and lagoons [1]. With only about 20-30 % of the generated fly ash being used as additive in cement and concrete manufacture, the managements of fly ash consequently becomes a global concern from the environmental and economic points of view [2]. Fly ash consists of crystalline aluminosilicate, mullite and α -quartz along with trace amounts of calcium, magnesium, potassium, sodium and titanium oxides, depending on the nature of the coal burned. The particle size distribution patterns of the spherically shaped fly ash are in the range of 1–100 μm based on the processing conditions [3, 4].

Due to the high silica and alumina content, fly ash can be converted into zeolite-like crystalline materials by chemical treatment, and would find use as adsorbents and ion exchangers in water and wastewater treatment [5, 6]. Rohatgi et al. [7] reported the application of fly ash as composites in reinforced glass and polymer matrix, composites with metals while Wang [2] and Dunens et al. [8] reported its application as catalyst supports. The application of fly ash for the remediation of environmental pollutants has also been widely reported [9 - 12] but the surface area of fly ash is exceptionally low. Hence, a need to improve the surface area and porosity of fly ash to enhance its adsorption capacity.

The aim of this study is therefore to enhance the physicochemical properties of fly ash by composition with nano metal oxide (nZnO), and to investigate the nature and morphology of the precursors and the nZnO/fly ash composite material using modern analytical techniques.

2 EXPERIMENTAL

2.1. Materials

Fly ash used in this study was obtained from Matla power station, Mpumalanga, South Africa. Zinc oxide NanoGard (nZnO) APS powder was purchased from Sigma Aldrich, USA. Methanol was supplied by Industrial Analytical, South Africa. Sodium Nitrate (NaNO_3) and potassium bromide (KBr) were supplied by Merck, Germany. Milli-Q water was used for all the analytical preparations.

2.2 Preparation of Composite

The nZnO/fly ash composite in the ratio 1:1 was prepared by dispersion of the precursors in 0.5 M HCl to form a slurry. The slurry was stirred and evaporated to dryness in an oven. The composite was then further washed with Milli-Q water, filtered and dried in an oven at 100 °C for 24 hours. The final product was ground to fine powder using agate mortar and pestle.

2.3 Instrumentation

The scanning electron micrograph (SEM) of fly ash, nZnO and the nZnO/fly ash composite was viewed under a FEITM scanning electron microscope (Nova Nano SEM 230). Euro Ea elemental analyzer was used to analyze for the percentage carbon, nitrogen and hydrogen contents. Fourier transform infrared spectroscopy (FTIR) absorption spectra were obtained using the potassium bromide (KBr) pellet method and the spectra of the samples were recorded over the range 4 000 – 400 cm⁻¹ using Perkin ElmerTM Spectrum 1000. Phase characterization by PAN-analytical PW 3830 x-ray diffractometer system with CuK α radiation. The specific surface area of the precursors and composite were obtained using a Tristar 3000 analyzer with N₂ adsorption at - 196 °C. The samples were first degassed at 200 °C for 4 hours prior to the analysis. The pH, point of zero charge (PZC), ash content and particle size of the samples were also determined.

3 RESULTS AND DISCUSSION

3.1 Scanning Electron Micrograph

The SEM of fly ash (Fig. 1a) showed that each of the particles of Matla fly ash is spherical with smooth and regular surfaces. The size of the spheres was found to be 0.6 - 26.2 μm with a mean particle size of $3.2 \pm 3.9 \mu\text{m}$. The cracks of some of the spheres show that the spheres are hollow. The SEM of nZnO (Fig. 1b) showed that the nZnO particles consist of uniform granules and more regular surfaces. The SEM presents granules of particle sizes ranging from between 15.9 - 144.7 nm with a mean particle size of $53.5 \pm 26.6 \text{ nm}$. The SEM of nZnO/fly ash composite (Fig. 1c) thus showed that the fly ash and nZnO particles were clustered together with large intergranular voids and crevices found. The SEM also showed that the fly ash and ZnO particles maintained their morphology after preparation of the nZnO/fly ash composite.

3.2 Carbon, Nitrogen and Hydrogen content

Table 1 showed that the fly ash, nZnO and nZnO/fly ash composite contained 1.54 %, 0.42 % and 0.79 % carbon, respectively. The nitrogen and hydrogen contents of fly ash and nZnO were below the detection limit. The nZnO/Fly ash composite contained 1.07 % hydrogen and the nitrogen content was also below the detection limit. The result showed that the carbon content of fly ash decreased by 48.70 % in the prepared nZnO/fly ash composite while the percentage hydrogen content in the composite was raised to 1.07 %.

3.3 FTIR

In the FTIR spectrum of nZnO/fly ash composite (Fig. 2), the absorption at 1097 cm⁻¹ (curve (a)) is assigned to the C–C stretching of fly ash while the absorption at 1110 cm⁻¹ (curve (d)) is assigned to the Zn = O stretching of nZnO and the absorption at 808 cm⁻¹ (curve (d)) is assigned to the Zn – O stretching of nZnO. It was found that the wavenumber of Zn – O stretching shifted from 808 cm⁻¹ of nZnO to 722 cm⁻¹ (curve (g)) of the nZnO/fly ash composite. The wavenumber of the absorption peak decreased by 86 cm⁻¹. The decreased wavenumber for the absorption peak indicated that the strength of Zn – O bond decreased. It could also be explained that a new C–O–Zn bond was formed during the preparation of the nZnO/fly ash composite.

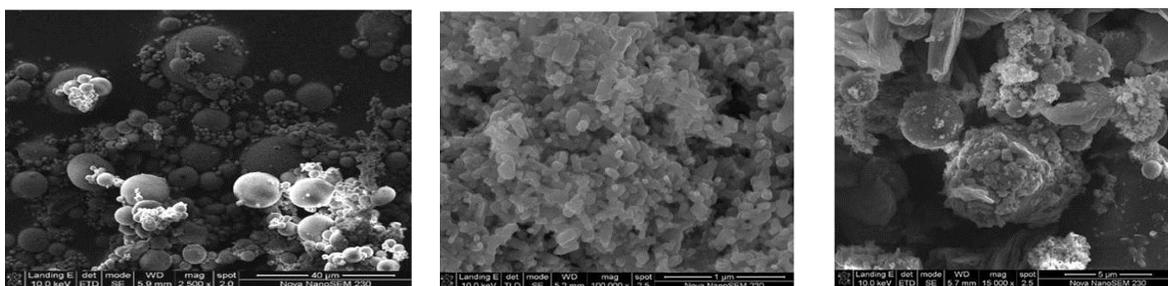
3.4 pH and Point of Zero Charge

Table 1 also shows that the preparation of nZnO/fly ash composite using fly ash (pH = 10.70) and nZnO (pH = 6.71) as precursors resulted to nZnO/fly ash composite of pH 6.96, the pH was lower than pH of fly ash by 34.9 % but higher than the pH of nZnO by 3.59 %. The result showed that the pH of the composite is a function of the pH of each of the component precursors that made up the composite materials. The PZC of nZnO/fly ash composite was 6.70. The PZC value was lower than the PZC of fly ash (12.17) and lower than the PZC of nZnO (6.80) by 44.95 and 1.47 %, respectively. The presence of nZnO in the fly ash therefore brought about a decrease in the PZC of nZnO/fly ash composite.

Since the pH of nZnO and fly ash is lower than the PZC value, the acidic water donates more protons than hydroxide groups, and so the adsorbent surface is positively charged (attracting anions) and will be favourable to the adsorption of anionic complexes and heavy metals. Conversely, the pH of nZnO/fly ash is higher than the PZC value, hence, the surface is negatively charged (attracting cations/repelling anions) and will be suitable for the adsorption of cationic complexes.

3.5 Ash Content

The ash content of the fly ash and nZnO are $97.4 \pm 0.14 \%$ and $99.2 \pm 0.14 \%$, respectively while $85.9 \pm 0.01 \%$ was recorded as the ash content of nZnO/fly ash composite. The result showed that the percentage organic materials present in the fly ash, nZnO and nZnO/fly ash composite are 2.6%, 0.8 % and 14.10 %, respectively. The result obtained showed that the precursors have the highest percentage of inorganic components as compared to the composite material.



(a) Fly ash (b) nZnO (c) nZnO/fly ash

Fig 1 Scanning electron micrograph (SEM) of fly ash, nZnO and nZnO/fly ash composite

Table 1 Physicochemical properties of fly ash, nZnO and ZnO/fly ash composite

Characteristics	Fly ash	nZnO	nZnO/fly ash
pH	10.70	6.71	6.96
PZC	12.17	6.80	6.70
Particle size	0.6 – 26.2 μm	15.9 – 144.7 nm	-
Surface area (m^2/g)	1.0600 ± 0.0030	14.4098 ± 0.0387	198.453 ± 0.0936
Micropore area (m^2/g)	0.3796	3.1780	5.4365
Ash content (%)	97.4 ± 0.14	99.2 ± 0.14	85.9 ± 0.01
Carbon content (%)	1.54	0.42	0.79

3.6 XRD

The diffractogram of fly ash (Fig. 3) showed that the fly ash is predominantly crystalline minerals mullite and quartz with large characteristic peaks of quartz (SiO_2). The intensity of quartz was also very strong. This result is similar to that reported for a fly ash investigated by Reynolds [13] and Sarkar, et al. [14]. Fig. 4 showed that the nano zinc oxide consists of ZnO with sharp peaks while nZnO/fly ash composite (Fig. 5) consists of mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$), quartz (SiO_2) (from the fly ash) and zinc oxide (from nZnO).

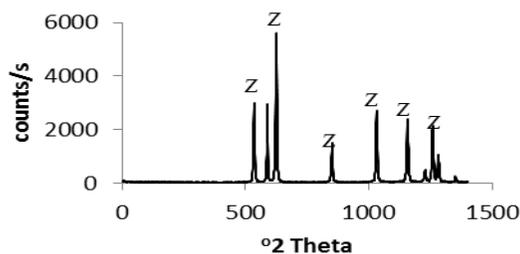


Fig 4 X-ray diffraction of nZnO

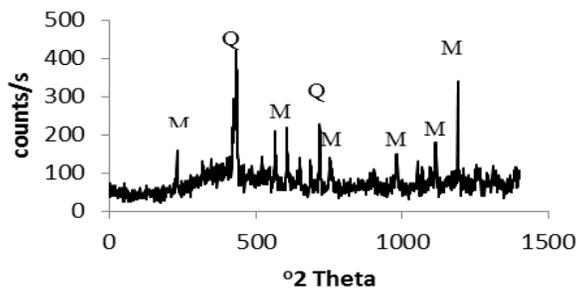


Fig 3 X-ray diffraction of fly ash

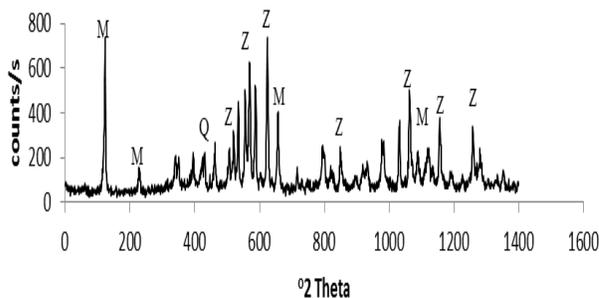
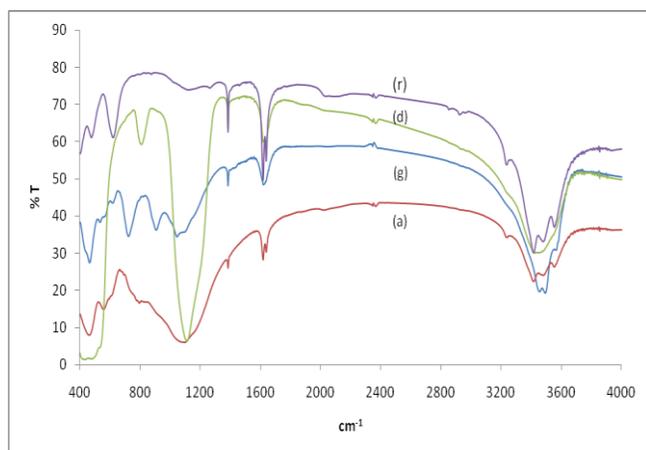


Fig 5 X-ray diffraction of nZnO/fly ash composite
M - Mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$), Q - Quartz (SiO_2), Z - Zinc Oxide (ZnO)



(r) – Reference, (a) – Fly ash, (c) – nZnO, (e) – Fly ash – nZnO composite

Fig. 2 FTIR spectrum of fly ash, nZnO and fly ash – nZnO composite

3.7 Surface and Micropore Area

Results obtained on the BET surface area and porosity determination of the precursors and the composite showed that the surface area of nZnO and fly ash are 14.4098 ± 0.0387 and 1.0600 ± 0.0030 m²/g, respectively while the surface area of nZnO/fly ash is 198.453 ± 0.0936 m²/g. The results showed that the use of ZnO for the preparation of nZnO /fly ash composite greatly accelerated the surface area of fly ash. The surface area of fly ash was therefore increased by 99.47 %.

The micropore area of nZnO/fly ash composite was 5.4365 m²/g while the micropore areas of fly ash, and nZnO were 0.3796 and 3.1780 m²/g, respectively. These values were thus smaller than the micropore area of the nZnO/fly ash composite material. It could therefore be concluded that the composition of nZnO with fly ash also increased the micropore area of fly ash.

4 CONCLUSION

In conclusion, values obtained for the PZC and pH showed that fly ash and nZnO are positively charged and will attract anionic complexes of heavy metals in wastewaters while nZnO/fly ash composite is negatively charged and will attract cationic complexes. The ash content determination showed that the level of inorganic materials present in the composite materials is a function of the precursors that make up the composite. Finally, the BET analysis showed that the composition of nZnO with fly ash increased the surface and micropore areas of fly ash which will make the composite a better adsorbent as compared to the precursors alone. Due to the presence of nano oxide in the composite material, it is also expected that the remediation mechanism by nZnO/fly ash composite will combine the synergistic effect of adsorption and oxidation

when it is used for the remediation of environmental pollutants from wastewaters and not adsorption alone.

We are currently working on the application of the precursors and the composite material for the remediation of environmental pollutants.

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