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Environmental remediation from heavy metal pollution using polyacrylamide–grafted gum arabic, *Moringa oleifera*, and blended products of *Moringa oleifera* and polyacrylamide-grafted gum arabic

M. B. ALANG [*], J. T. BARMINAS, S. A. OSEMEAHON, H. M. MAINA and
R. USAKU

Department of Chemistry, Federal University of Technology, P.M.B 2076 Yola, Nigeria.
[*] *Corresponding author, E-mail: alangmibong@agat.net*

ABSTRACT

Graft copolymers of polyacrlamide-grafted gum arabic were synthesized, blended with *Moringa oleifera* and characterized by IR spectroscopy. The potentials of the products to remove heavy metals from aqueous solutions were studied at room temperature (30 $^{\circ}$C) and this was experimented on iron (III) ions (Fe^{3+}). The extent of metal ions removal was determined from sorption capacity values of several sorbents. The results showed that all the polymeric products investigated displayed significant sorption capacities. The abilities of the grafted product polyacrylamide-grafted gum arabic (GA-g-PAAM) to clarify wastewater to a high degree and also remove heavy metals from contaminated water systems, are good indications of the importance of material transformation, especially gum arabic which is hitherto, an emulsifier, and other products of phyto-origin. The sorption capacities of the synthesized and natural products could lead to a blissful expansion of the spectrum of substances that can be used to detoxify our environment through well guided technologies.
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Keywords: Gum arabic, *Moringa oleifera,* sorption capacity, sorbent, phyto–products, detoxify, environment.

INTRODUCTION

Natural substances as well as their synthetic alternatives exhibit characteristic properties and perform varied functions depending on their chemical constitution and environmental constraints. Pure materials alone seldom proffer satisfactory performance when applied singly and when they do, their performances are shrouded with a plethora of limitations (Tripathy and Singh, 2001; Jideoniwo and Okieimen, 2006). The inefficiencies of certain materials may be attenuated or the efficiencies of such materials can be enhanced through the chemical modification of their structures. This can be done through chemical inclusion of desirable functional groups or exclusion of unwanted and unproductive or counterproductive molecular fragments, alteration of stereo-chemical or conformational structures if one intends to come out with a compatible hybrid structure of material with befitting properties for a specified application. Such is the intent of scientific and technological drift towards the formulation of bona fide, authentic and long lasting water and wastewater treatment chemicals tailored to the upgrading of water quality standards as recommended by the

World Health Organization (W.H.O), Environmental Protection Agency (E.P.A), Food and Agricultural Organization (F.A.O) or other socially and environmentally affiliated agencies and organizations such as the Standard Organization of Nigeria (S.O.N) and the National Agency for Food and Drug Administration and Control (N.A.F.D.A.C). This goes a long way to protect growing interest and concern for a healthier (disease-free) human population, social welfare and general environmental protection and conservation. Thus, paving the way to a richer flora including, the proliferation of medicinal plants (Falodun et al., 2009; El-Mahmood, 2009). Consequently, pertinent research has been done and more research is still going on to produce more authentic products for intended end-use as previous flocculants, though have significantly ameliorated the situation of water and wastewater treatment, are still shrouded and perturbed with a myriad of shortcomings which call for scientific and technological attention and reaction. Substances for water treatment are essentially of polymeric origin or nature, some being natural and others synthesized in the laboratory. Synthetic products are more likely to yield expected fruits as the raw materials for their production are meticulously selected to produce products with desirable qualities. There is however growing interest and research into the production of polymeric material usually of polysaccharide origin such as gum exudates and synthetic polymeric materials such as polyacrylamide. The scientific union between natural and synthetic polymeric counterparts is sealed by the technological process termed graft copolymerization. This process has the potential of promoting or causing up-shoot in values and awareness of some important but latent natural raw materials with a resultant blissful broadening of the field of scientific research in phyto- products. Tripathy and Singh (2001) demonstrated that polymeric grafted flocculants of polyacrylamide and sodium alginate possess better flocculating properties than polycrylamide alone. It is the

intent of further research to sort out other plausible combinations with acrylamide, which might exhibit greater performance, especially from phyto- products such as gum exudates. Some of these natural polysaccharide and polymeric materials include starch, guar gum, xanthan gum and gum arabic (Baid, 1988 and Barminas, 2004). The grafted products have more extended and ramified structures, which transform them into efficient encapsulating agents (Baldwin et al., 1998). Tripathy and Singh (2001) propounded that the better flocculating efficiency of grafted copolymers as compared to the linear polyacrylamide was due to enhanced proximity or better approachability of the branched chains to the colloidal particles. This efficiency allegedly increased with increase in polyacrylamide branched chain lengths. Hitherto, proper characterization of flocculating capabilities of grafted copolymers of polyacrylamide and natural polysaccharide is being awaited. A credible water treatment procedure actually encompasses a stringent removal of colloidal particles in general and a drastic attenuation or approximate extinction of the embedded pathogenic microbial load in the water system in particular (Friedman, 1997; Hazen, 1997; Tchobanoglous, 1997). A natural product venerated for such an important, scientific attractive quality is 'Zogale' *(Moringa oleifera)* tree seed extract (Muyibi and Sani, 2001). It has been reported that bacteria and pathogenic load reduction by *Moringa oleifera* seeds lie in the range of 90-99%. Due to the quest for higher quality and efficiency at a reduced cost, research remains relentless towards formulation of more versatile products with wider scopes of application. Pertaining to water and wastewater treatment, there is a greater deal of focus on grafted copolymeric flocculants which could possibly be obtained through blending with cheaper natural products like *Moringa oleifera* with the potential of greater performance. *Moringa oleifera,* in addition to supplementing flocculation, has the added advantage of microbial pathogenic population reduction from water supplies (Sutherland et

al., 1994). The development of new commercial industrial products from natural materials is therefore a target for progressive research in both large and medium size research institutions. Relevant studies carried out in this area of research include the ceric ion induced graft copolymerization of polyacrylamide onto Sodium Alginate and investigation of flocculation properties of the product (Tripathy and Singh, 2001; Okieimen, 2004). The study did not however evaluate the heavy metal remediation properties of the grafted product if applicable. Osemeahon (2003) and Osemeahon et al. (2008) used grafted membranes of polyacrylamide – grafted konkoli gum to absorb some metal ions like Cd^{2+}, Fe^{2+}, and Zn^{2+} ions from aqueous solutions but did not investigate the removal of heavy metal ions of higher charge densities and hence higher oxidizing power like Fe^{3+} *inter alia.* The study, similarly did not report the effects of grafted and blended membranes on wastewater remediation. This research was thus undertaken to clear the air on some of these enunciated predicaments and then proceeded to synthesize grafted and blended products of polyacrylamide-grafted gum arabic and *Moringa oleifera* and further proceeded to evaluate their effectiveness in heavy metal remediation from polluted water systems.

MATERIALS AND METHODS
Materials

Gum arabic (GA) was purchased in powdered form from processing factories in Kano city - Nigeria. *Moringa oleifera* (MO) seed pods were purchased from farmers in Yola-Nigeria. Ceric ammonium nitrate (CAN), acrylamide (AM), acetone, hydroquinone, ethanol, acetic acid, ferric nitrate nonahydrate and methanol were purchased from BDH laboratories and used as supplied without further purification. In addition to these, laboratory apparatus were made use of, including instruments, glass wares distilled water and detergents.

Preparation of gum arabic and *Moringa oleifera*

Gum arabic (grade one *Acacia senegal*) dried exudates were purchased in powdered form from processing factories in Kano-Nigeria and stored at room temperature (30 ^{o}C) for subsequent use in graft copolymer synthesis. Meanwhile matured pods of *Moringa oleifera* (MO) seed pods were collected from neighborhood farms and gardens in Yola-Nigeria where the plant grows in relative abundance. The seed kernels were treated following the procedure outlined by Schwarz (2000) and Abdulkarim et al. (2004). The seeds were removed from dry pods and about 200 g of undamaged seeds were sorted out. The seeds were then shelled (to ease crushing) and powdered using a mortar and pestle. The resulting powder was sieved using a 500 µm mesh to screen out coarse particles and the fine powder was packaged in a polyethene bag and kept under dry cool conditions pending usage.

Synthesis of grafted products and blending with *Moringa oleifera*

The polymeric product (GA-g-PAAM) earmarked was synthesized by the ceric – induced solution polymerization method (Tripathy and Singh, 2001; Osemeahon et al., 2008) and purified by solvent extraction. The blending reactions were conducted in conformity with the procedure of Tripathy and Singh (2001). The products were all characterized by IR spectroscopy.

The potential of natural, grafted and blended products to remove heavy metals from aqueous solutions

The abilities of the natural flocculant (MO), grafted product (GA-g-PAM) and reactive blends to remove heavy metals from aqueous solutions were investigated. The sorbents investigated were MO, GA-g-PAAM, and reactive blends of MO and GA-g-PAAM (1:1 and 3:1). This was done using simulated aqueous solutions of metal ions and focus was on aqueous solutions of Fe^{3+} from ferric nitrate nonahydrate [Fe $(NO_3)_3.9H_2O$].

Preparation and analysis of Fe^{3+} ions

The determination of the sorption capacity of the earmarked sorbents was similar to the procedure earlier followed by Otuonye (2008). This determination was then preceded by the preparation of a calibration curve using ferric nitrate salt. 1000 ppm of Fe (III) stock solution was prepared by dissolving 7.21 g of ferric nitrate nonahydrate – $Fe(NO_3)_3.9H_2O$ in distilled water and making up the volume to 1litre in a 1000 ml volumetric flask and from this working standards of 10 ppm to 100 ppm Fe solutions were prepared by serial dilution as described by Christian (2007). From here, the principles of atomic absorption spectroscopy (AAS) as outlined by Ogubuaja (2000), were employed to determine the concentrations of residual metal ions in solution. The absorbance of each solution was measured using an atomic absorption spectrophotometer (UNICAM 969) with computer interface at 800 nm from a calibration curve was constructed. The atomic absorption spectrophotometer plotted the calibration curve and extrapolated the concentrations of the residual Fe^{3+} ions in the various filtrates treated with sorbents at different times. For each sample, the spectrometer took three cycles of readings and gave the corrected value in each case as well as the standard deviation. The corrected values were used as the data collected from the measurements.

A similar stock solution of iron (III) ions (1000 ppm) was prepared from this stock solution and working standard solutions were similarly prepared by serial dilution to obtain 50 ppm in 50 ml each. To every 50 ml of 50 ppm iron (III) solution, 0.1 g of sorbent was added, agitated for five minutes, filtered and then the concentration of residual Fe^{3+} ion in the filtrate was determined using AAS. This procedure was repeated for each sorbent at determined time intervals. This involves treating 50 ml of 50 ppm iron (III) solution with 0.1 g of sorbent and agitating for 5 minutes, 10, 20, 30, 40, 60, 90 and 120 minutes, each time filtering and measuring the concentration of residual metal ions in the filtrate. Filtration was accomplished with the aid of a whatman filter paper. The entire procedure above for the adsorption of metal ions was applied to the rest of the sorbents.

Adsorption capacity of sorbents

The adsorption capacity of each sorbent was investigated to classify the substances in order of their ability to extract heavy metals from aqueous solutions. 50 ppm Fe (III) solution was prepared from the stock solution. 50 ml aliquots of this solution were transferred into 5 different conical flasks and 0.1 g of sorbent was added to each and stirred and agitated thoroughly at room temperature (30 °C) for 10, 20, 30, 40, 60, 90, and 120 minutes. After each agitation time, the sample was filtered and the concentration of the metal ions in the filtrate was determined by AAS. The adsorption capacity of each adsorbent which refers to the amount of metal removed from aqueous solution was calculated using a formula earlier used by Otounye (2008).

$$\text{Adsorption capacity (q)} = \left(\frac{C_0 - C_e}{m}\right)v$$

where V is the volume of the solution in litres, m is the mass of the sorbent (g), C_o is the initial metal ion concentration; C_e is the residual concentration of the metal ions in the filtrate. The amount of metal removed in terms of mg/g and the percent removal were calculated. The percentage of metal removal is defined mathematically as follows;

$$\%\,\text{removal} = \left(\frac{C_0 - C_e}{C_0}\right)\times 100 \; ; \text{ where } C_o \text{ is}$$

the initial concentration of the metal ions, C_e is the residual concentration of the metal ions in the solution (filtrate). A plot of adsorption capacity (q) in mg/g versus adsorption time in minutes was done to observe the adsorption profile of each sorbent.

RESULTS

Graphical representations of the sorption profiles are given in Figure 1, while the sorption data for all the products investigated are presented in Tables 1 to 4. All the four products experimented had laudable

sorption capacities. The adsorption capacity of a sorbent was directly proportional to its percentage removal of metal ions from solution. The best sorbent amongst the products investigated was the 3:1 reactive blend whose percentage removal of metal ions ranged from 86.93% - 99.86%. The next was the 1:1 reactive blend, whose percentage removal spanned from 85.65% - 90.62%. Then followed *Moringa oleifera* whose percentage removal of iron ions ranged from 75.46% to 80.99%. GA-g-PAAM ranked lowest in the list with removal percentages of metal ions ranging from 15.12% to 84.95%. Details are shown in Tables 1 to 4.
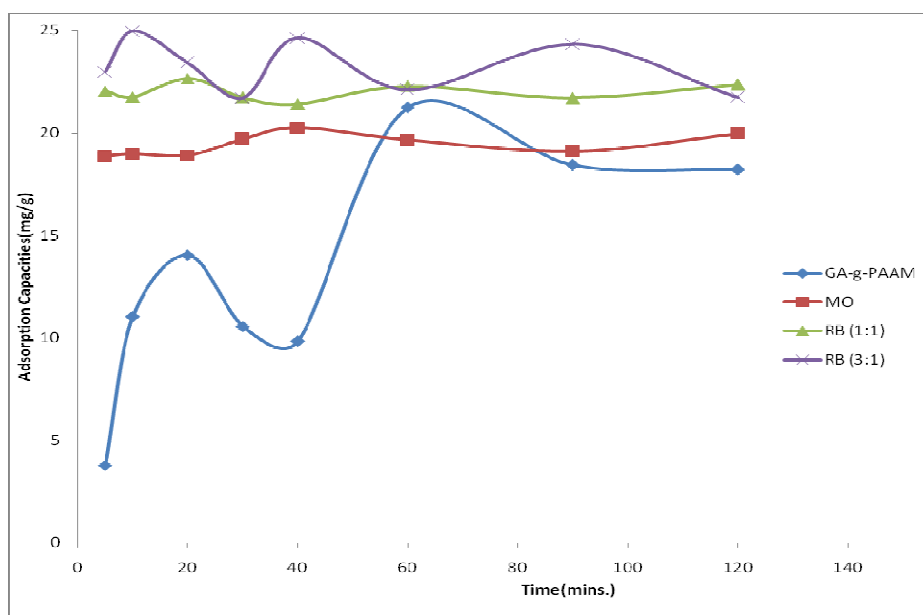

Figure 1: Adsorption profiles for MO, GA-g-PAAM, RB (1:1) and RB (3:1).

Table 1: Adsorption data for *Moringa oleifera.*

Vol. of analyte taken /ml	Amt. of sorbent added/g	Agitat. time /min	Initial conc.(C_o) of analyte /ppm	Residual conc.(C_e) of analyte / ppm	Adsorbed conc. ($C_o – C_e$)/ Ppm	Adsorp. capacity (q) in mg/g	Percent removal of metal ions (%)
50	0.1	5	50	12.2707	37.7293	18.86	75.46
50	0.1	10	50	12.0305	37.9695	18.98	75.93
50	0.1	20	50	12.2100	37.7900	18.90	75.58
50	0.1	30	50	10.6068	39.3932	19.70	78.79
50	0.1	40	50	09.5051	40.4959	20.25	80.99
50	0.1	60	50	10.7162	39.2838	19.64	78.57
50	0.1	90	50	10.7907	38.2093	19.10	76.42
50	0.1	120	50	10.0879	39.9121	19.96	79.82

Table 2: Adsorption Data for GA-g-PAAM.

Vol. of analyte taken /ml	Amt. of sorbent added/g	Agitat. time /min	Initial conc.(C_o) of analyte /ppm	Residual conc.(C_e) of analyte / ppm	Adsorbed conc. ($C_o - C_e$)/ Ppm	Adsorp. capacity (q) in mg/g	Percent removal of metal ions (%)
50	0.1	5	50	42.4385	7.5615	3.78	15.12
50	0.1	10	50	27.9159	22.0841	11.04	44.17
50	0.1	20	50	20.9950	29.005	14.03	58
50	0.1	30	50	28.8841	21.1216	10.56	42.23
50	0.1	40	50	31.8313	18.1687	9.84	36.34
50	0.1	60	50	7.5220	42.4780	21.24	84.95
50	0.1	90	50	13.1151	36.8849	18.44	73.77
50	0.1	120	50	13.5651	36.4349	18.22	72.87

Table 3: Adsorption data for M.O and GA-g-PAAM, 1:1 reactive blend.

Vol. of Analyte taken /ml	Amt. of Sorbent added/g	Agitat. Time /min	Initial Conc.(C_o) of analyte /ppm	Residual Conc.(C_e) of analyte / ppm	Adsorbed Conc. ($C_o - C_e$)/ Ppm	Adsorp. Capacity (q) in mg/g	Percent Removal of metal ions (%)
50	0.1	5	50	5.8918	44.1o82	22.05	88.22
50	0.1	10	50	6.5234	43.4766	21.74	86.95
50	0.1	20	50	4.6911	45.3089	22.65	90.62
50	0.1	30	50	6.5337	43.4663	21.73	86.93
50	0.1	40	50	7.1769	42.8231	21.41	85.65
50	0.1	60	50	5.4352	44.5648	22.28	89.13
50	0.1	90	50	6.5924	43.4076	21.70	86.82
50	0.1	120	50	5.2663	44.7337	22.37	89.47

Table 4: Adsorption data for M.O and GA-g-PAAM 3:1 reactive blend.

Vol. of analyte taken /ml	Amt. of sorbent added/g	Agitat. time /min	Initial conc.(C_o) of analyte /ppm	Residual conc.(C_e) of analyte / ppm	Adsorbed conc. ($C_o - C_e$)/ Ppm	Adsorp. capacity (q) in mg/g	Percent removal of metal ions (%)
50	0.1	5	50	4.0414	45.9586	22.98	91.92
50	0.1	10	50	0.0725	49.9275	24.96	99.86
50	0.1	20	50	3.1873	46.8127	23.41	93.63
50	0.1	30	50	6.5875	43.4125	21.71	86.82
50	0.1	40	50	0.7456	49.2544	24.63	98.51
50	0.1	60	50	5.8018	44.1982	22.10	88.40
50	0.1	90	50	1.3381	48.6615	24.33	97.32
50	0.1	120	50	6.5368	43.4632	21.73	86.93

DISCUSSION

Heavy metals are metallic elements with high atomic weights most of which are generally toxic in low concentrations and exhibit biological accumulation. Examples of heavy metals include mercury, chromium, iron, cadmium, lead, and Arsenic (Lacy et al., 1997). The potential of the synthesized products to adsorb heavy metals such as iron from aqueous solutions was investigated. Four products were experimented for sorption capabilities and included GA-g-PAAM, *M. oleifera,* M.O and GA-g-PAAM (1:1) reactive blend and M.O and GA-g-PAAM (3:1) reactive blend. The residual concentrations of Fe in the filtrates were determined by AAS and hence the adsorbed concentration in ppm for each sorbent and at each reaction time was calculated as well as their respective adsorption capacities in mg/g. Also from the initial and residual concentrations, the percentage removal of heavy metal ions by each sorbent was calculated, which is likewise an indication of the efficacy of each product as a sorbent. The remediation of heavy metals may be thought of as taking place through processes like complexation, methylation and changes in valence state (Alang, 2009). This research is in line with contemporary works on pollution control and attenuation through the use of polymeric materials that have a high affinity for heavy metals in aqueous media (Osemeahon, 2003; Osemeahon et al., 2008a, 2008b).

Most industrial process formulations usually give priority to economic and environmentally friendly procedures (Osemeahon et al., 2009) and where the leaching of contaminants from manufacturing plants is inevitable, corrective measures to right the wrongs are taken such as treating wastewaters and industrial effluents with products of the type proffered by this research.

Heavy metals have health implications on both fauna and flora which may be contracted through water or smoke (Yebpella et al., 2011). Some plant species like the tobacco plant amongst others have been found to contain toxic metals most probably absorbed from the soil, fertilizing products or from pesticides (Yebpella et al., 2011). Some of the plants exposed to heavy metal contaminants are medicinal plants used for various disease therapies (Falodun et al., 2009). The solution to the enunciated predicaments above lies in the results of this research.

Finally, industries that operate on the principle of "zero liquid effluent" (Ahmad et al., 2007) in areas of acute water shortage will find this research results very palatable since the recovery and reuse of water has the propensity of increasing the concentration of organic and inorganic contaminants including heavy metals and bacteria load (Ahmad et al., 2007), if the recycled water is not appropriately treated and will go a long way to attenuate the quality of products and cause damage to equipment.

However, an expected equilibrium contact time for maximum absorption of heavy metals by sorbents as reported by Otuonye (2008) was not observed in this research, probably due to non-optimization of sorption conditions. Consequently, further research may be recommended so as to tract optimum adsorption conditions of heavy metals by the investigated sorbents.

Conclusion

The results from this segment of research unravel the affinity to heavy metals and consequent withdrawal from aqueous systems by the grafted and blended polymeric products as well as that of *Moringa oleifera.* These substances can thus be employed as bona fide agents for environmental sanitization most especially industrial effluents. Further investigation may be required to sort out optimum conditions for the sorption of heavy metals by the grafted and blended products.

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