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Green Synthesis of *Moringa oleifera* Seeds Grafted Acrylamide and its Flocculation Performance in Low Turbid Surface Water

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ABSTRACT

A green, highly efficient flocculant based on Moringa oleifera grafted acrylamide was prepared via microwave assisted synthesis. The grafted sample was characterized using Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM) and X-ray diffraction (XRD) techniques. The flocculation performance of the grafted sample was evaluated. The residual turbidity of the surface water decreased from original 34.5 NTU to 3.3 NTU with removal efficiency of 97%. The pH of the water did not change after the treatment processes. Therefore, grafted Moringa oleifera could be considered as alternative for replacement of alum in surface water treatment.

1. INTRODUCTION

Water is an extremely important resource for the existence of life. Several human activities, such as mining, agriculture, discharge of sewage and industrial effluent without proper treatment, and dumping solid wastes in inappropriate places, etc., are leading to the contamination of most of the Earth's water resources (Chaudhuri and Sarah, 2009). Many impurities in water and wastewater are present as colloidal particles that take longer time to settle by ordinary sedimentation. Coagulation and flocculation are essential processes in water and wastewater treatment (Dalen et al., 2010).

Conventionally, there are two main chemicals used to aid coagulation, these are aluminium sulphate ($Al_2(SO4)_3$) and ferric sulphate ($Fe_2(SO_4)_3$) which are popularly known as alum and ferric respectively. Despite the good performance of these inorganic coagulants, they require pH and alkalinity adjustments, and also generate high volumes of sludge (Liew et al., 2006).

Many plant extracts have been reported to have shown the coagulation effects which include; *Moringa oleifera, Jatropha curcas, Guar gum, Strychnos potatorum, Hibiscus sabdariffa and Clidemia angustifolia* (Bhatia et al., 2007).

The potential of *Moringa oleifera* (MO) seeds as primary coagulant/flocculants in sludge and surface water treatment has been reported by several researchers (Muyibi and Okuofu 1995; Ndabigengesere et al., 1995; Ndabigengesere et al., 1998; Bhuptawat et al., 2007). It has been established that the active component of MO seeds responsible for coagulation effect is a soluble protein that acts as a natural cationic polyelectrolyte which causes coagulation in turbid water (Ndabigengesere et al., 1995). MO is a plant tree that belongs to the Moringaceae family, which grows well in tropical regions and in most parts of Africa and Asia (Pritchard et al., 2010).

To enhance the performances of coagulant properties of plant extracts, certain synthetic polymers such as polyacrylamide (PAM), polyacrylic acid and polystyrene sulfonic acid have been incorporated (Nayak and Singh, 2001). Polysaccharide-based graft copolymers have shown better flocculation performance in the treatment of wastewaters than polysaccharide alone in many studies reported (Singh et al., 2000). The most attractive technique in graft copolymer synthesis involves the use of microwave radiations to initiate the grafting reactions. The merit of this technique over other conventional technique has been well discussed in earlier studies (Mishra, et al., 2012; Pal et al., 2012, Rani et al., 2012 and Salisu and Sale, 2018).

The present study is aimed at synthesizing MO seeds grafted acrylamide using microwave radiation and determining its flocculation performance in low turbid surface water.

2. MATERIALS AND METHODS

2.1. Materials/Equipment

Acrylamide and potassium persulphate were purchased from Loba Chemie (England). n-hexane and acetone were purchased from Zayo-Sigma, Nigeria. Aluminum sulphate (alum) was kindly donated by the Head Chemistry Laboratory, Ajiwa water treatment plant. Other chemical reagents were of analytical grade and used as received. Raw water sample was collected in a cleaned 5L plastic Gallon from Ajiwa dam (Ajiwa water works) Katsina State, Nigeria. pH measurements were carried out by using Philips PW 8418 pH meter. Flocculation tests were carried out using a Stuart Scientific SW1 (England) 4 paddle jar test apparatus. Turbidity was measured with a Hach 2100N turbidity meter. Conductivity was measured with a NAAFCO, YF87001 conductivity meter.

2.1.1. Samples collection and pretreatment

The seed of Moringa was collected from Wagini villages in a Batsari local Government Area, Katsina State, Nigeria and was identified by a Botanist in the Department of Biology, Umaru Musa Yar'adua University, Katsina. The seeds were air-dried for two days. The shells surrounding the seed kernels were removed using a knife and the kernel was ground to a powder using laboratory mortar and pestle and sieved using a strainer with a pore size of 2.5 mm to obtain a fine powder. The powdered (50 g) was subjected Soxhlet extraction using petroleum ether to remove the oil.

2.2. Graft Copolymerization of Acrylamide onto *Moringa oleifera* Seeds

In this reaction, the procedure reported by Mishra et al. (2011) was adopted with little modifications. Moringa seeds powder (1 g) was dissolved in 10 mL distilled water in a 200 mL Bomex beaker and 0.2 g of potassium persulfate (KPS) were added and mixed well. The reaction vessel was placed at the center of a rotating ceramic plate in the domestic microwave oven (Model WMO20L-MGSB, Skyrun, Nigeria). The reaction vessel was then exposed to microwave radiation at 900 W power for two minutes. After every 30 seconds, the microwave irradiation was paused and the reaction mixture cooled by placing the reaction vessel in cold water. The polymer was precipitated by adding cold methanol. The grafted sample thus obtained was dried in hot air oven at 50 °C. The product was washed with acetone solvent to remove acrylamide homopolymer using Soxhlet extractor. The percentage grafting was determined using Equation (1).

$$(\%)\ \text{Grafting} = \frac{W_2 - W_1}{W_1} \times 100 \quad (1)$$

Where W_1 is the initial weight of the fiber sample, W_2 is the weight of the grafted sample after extraction of unreacted polymer (Salisu and Sale, 2018). The reaction scheme is shown in Figure 1.

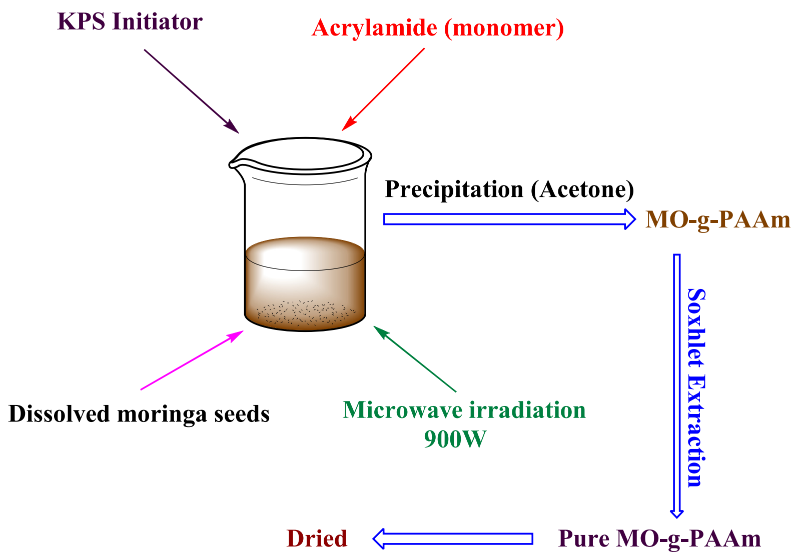

Figure 1: Scheme of graft copolymer synthesis

2.3. Characterization Techniques

Fourier Transform Infrared analysis was conducted using FTIR VERTEX 70/70v spectrophotometer (Agilent Technologies, USA). The scanning electron microscope (SEM) micrographs of the fiber and its surface morphology were examined using PHENOM PRO X (Netherland). Powder X-ray diffraction patterns were recorded on ARL X'TRA X-ray Diffractometer (Thermoscientific, Switzerland) using graphite monochromatic CuKα1 (1.5406Å) and Kα2 operated at 40 kV and 30 mA.

2.4. Coagulation Experiment

The procedure reported by Muyibi and Okuofu (1995) was adopted, where 500 ml of water sample (with physicochemical properties shown in Table 1) was poured into a 1 L beaker and placed under the jar test apparatus. The specified amount of the unmodified Moringa seeds and the grafted MO were added separately into the beakers contained the raw water. The solutions were stirred at 100 rpm for 5 minutes, followed by 20 minutes settling time. Afterwards, the supernatant liquid was collected and turbidity measured in a calibrated nephelo-turbidity meter (Digital Nephelo-Turbidity Meter).

Table 1: Physico-chemical properties of the surface water

Physical parameters	Values
Conductivity (µs)	24.90
Turbidity (NTU)	34.5
pH	7.82

3. RESULTS AND DISCUSSION

3.1. Synthesis of Acrylamide Graft MO Seeds by Microwave Radiation

Various samples of the graft copolymer were synthesized by varying the potassium persulphate (KPS) concentration, in each case, and keeping the acrylamide concentration constant (S/N 1, 2, 3 and 4). Thereafter, optimization with respect to acrylamide concentration, keeping KPS concentration constant (S/N 5, 6, 7 and 8) was done. From Table 2, it was observed that the grafting is optimized at an acrylamide concentration of 5 g and KPS concentration of 0.3 g with the highest percentage grafting of 56% by keeping irradiation time constant.

Table 2: Optimization of monomer and initiator concentrations

S/N	Wt of MO (g)	Wt of AM (g)	Wt of KPS (g)	Time (s)	% grafting
1	1.0	5	0.1	120	26
2	1.0	5	0.2	120	32
3	1.0	5	0.3	120	56
4	1.0	5	0.4	120	47
5	1.0	2.5	0.4	120	11
6	1.0	7.5	0.4	120	28
7	1.0	5	0.5	120	19

3.2. Characterization

3.2.1. Fourier transforms infrared spectroscopy

Previous study revealed that a Moringa oleifera seed has four (4) principal elements, namely carbon (C), oxygen (O), hydrogen (H) and nitrogen (N). The principle groups of the above constituent are proteins, carbohydrates, lipids, lignin and free amino acids (Ndabigengesere et al., 1995). From this study, an FTIR spectrum of Moringa seeds before modification is shown in Figure 2. The absorption peaks at 3279 cm^{-1} and 2921 cm^{-1} were assigned to O-H and C-H stretching vibrations in carbohydrate group. The absorption peaks at 1748 cm^{-1} and 1652 cm^{-1} could be due to carbonyl carbon (C=O) stretching in esters/lipids and proteins, respectively. While, in the FTIR spectrum of grafted MO seeds is shown in Figure 3, two new absorption peaks appeared at 3197 cm^{-1} and 1659 cm^{-1} which were attributed to N-H (primary amide) and C=O group in acrylamide respectively, which confirmed the formation of the graft copolymer.

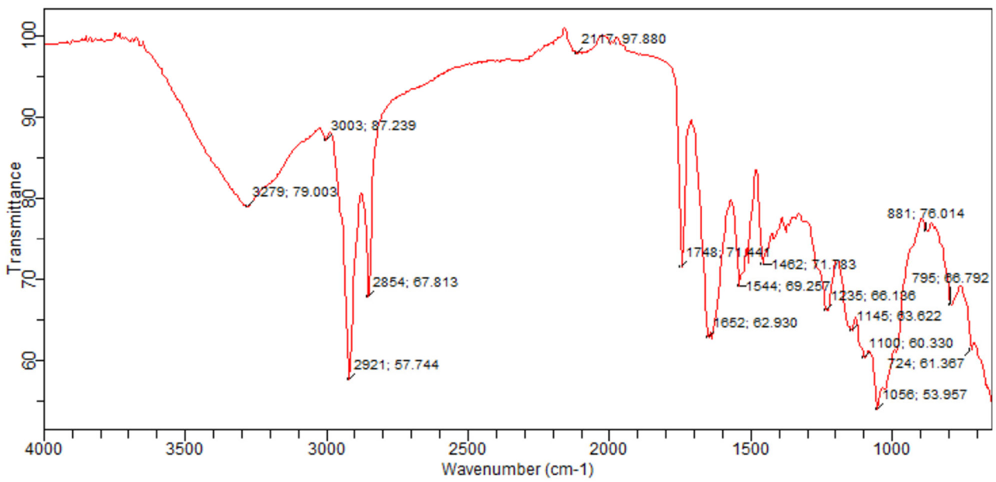

Figure 2: FTIR spectrum of MO seed

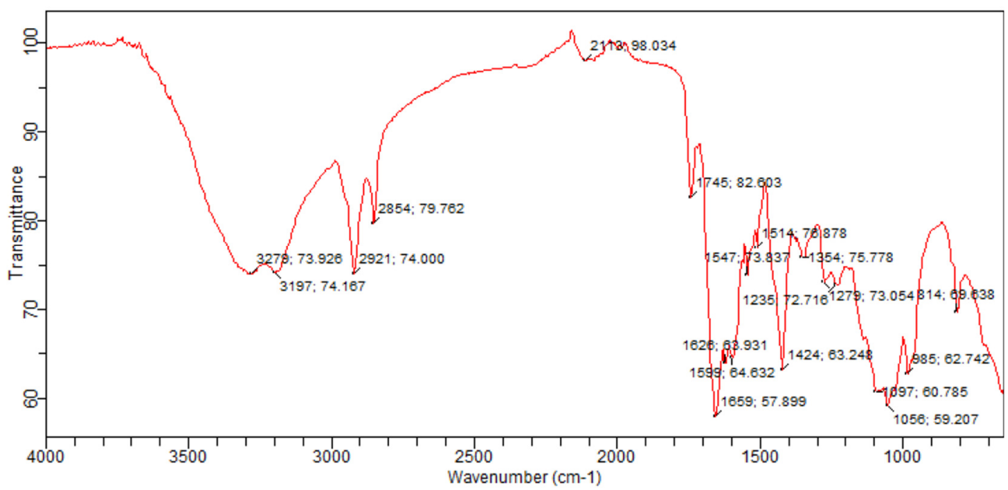

Figure 3: FTIR Spectrum of modified MO (MO-g-PAM)

3.2.2 X-Ray Diffraction (XRD) study

The XRD pattern of MO seed before and after grafting is shown in Figure 4. As can be seen from the pattern, MO seeds indicate significant amount of crystalline phase. However, after grafting, the crystalline phase decreased greatly due to change of the structure to amorphous nature of polyacrylamide chains. Similar observations were reported by Sen and Pal (2009).

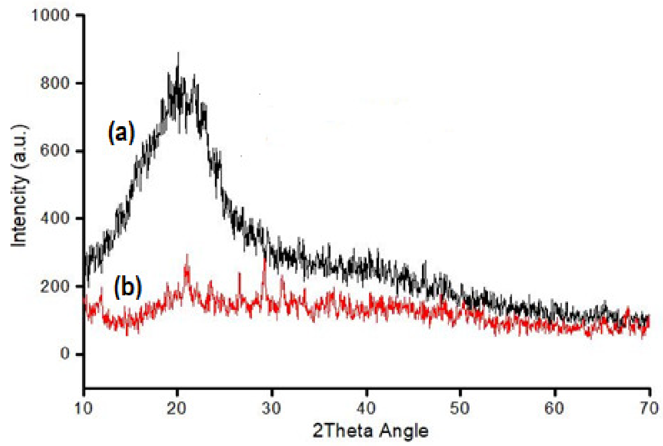

Figure 4: X-ray diffractogram of (a) MO seeds and (b) Grafted MO seeds

3.2.3. Scanning electron microscopy (SEM)

The SEM image in Figure 5a showed the surface morphology of MO seeds before the modification. It is clear that the surface was smooth with some micro fibrils on the surface. However, the surface structure of the grafted MO revealed polyacrylamide polymer deposited and some pores appeared as can be seen in Figure 5b. This has also confirmed the formation of the graft copolymer on the surface MO seeds.

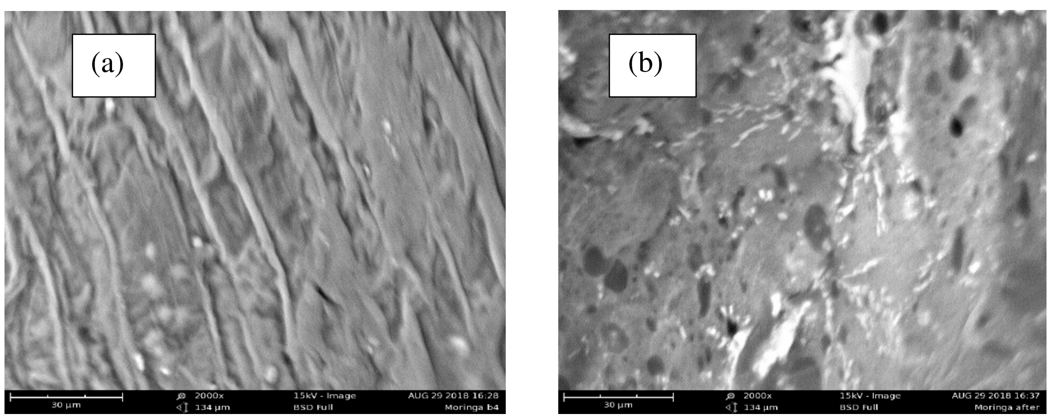

Figure 5: SEM images of (a) MO seeds and (b) Grafted MO seeds

3.3. Flocculation Study

In order to assess the applicability of grafted sample, flocculation efficiency was evaluated using low turbidity dam water with initial turbidity of 34.5 NTU as shown in Table 1. However, Table 3 shows flocculation performance of MO seed before modification at different dosages. It was observed the maximum turbidity removal was obtained at 0.5 g of MO seed with residual turbidity of 6.5 NTU. However, at higher MO dosage turbidity removal decreased. This observation could be attributed to stabilization of the suspended particle which became over saturated. Similar result was reported by (Muyibi and Okuofu, 1995).

Flocculation performance of the grafted MO is shown in Table 4. It was observed the efficiency of MO was improved after grafting of acrylamide for all dosages tested. The initial turbidity of 34.5 was reduced to 3.3 at 0.5 g dosage. For comparison, the flocculation performance of standard coagulant (alum) was also assessed. The grafted MO was comparable to standard alum in term of flocculation efficiency. However, both MO and grafted MO did not affect significantly the pH value of the initial raw water, which remained almost constant at 7.2 for all dosages tested. In contrast, the pH value decreased from 7.82 to 4.2 for alum, which required further pH correction.

Generally, flocculation efficiency is affected by settling time. Thus, time dependence of residual turbidity of grafted MO was also determined and the results are shown in Figure 6. It was observed that flocculation performance increased as settling time was increased up to the optimum time of 20 minutes. It has been established that the two major mechanisms of flocculation exhibited by polymers were charge neutralization and bridging model (Nayak and Singh, 2001).

Table 3: Flocculation performance of MO seeds

S/N	MO dose, (g)	Residual turbidity, (NTU)	pH
1.	0.5	6.5	6.75
2.	1.0	10.7	6.64
3.	1.5	16.3	6.69
4.	2.0	9.4	6.52
5.	2.5	17.6	6.55
6.	3.0	19.8	6.49

Table 4: Flocculation performance of grafted MO seeds

S/N	Grafted MO (g)	Residual Turbidity, (NTU)	pH
1.	0.5	3.3	7.25
2.	1.0	4.1	7.14
3.	1.5	8.3	7.19
4.	2.0	8.6	7.02
5.	2.5	13.1	7.05
6.	3.0	13.8	6.99
Alum	0.5	2.2	4.2

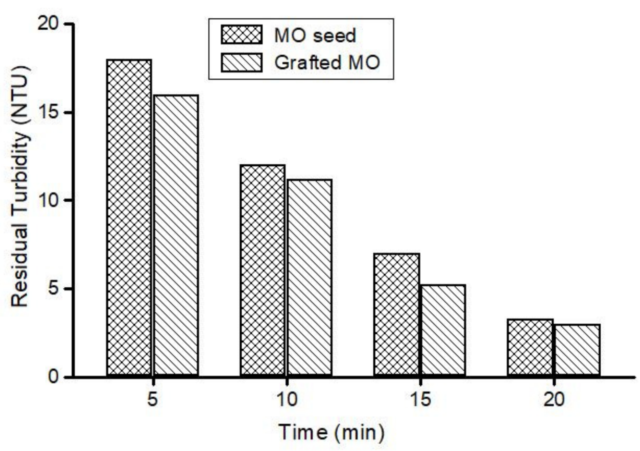

Figure 6: Effects of settling time of grafted MO seeds (0.5 g) at initial turbidity of 34.5 NTU

4. CONCLUSION

Moringa oleifera grafted acrylamide (MO-g-PAM) has been synthesized by microwave assisted technique, which involved a synergism of microwave radiation and potassium persulfate (chemical free radical initiator) to initiate the free radical grafting reaction. The synthesized graft copolymer was characterized by FTIR, SEM and X-ray diffraction techniques. The flocculation efficacy of the graft copolymer was appreciable in low turbid surface water, at an optimized dosage of 0.5 g and settling time of 20 minutes. It is suggested that the modified *Moringa oleifera* seeds could be used in surface water and wastewater treatment as an alternative to conventional alum.

5. ACKNOWLEDGEMENT

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6. CONFLICT OF INTEREST

There is no conflict of interest associated with this work.

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