INVESTIGATION OF THE SYNTHESIS AND CHARACTERIZATION OF MANGANESE NANOPARTICLE AND ITS ASH RICE HUSK SUPPORTED NANOCOMPOSITES.

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Abstract

This research paper reported the investigation of the synthesis of Nano-scaled zerovalent manganese and its rice husk supported nanocomposites (nZVMn and ARH-nZVMn) by bottom–up approach via chemical reduction using sodium borohydride. nZVMn was characterized using Ultraviolet-Visible (UV-VIS) Spectroscopy and Fourier Transform Infrared Spectroscopy (FT-IR). The UV-VIS surface plasma resonance absorption band occurred at 380nm. Both nZVMn and ARH-nZVMn were further characterized byScanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), Energy Dispersive X-ray (EDX) and Points of Zero Charge. The surface texture and morphology were revealed by SEM and TEM micrographs while the EDX spectra gave the information on elemental and percentage composition coupled with surface atomic distribution of nZVMn and ARH-nZVMn. Their points of zero-charge are 7.80 and 7.90 for nZVMn and ARH-nZVMn respectively. The unique characteristics possessed by nZVMn and ARH-nZVMn enlisted them as novel, promising and potential adsorbents for heavy metal removal.

Keywords: EDX, FTIR, nanoparticles and nanocomposites, SEM, TEM and UV-VIS

Introduction

The concept of nanotechnology is considered as modern science and it is on the increase per day as its applicability attractsthe interest of researchers owing to the fact that it gives room for several innovations. A number of physical phenomena become more prominent as the size of the system increases from macro or micro to nano scale. This size of the nano-material is one of the major superiorities of nanotechnology (Prathna*et al*., 2012). The mechanical, thermal and catalytic properties of the material are affected by surface area. The increase in surface area to volume ratio leads to increasing dominance of the behaviour of atoms on the surface of the particle over that of those in the interior of the particle, thus altering the properties (Jain *et al*.,2007). Effort has been made by different researchers to prepare silver, gold and iron nanoparticles by chemical reduction which is the bottom up approach using sodium borohydride, starch, sodium citrate, and medicinal plant extract (Roosta*et al*., 2014; Wojtysiak and Kudelski, 2012; Prasad and Elumalai, 2011; Kumar and Yadav, 2011; Xi*et al*., 2011 and Chen *et al*.,

2011). The pollution challenges in the environment as a result of industrial globalization and the quest for novel and active adsorbent propel the authors into the investigation of the synthesis and characterization of manganese nanoparticle and its ash rice husk supported nanocomposites which are the objectives of this research.

Experimental

Materials and Preparation.

All the reagents used are of analytical grade. Deionized deoxygenated water (sparged with nitrogen gas) was used all through for this preparation. Sodium Borohydride purchased form Sigma-Aldrich was used for the chemical reduction, $MnCl_4.4H_2O$ (Xilong Chemical), Absolute Ethanol (BDH), HNO_3 (Sigma-Aldrich).

Rice husk collected from a local mill in Ilorin was used to prepare Ash Rice Husk. This serves as a base (supporting) material, it is locally available and cost effective.Rice husk was screened, washed and dried in the oven at about 80 - 90^{o}C for 2 days. About 140g of the dried sample of rice husks was calcined at 550°C for 3hours in the muffle furnace resulting into about 16.35g of rice husk ash (RHA) following the procedure reported in the literature (Atta et al. 2012). Ash rice husk (RHA) was cool and stored in the desiccator for further uses.

For the synthesis of ZVMn, the procedure reported by Hariljeet*et al*., 2010 was followed. In a typical procedure for nano-scaled zerovalentmangansese synthesis,4.55g of 0.023M of $MnCl_4.4H_2O$ was prepared and tagged solution A and 4.73g of 0.123M $NaBH_4$ was prepared and tagged solution B. Manganese Chloride was reduced to zerovalent Manganese according to the reaction:

$Mn^{2+} + 2BH_4^- + 6H_2O \rightarrow Mn^0 + 2B(OH)_3 + 7H_2\uparrow$

Under anaerobic condition in a glove box, solution B was drop wisely added to solution A in a three-neck-round bottom flask and rapid formation of zerovalent manganese with faint milky colour was observed with a large evolution of hydrogen gas.As soon as the borohydride solution was added to Manganese Chloride solution, a faint milky particles of (nZVMn) appeared and the mixture was further stirred for 3h. The mixture was allowed to age overnight for better formation of nZVMn. Manganese powder was separated from the solution using vacuum filtration apparatus and a cellulose nitrate membrane filter (Millipore filter) of 0.45μm. Mn^0 (nZVMn) was further washed with absolute ethanol three times and dried in a Genlab oven at 50°C overnight to obtain a deep brown colour of nZVMn.

The preparation of Ash Rice husk supported nanoscaledzerovalent manganese was carried out following the proceure reported for the preparation of betonite supported iron nanoparaticles by Chen *et al.*,2011. The preparation consisted of ARH-nZVI with an manganese/ARH mass ratio of 1:2, 50mL of 0.023M $MnCl_2.4H_2O$ earlier prepared using deionized deoxygenated (sparged with nitrogen gas), add Ash

Rice Husk (6.00 g). The mixture was stirred with a magnetic rod for 30 min in a nitrogen atmosphere and then 0.123M $NaBH_4$solution (100 mL) was added at the speed of 1–2 drops per second drop by drop into this mixture and vigorously stirred continuously under nitrogen atmosphere. The mixture changes from milky color to light brown and then eventually to deep brown in a three-neck flask.After all of the $NaBH_4$solution had been added, the mixture was stirred under the nitrogen atmosphere continuously for another 3h and later was left over night to allow ageing of the ARH-nZVMnnanocomposite and deplete all the $NaBH_4$ solution. Vacuum filtration was employed to collect the ARH-nZVMn particles using a milliporefilter paper (0.45μm) and these were quickly rinsed three times with absolute ethanol and dried in a Genlab oven at 50°C overnight to obtain a deep brown powder of ARH-nZVMn.

Characterizations of nZVMn and ARH-nZVMn

The Absorption band arising from the surface plasmon resonance in the nZVMn was determined using a Beckmann Coulter DU 730 Life Science UV-VIS spectrophotometer in the Department of Chemistry, University of Ilorin.

The information on the molecular environment of nZVMn and ARH gotten from the IR spectra was obtained from the Shimadzu FT-IR spectrophotometer in the department of Chemical Sciences, Redeemers University, Nigeria.

The surface morphology and elemental analysis was done using a scanning electron microscopy (SEM) integrated with energy dispersive x-ray (EDX) analyzer. SEM images and EDX spectra were obtained using a TESCAN Vega TS 5136LM typically at 20 kV at a working distance of 20 mm.Samples for SEM analysis were prepared by coating them in gold using a Balzers' Spluttering device.

The Transmission electron microscopy was carried out usingA Zeiss Libra 120 transmission electron microscope at 80KV voltage to determine the size and shape ofthe microstructures.Samples were well dispersed, supported on a copper grid and dried at ambient temperature.

The Point of Zero charge which is the pH at which the nZVMn and ARH-nZVMn surfaces submerged in an electrolyte (0.1M $NaNO_3$) exhibiting zero net charge was carried using a procedure reported by Srivastava*et al*., 2005. The pH was varied from 2 to 12 using 0.1M HNO_3 and 0.1M NaOH.

Results and Discussion

UV- VIS Analysis

The reduction of $Mn^{2+}$to Mn^0 (nZVMn) when it reacted with sodium borohydride followed by a gradual colour change. The spectrum of deep brown colour of nZVMn was obtained by carrying out a wavelength scan of dispersed nZVMn in a quartz cuvette with a 1 cm optical path. A small aliquot was drawn from the reaction mixture and a spectrum was taken on a wavelength from 200nm to 800nm.

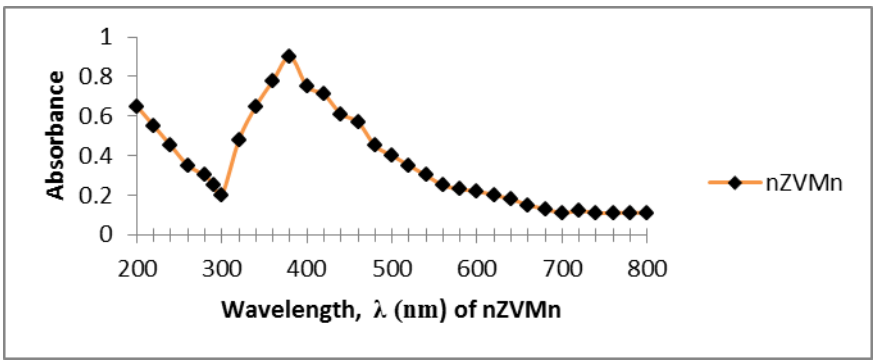

Fig. 1: UV-VIS spectrum of nZVMn

The absorption spectrum of nZVMn was depicted on Fig 1. The maximum wavelength was observed around 340nm 345nm as a result of surface plasmon resonance (SPR). The surface of plasmon resonance (SPR) is the collective oscillation of the conduction electrons in resonance with the light field due to electron conferment in nZVMn. The SPR depends three (3) factors namely: the nature of the metal, the morphology(size and shape) of the nanoparticles and the dielectric properties of the environment medium of dispersion (Jain *et al*., 2007). The result obtained was in support with the report of Waghmare, et al., 2012

FTIR Analysis

Figure 2 represents IR spectrum of Manganese Nanoparticles with some vibration bands at 3288, 1636, 1307, and 504 cm^{-1}. The peak at 3288 cm^{-1} stands for O–H broad from the alcohol where the manganese nanoparticle is kept for preservation, H-O-H stretching (1636 cm^{-1}) , C─O stretching of alcohol at 1309cm^{-1} and the peak at 504 cm^{-1} stands for Manganese nanoparticle, nZVMn as summarized on table 1 below (Sinha*et al.*, 2011, Li *et al.*, 2009).

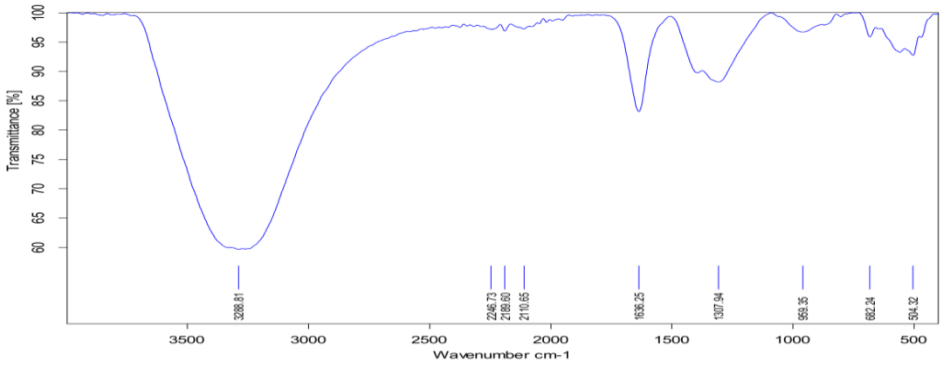

Fig. 2. FT-IR spectrum of nZVMn

Table 1: Summary of the Functional groups and vibration frequencies on the IR spectrum of nZVMn

Functional group	**O–H str of alcohol**	**H–O–H str**	**-C–O**	**Mn^0**

$\tilde{V}/cm^{-1}$	3288	1636	1309	504

SEM, TEM and EDX Analyses

The SEM micrograph is portrayed in Fig 3, 4, 5 and 6. Figure 3 shows the SEM micrograph of Ash rice husk. The picture reveals the surface texture and porosity of ARH. It shows that ARH is a very fine particle size to the order of a millimeter or less and that there are pores of varying sizes within the particle. However, this is in accordance with the report in the literature [Srivastava, *et al.,* 2005].

Figure 4 depicts the SEM image of zerovalent manganese nanoparticle. The picture reveals coarse, rough and crake surface, the sample exhibits odd and unspherical particle. Presence of some pores on the surface makes it a promising adsorbent for adsorption studies [Morsali*et al.,* 2009].

SEM micrographs on Fig 5 and 6 show morphology of ash rice husk supported manganese nanocompoisteof different magnifications. Fig 5 reveals a closely pack, curled and crumpled surface while Fig 6 shows a larger magnification of the nanoparticles seen of Fig 5. An evidence of manganese forming a composite with ash rice husk is seen. The flake-like particle of large surface area gives an assurance that this novel adsorbent will be effective in sorption studies [Srivastava, *et al.,* 2005]

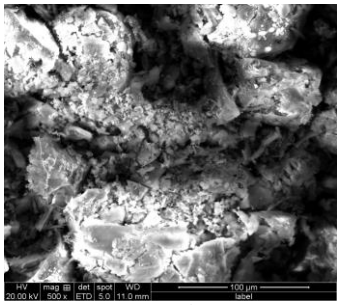

Fig 3: SEM for ARH

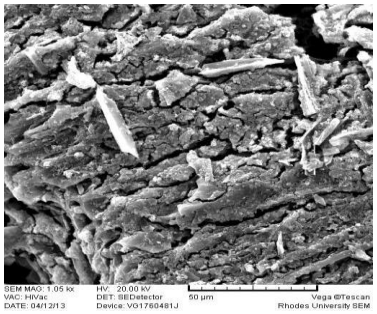

Fig 4: SEM for NZVMn

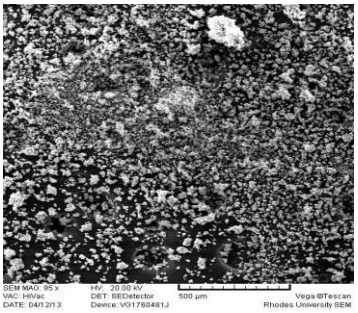

Fig 5: SEM for ARH-nZVMn

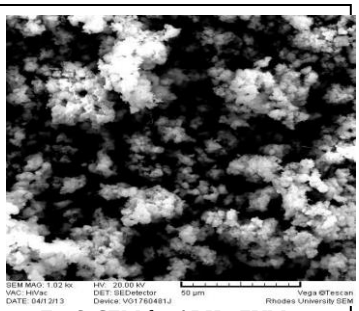

Fig 6: SEM for ARH-nZVMn

The TEM micrographs on Fig 7 and 8 reveal the images of NZVMn, NZVMn-ARH respectively. Fig. 7 shows some dispersion and agglomeration of manganese nanoparticle. On Fig 8, it was observed that there are traces of dispersions and whiskers which are attribute of manganese nanoparticles as reported in the literature [Giovannelli, *et al.*, 2012; Waghmare*et al*., 2011; Lisha, *et al.,* 2010]. To the best of my

knowledge, ARH- nZVMnnano-composites has not been reported therefore they are novel and potential composites which might be useful for on adsorption studies.

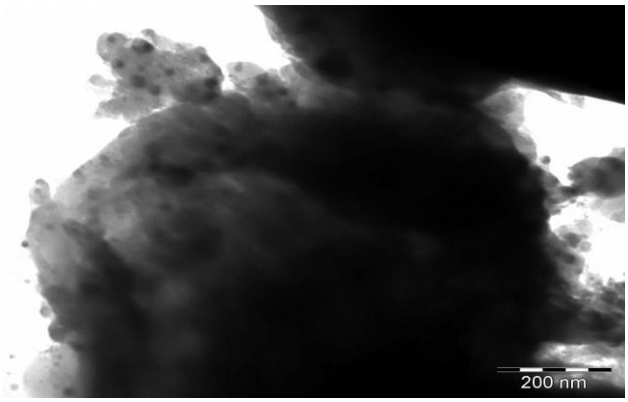

Fig 7: TEM for NZVMn

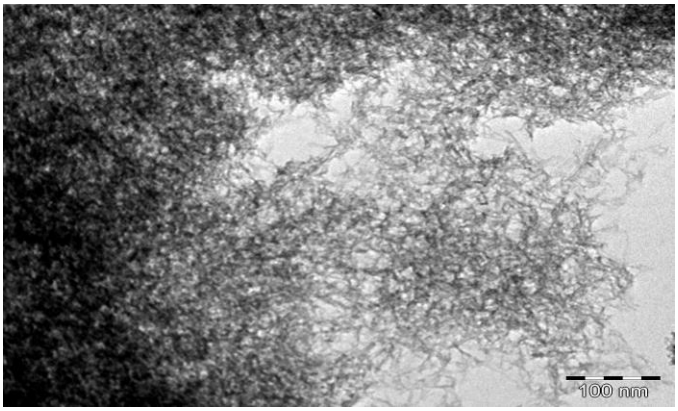

Fig 8: TEM for ARH-nZVMn

ARH-nZVMn and 10). The

atomic distribution and the chemical elemental composition couple with the percentage compositions are stated on tables 2, 3, 4, and 5. The presence of other elements may arise from the reagents during the synthesis or additives during the analysis.

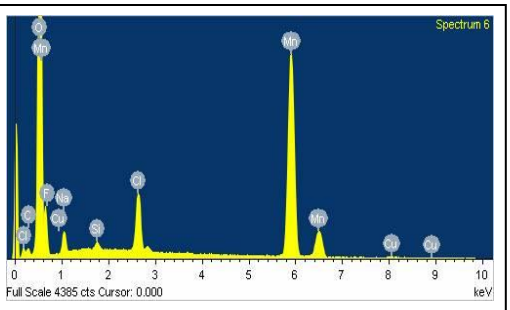

Fig 9: EDX for NZVMn

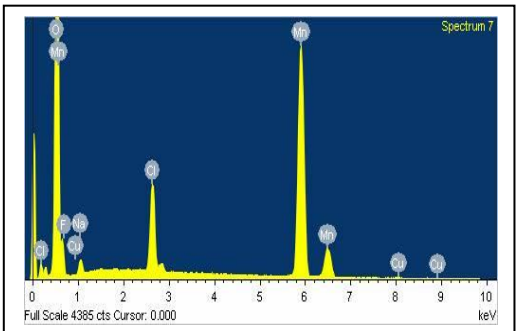

Fig 10: EDX for ARH-nZVMn

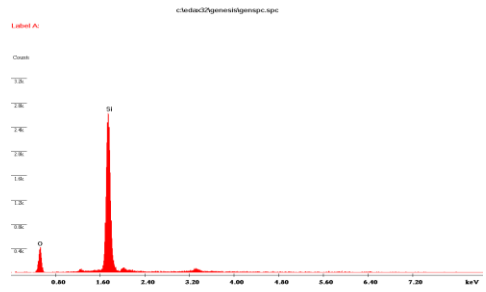

Fig 11: EDX for ARH

Table 2: Information extracted from the EDX spectra

S/N	Fig	Nanoparticles/Nanocomposites	Element with intense Peak(s) with their binding energy (keV)	Other elements
1	9	NZVMn	Mn^0 (0.6, 6.0, 6.4)	O, C, Cl, F, Na, Cu, Si,
2	10	NZVMn-ARH	Mn^0 (0.6, 6.0, 6.4)	O, C, Cl, F, Na, Cu, Si,
3	11	ARH	Si (1.8)	O

Table 3: EDX Elemental percentage composition of nZVMn

Element	Weight%	Atomic%
O K	48.74	72.64
F K	2.40	3.01

Na K	1.60	1.66
Cl K	5.49	3.69
Mn K	43.57	18.91
Cu K	0.25	0.09
Totals	102.04	100

Table 4: EDX Elemental percentage composition of ARH-nZVMn

Element	Weight%	Atomic%
C K	4.00	4.55
O K	82.29	70.29
F K	5.17	3.72
Na K	3.81	2.26
Si K	0.59	0.29
Cl K	6.17	2.38
Mn K	65.94	16.40
Cu K	0.49	0.11
Totals	168.46	100

Table 5: EDX Elemental percentage composition of ARH

Element	Weight %	Atomic %
O K	32.35	46.59
Mg	1.65	1.56
Si	52.78	43.30
P	5.14	3.82
K	5.5	3.24
Ca	2.58	1.49

Point of Zero Charge (PZC)

This was determined by salt addition method following the procedure reported by Srivastava *et al.*, 2005. In a typical step, to a series of 100 cm^3 plastic bottles, 50 cm^3 of 0.1M $NaNO_3$ solution of known strength was transferred. 100mg of nZVIwas added to 50 cm^3 of 0.1M $NaNO_3$ with varying pH from 2 to 12 and capped immediately. The suspensions were then agitated on the orbital shaker and allowed to equilibrate for 48 h with intermittent shaking. The pH values of the supernatant liquid were noted. The difference between the initial and final pH (pH_f) values ($pH=pH_i - pH_f$) was plot-ted against the pH_i. The point of intersection of the resulting curve at which pH_i gave the point of zero charge. The procedure was repeated for ARH-nZVMn and ARH for comparison. The figures below represent the PZC for nZVMn, ARH-nZVI and ARH

As determined in the laboratory, the PZC for nZVMn (Fig. 12), ARH- nZVMn (Fig. 13) and ARH (Fig. 14)are 7.80, 7.90 and 8.00 respectively. The significance of this kind of plots is that nZVMn, ARH- nZVMn, and ARH will have positive charge at solution pH values less than the pzc and thus be a

surface on which anions may adsorb. On the other hand, they will have negative charge at solution pH values greater than the pzc and thus be a surface on which cation may adsorb. The result reported here is similar to the findings Srivastava *et al.,* 2005. This information is a useful tool showing that the nanoparticles (nZVMn) and nanocomposites (ARH-nZVMn) can serve as active, efficient and effective novel adsorbents for treatment of waste.

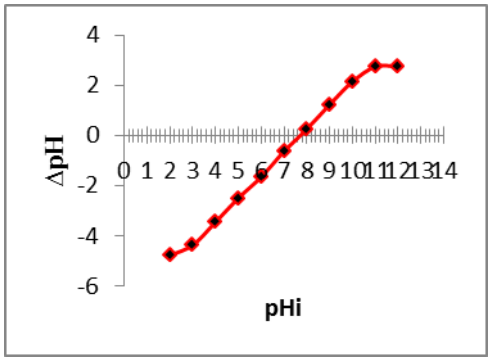

Fig 12: Point of Zero Charge for NZVMn

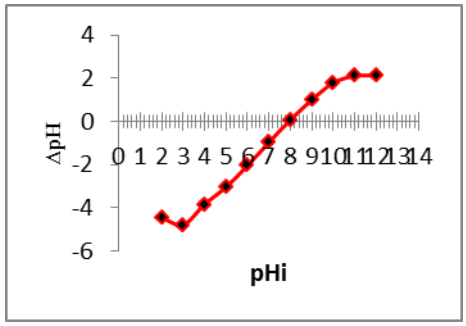

Fig 13: Point of Zero Charge for ARH-NZVMn

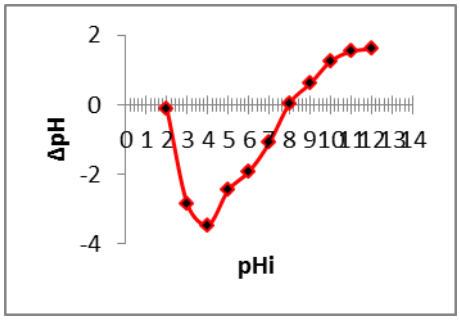

Fig 14: Point of Zero Charge for ARH

Conclusion.

Nano-scaled Zerovalentmanganese (nZVMn) and Ash rice husk supported nano-scaled zerovalent manganese (ARH-nZVMn) have been successfully prepared and characterized using UV-VIS spectroscopy showing their surface plasmon resonance,FTIR revealing the component of their molecular environment, SEM revealing the nature of their surface texture and porosity, TEM showing their morphologies, EDX revealing their elemental compositions and PZC showing the suitable pH for the adsorption studies. The unique characteristics shown by both nZVMnand ARH-nZVMn revealed that they are potential novel adsorbents for toxic pollutants in waste water.

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