

MAIZE TASSEL–MULTIWALLED CARBON NANOTUBES AS NOVEL SORBENT FOR THE REMOVAL OF ATRAZINE FROM AQUEOUS MEDIA.

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Introduction

Maize tassel (MT), an agricultural waste material has been used for the removal of Pb from borehole water contaminated with mine wastewater². Furthermore, it has been shown that maize tassel contains functional groups such as –OH and N-H. It is postulated that the functional groups in maize tassel can be used to functionalise MWCNTs. Atrazine (ATZ) is one of the s-triazine herbicides that is widely used in agriculture to destroy broadleaf and grassy weeds in corn and other crops in order to improve crop production and quality¹. Adsorbents such as functionalized multiwalled carbon nanotubes (MWCNTs), C₁₈ silica that are readily available have been used to extract atrazine. However, they are considered to be very expensive. Therefore, there is a need to develop an affordable but efficient adsorbent for solid phase extraction (SPE) of ATZ. This study, therefore, reports the development of an affordable adsorbent material based on MT-MWCNTs nanocomposite for the effective removal of atrazine and its primary metabolites, deethylatrazine (EDA) and deisopropylatrazine (DIA). The authors are not aware of any report on the use of MT to functionalise MWCNTs with the development of a nanocomposite material (MT-MWCNTs) that can be used to extract ATZ from aqueous solution.

Materials and methods

The non-functionalized multiwalled carbon nanotubes were purchased from (Sigma–Aldrich, South Africa); 98% carbon basis, O.D x I.D x L 10 ± 4.5 nm ± 0.5 nm x 3 ~ - 6µm; TEM. Before use, they were dried in an oven at 80°C for 2 h. Maize tassels, with a cultivar number: *variety star 7714* was collected from a farm in Brits, South Africa. The maize tassel plant was first air-dried, thoroughly washed and rinsed with deionised water and thereafter oven-dried for 24 h at 100 °C. The maize tassels were then milled using a 500-µm sieve laboratory hammer mill to a fine powder. The powder was then fractionated into different sizes using laboratory analytical sieves. Particles with diameters ranging from 150-500µm were obtained and used for the preparation of the nanocomposite. About 1.5 g of maize tassel was sonicated for 2 h in 50 ml of deionized water in the presence of a few drops of acetic acid until the solution was homogenous. Approximately 0.5 g of MWCNTs were suspended separately in deionized water and sonicated for 2 h. The two suspensions were mechanically mixed, sonicated for 4 h to increase the homogeneity and cross-linked with glutaraldehyde (GA), and left to dry overnight in a vacuum oven at 60 °C followed by mechanical grinding³. The composite material was synthesised by varying the ratio of maize tassel and multiwalled carbon nanotubes, i.e., 1:1, 2:1, and 3:1 and 5:1, respectively. The produced nanocomposites were coded as i.e. MT-MWCNT (1:1), MT-MWCNT (2:1), MT-MWCNT (3:1), and MT-MWCNT (5:1).

River, dam and borehole samples as well as field and method blanks were collected and analysed to evaluate the feasibility of the developed method and deionised water. Before the environmental water samples were used, they were filtered through 0.22µm micropore membranes and stored in an amber glass bottles at 4 °C. The effluents collected were also analysed using LCMSMS-8030 serial No (010255270012) from Shimadzu was used for analysis of samples the system was equipped with a quaternary pump, micro degasser (DGU-20A3R, high-performance well-plate auto sampler and thermostated column compartment. The column from Leco Africa used was a Luna Omega 3 µm Polar C18 1005 (100 x 2.1mm) Phenomenex and the column temperature was designed to be 40 °C. The elution was made with the gradient mode running with the conditions: 0-0.4 min, 90% A (water solution containing 0.5% formic acid and 10 mmol ammonium acetate) + 10% B (acetonitrile solution containing 0.5% formic acid); 0.4– 12 min, changing from 90% A + 10% B to 55% A + 45% B; 12–14 min, changing from 55% A + 45% B back to 90% A + 10% B and maintaining for 1 min in order to equilibrate the flow. The pump flow for (A) was 0.05 ml min⁻¹ and for (B) was 0.15 ml min⁻¹. The flow-rate was 0.9 mL min⁻¹, the injection volume was 5.0 L. All mass spectrometry analysis was performed by a Shimadzutriple quadrupole mass spectrometer fitted with electrospray ionization (ESI) source and controlled by Mass Hunter (Version B.01.03) software. The Nitrogen nebulizer pressure was set at (A) 1100 psi (B) 1082 psi and the nitrogen drying gas was set at 40 °C with a flow rate 15 L min⁻¹. Pure nitrogen was used a collision gas. To optimize the multiple reaction monitoring (MRM) each herbicide standard were injected at a concentration of 1 mg L⁻¹.

Results and discussion:

Table 1 shows a summary of the characterization results from BET isotherm on raw maize tassel and nanocomposites. The surface area of the MT-MWCNTs composites decreased with increase in MT mass ratio. This could be due to the deposition or infusion of MT powder into the MWCNTs, which filled the pore sites of the MWCNTs and contributed to the increase in pore size. There is also a decrease in pore volume as the ratio of MT increased. However, the pore size increased with increase in MT ratio and this can be attributed to the formation of pseudo pores.

Table 1: Adsorption Parameters Obtained by BET Model to Adsorption Isotherms of N₂ at -196 °C

Sample	Surface area Single point P/P ₀ m ² /g	BET surface area (cm ² g ⁻¹)	Pore Volume (cm ³ g ⁻¹)	Pore size (nm)
MT	0.1120	0.0991	¹ Na	Na
MWCNTs	281.3950	281.3950	1.046057	14.86959
MT-MWCNTs (1:1)	86.2199	92.0310	0.643441	27.96627
MT-MWCNTs (2:1)	53.1005	57.8821	0.438790	30.32301
MT-MWCNTs (3:1)	32.9588	36.5263	0.241300	26.42483
MT-MWCNTs (5:1)	18.2076	20.5146	0.152555	29.74569

¹Not Applicable

Figure 1 shows the nitrogen adsorption–desorption isotherm measured at -196 °C. The isotherm of the tassel adsorbent is characteristic of materials without micropores because the adsorption–desorption curve is typical type IV isotherm.

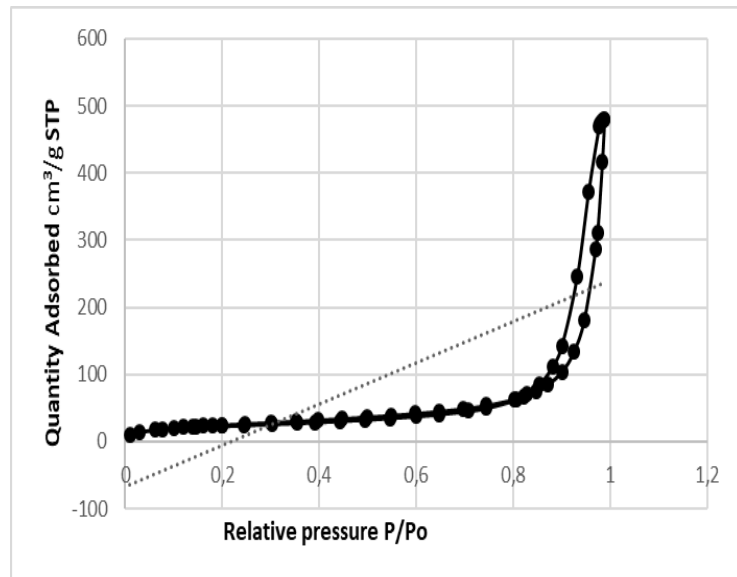


Figure 1: Adsorption- desorption curve for MT-MWCNTs (1:1)

The micrograph in Fig. 2(a) shows a flat and smooth structure of maize tassel, while Fig. 2(b) shows the tangled and tubular form of multiwalled carbon nanotubes. The tangled and tubular forms of multiwalled carbon nanotubes are retained in Fig. 2(c) indicating the dominance of the multiwalled carbon nanotubes. The trend observed in Fig. 2(c) is repeated in Fig. 2(d), although to a lesser extent. Fig. 2(e) shows a micrograph of a complete mixture of MT-MWCNTs composite. The MT-MWCNTs composite have cleaved well indicating proper infusion of the MT and the MWCNTs.

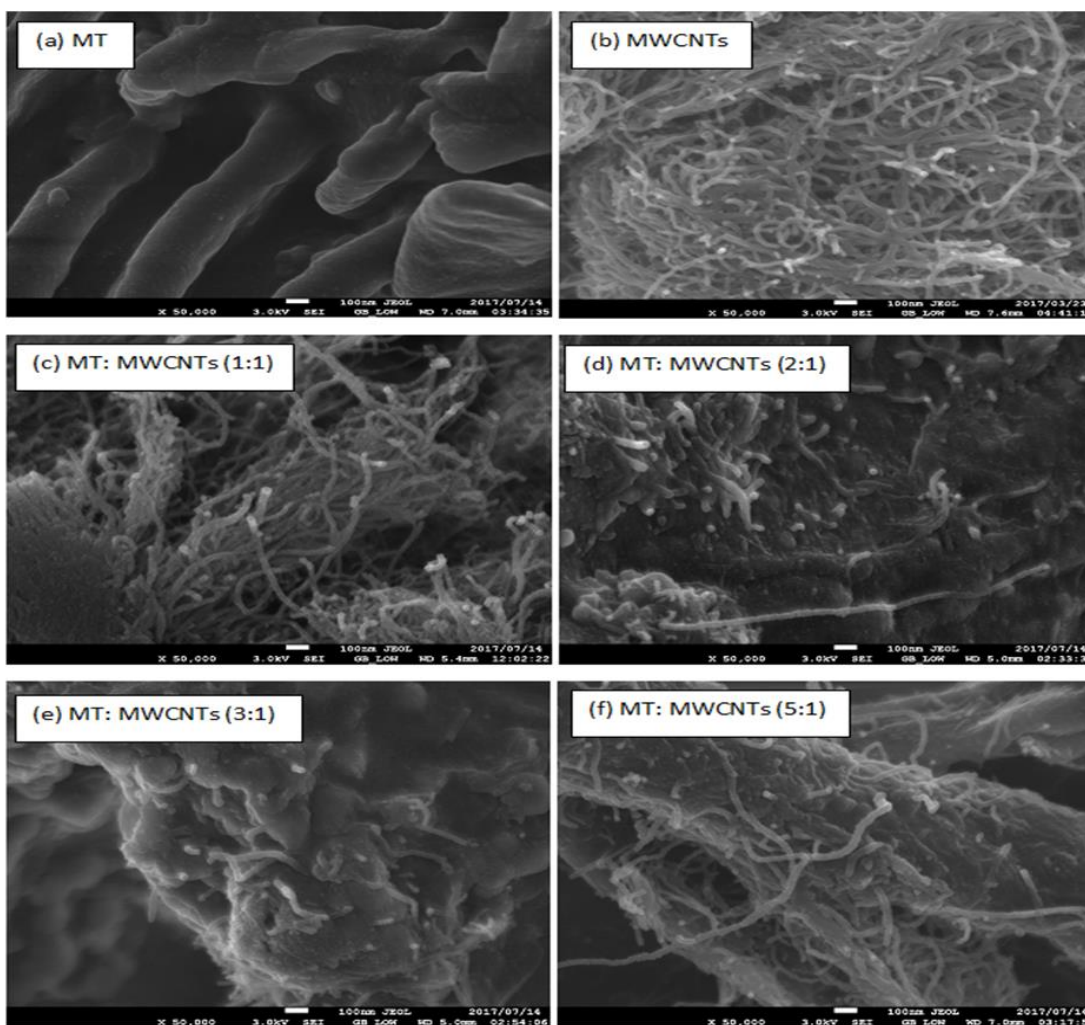


Figure 2: SEM images of MT, MWCNTs and MT-MWCNTs nanocomposites

It can be seen in Fig. 3 the presence of, -C-Cl, -C=C, -C-O, -N-O, C-H, -C-C, and -OH on MT attributed to intensities of 600 cm^{-1} , 896 cm^{-1} , 1200 cm^{-1} , 1500 cm^{-1} , 1700 cm^{-1} , 2950 cm^{-1} , and 3500 cm^{-1} , respectively.

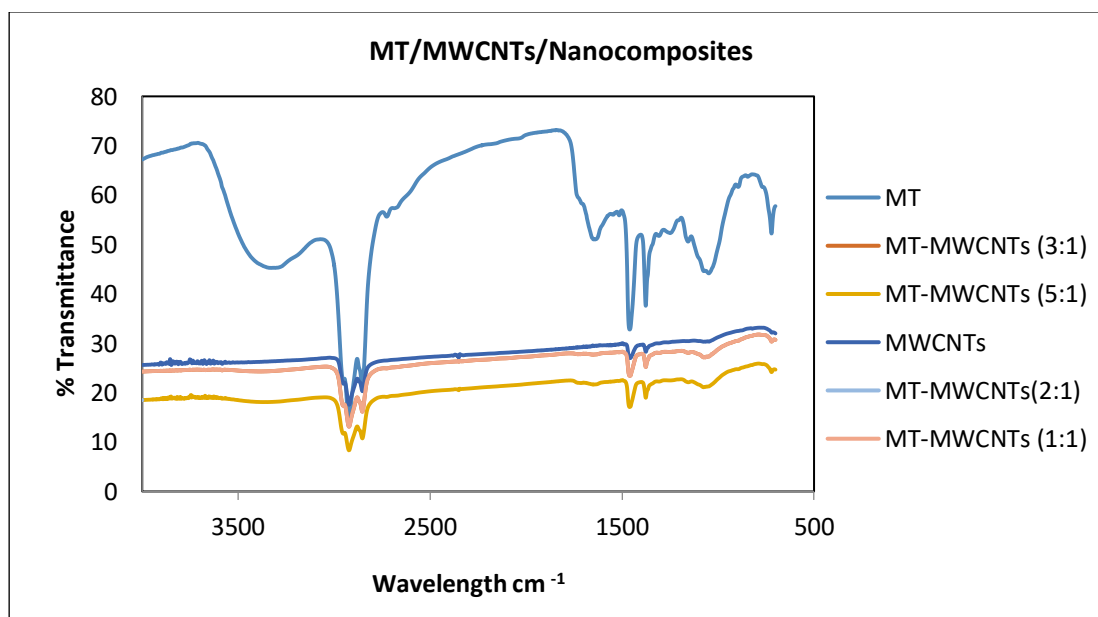


Figure 3: FTIR spectra of raw MT, MWCNTs and MT-MWCNTs nanocomposite

Figure 4 shows the effect of adsorbent dosage on the adsorption of ATZ, DEA and DIA. The results obtained indicate increase in percentage removal with increase in adsorbent dosage from 0.1g - 0.5g. This might be due to the availability of active adsorption sites on the composite for triazine adsorption. Figure 5 shows the effect of pH range from pH 2-12. The optimum pH efficiency was achieved at pH 8, because there is a slight increase of adsorption. pH above pH 9 or below pH 7 caused a decrease in extraction of atrazine and this might be due to the pKa value of the three compounds. Figure 6 shows the influences of initial concentration of adsorbate on the adsorption of ATZ, DEA and DIA compounds on the nanocomposite sorbent. The results show that among all the analytes, DIA exhibited the highest adsorption compared to the other analytes. It was observed that an increase in initial concentration of the solute resulted in increasing adsorption of all the analytes. This is because increasing the initial concentration increased the adsorption capacity between the solid and liquid phase of the adsorbate. The nanocomposite was tested on environmental samples (Fig.7). The optimum conditions were pH 8, sorbent dosage 0.5g, initial concentration 100 mg L⁻¹. The study shows that the removal of ATZ, DEA and DIA was effective in the range of 99.5% - 99.9%.

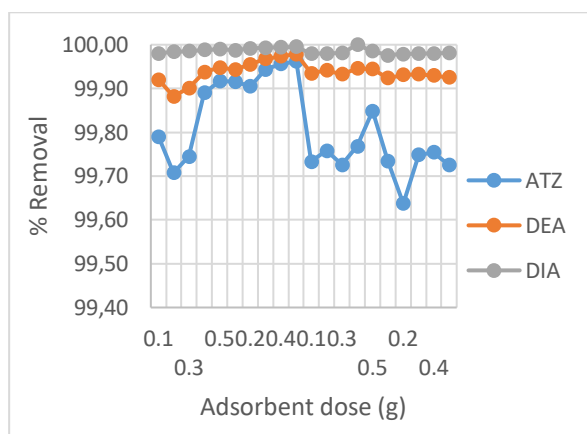


Figure 4: Effect of adsorbent dosage

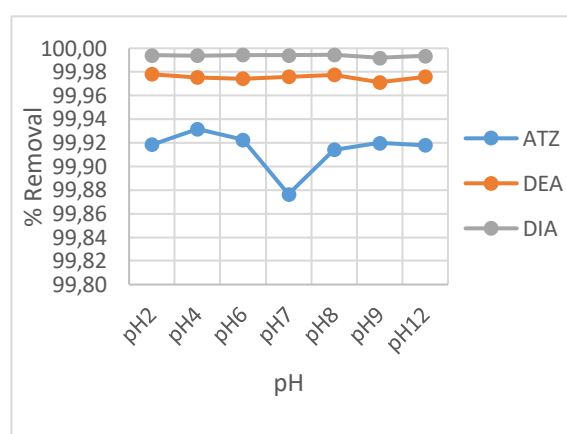


Figure 5: Effect of pH

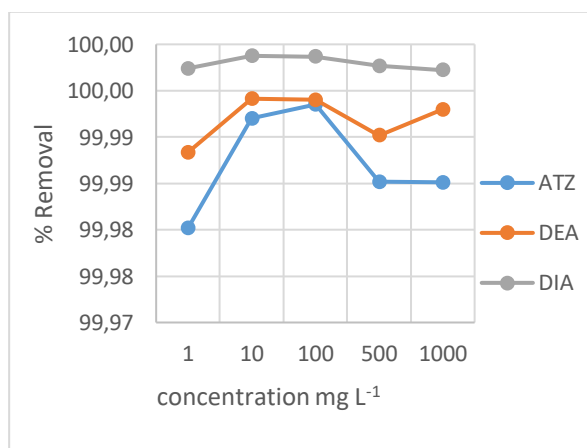


Figure 6: Effect of initial concentration

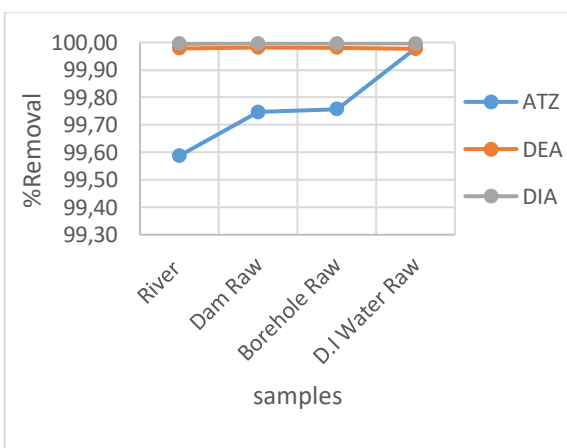


Figure 7: Real water samples

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References:

1. Udiković-kolić N, Scott C, Martin-Laurent F (2012) *Appl. Microbiol. Biotechnol.* 96(5): 1175-1189.
2. Zvinowanda C, Okonkwo J, Sekhula M, Agyei N, Sadiku R (2009) *J. Hazard. Mater.* 164(2): 884-89.
3. Salam M, Makki M, Abdelaal M (2011) *J. Alloys Compd.* 509(5): 2582-2587.
4. Yu Z, Qin Z, Ji H, Du X, Chen Y, Pan P, Wang H, Liu, Y (2010) *Chromatographia.* 72(11-12):1073-1081.