Application of Moringa Oleifera Seed Cake as a Natural Coagulant for the Removal of Oil from Model Oil-Water Emulsions

E. Lester-Card[1], G Smith[2], J. Widdowson[1], C. Tizaoui[1]
[1]: College of Engineering, Swansea University, Swansea, Wales, SA1 8EN, United Kingdom
[2]: Tata Steel, Port Talbot, SA13 2NG
Keywords: Moringa Oleifera, Natural Coagulant, Oil-Water Emulsions.
Presenting author email: 706749@swansea.ac.uk; Correspondence to: c.tizaoui@swansea.ac.uk

Introduction Traditional wastewater treatment chemicals used to coagulate and flocculate oily wastewater include metal salts such as aluminum sulphate and synthetic polymers. However, these have drawbacks such as hazardous non-biodegradable voluminous sludge, sensitive pH and dosage conditions (Bratby 2006). Additionally, aluminum has been linked with Alzheimer's disease (Rondeau 2008). Consequently, there is a demand for natural coagulants which are non-toxic, biodegradable, and safe to handle. One such natural coagulants can be extracted from the seeds of the plant *Moringa Oleifera* (MO). The main financial value of the MO seeds is the oil they contain (30-40% by weight). Once the oil is removed from the seeds the remaining residue is known as moringa seed cake and is rich in coagulating proteins. The waste seed cake currently has little industrial use and is often regarded as a waste material and on occasions is used as a fertilizer or green manure (Gopalakrishnan 2016). Consequently, alternative uses for the seed cake, such as a natural coagulant, are a novel and keen research interest. The aim of this study is to investigate the effectiveness of extracted coagulant from de-fatted moringa seed cake following a basic extraction procedure and compare to alum and a synthetic polymer coagulant for the treatment of oily wastewater (Bhatia 2006), (Bhatia 2007), (Bhatia 2007) and (Jagaba 2020).

Materials and Method **Coagulants** – Moringa Oleifera seeds, aluminium sulphate (alum) and a cationic synthetic polymer commonly used for oil removal. **Moringa coagulant extraction procedure** – De-shelled moringa seeds are crushed to a powder with a mortar and pestle. Natural oil/fat is removed with solvent extraction (95% ethanol, 5% de-ionised water). The mixture is centrifuged to separate the solids and ethanol-oil waste liquid leaving the protein rich seed cake. The seed cake is extracted in a salt solution (1M NaCl) and filtered to remove the insoluble solids and obtain a liquid coagulant extract (MOCE). **Moringa coagulant dosage** – As MOCE is a protein-based coagulant, it is important to determine the protein concentration in MOCE. Protein analysis was done by the Bradford assay at a dilution factor of 20; the stock protein concentration was around 8,000 mg/L. **Preparation of model oil-water emulsions** – Preparation used a synthetic motor oil, sodium dodecyl sulfate (SDS) as a surfactant and tap water. 0.025g of SDS was added to 400mL of tap water along with 0.3g of oil which was then mixed at 2000rpm for 45 minutes.

Table 1: Characterization of the model oil-water emulsion

Parameter	pH	Turbidity (NTU)	Absorbance	TOC (mg/L)	Particle Size (nm)	Zeta Potential (mV)	Surfactant (mg/L)	Oil (mg/L)
Model Emulsion	7.8	94.5	1.3	108.0	395.2	-30.9	62.6	128.5

Jar test experimental procedure – Each experiment started with 6 beakers filled with 400mL emulsion. Following coagulant addition, there was a rapid mixing stage (250rpm) for 2 minutes followed by a slower mixing stage (45rpm) for 15 minutes before the paddles were removed and the emulsion was left to settle for 15 hours. Experiments included pH variation (3-11), coagulant dosage alum (Al^{3+} 0-100mg/L), polymer (0-100mg/L), and MOCE (0-100mg/L) and settling time (0-900 minutes) with samples being taken at: 0, 15, 60, 90, 120, 390 and 900 minutes. **Parameters analysed** – pH, absorbance (254nm), turbidity, total organic carbon (TOC), zeta potential, chemical oxygen demand (COD) and oil concentration via an FTIR following a solvent extraction procedure. **Purification and characterisation of MOCE** - Fractionation of MOCE was done with Polyether Sulfone membranes of different sizes (300 and 100kDa) using dead-end filtration to investigate the effect on organic load and protein concentration in the permeates and retentate. The selected fraction was then freeze dried to obtain a solid product. SDS-PAGE (Polyacrylamide Gel Electrophoresis) was also completed on MOCE and membrane purified MOCE to obtain molecular weights of the coagulating proteins.

Results and Discussion **Effect of initial pH and coagulant dosage on turbidity, absorbance, and final pH -** It is clear from Figure 1. (a, b and c) that MOCE is not affected by initial pH unlike alum and the cationic polymer. This is a key advantage of MOCE and means that pH adjustment and control is not necessary, additionally, the final pH of the emulsion is unchanged unlike the alum coagulant which dramatically consumes alkalinity meaning that additional chemicals such as lime or soda ash are required to restore the alkalinity bringing the pH to neutral conditions. It can also be seen that MOCE is the superior coagulant in the acidic pH range (3-6). When considering coagulant dosage (Fig1. d, e and f) it is clear that MOCE does require a higher optimum dosage (50mg/L, protein equivalent) compared to alum (10mg/L, Al^{3+} equivalent) and polymer (2.5mg/L). Fig1 (d and e) also show that the polymer is very dosage sensitive since its removal efficiencies sharply drop as its concentration changes from about 1.25 mg/L.

Effect of settling time on turbidity, absorbance and oil removal - When considering the effect of settling time as shown in Figure 2 a, b and c. It is observed that MOCE is much faster than alum and the polymer achieving turbidity, absorbance and oil removals of 75%, 63% and 100% in 60 minutes.

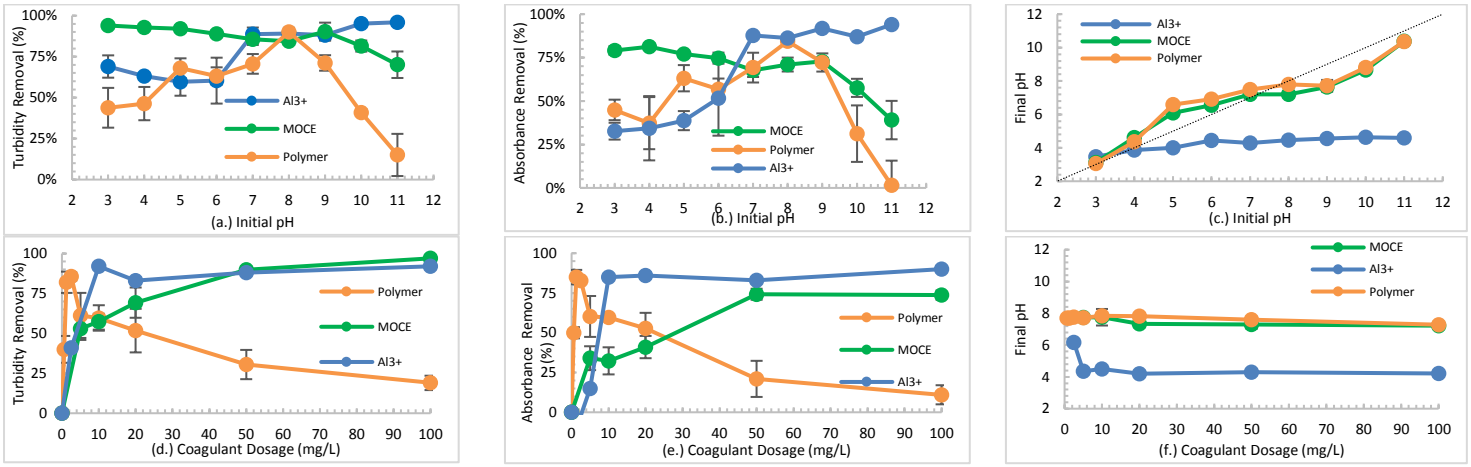

Figure 1: Initial pH vs turbidity removal (a.), absorbance removal (b.), final pH (c.). Experimental conditions, coagulant dosage Al^{3+} 10mg/L, polymer 2.5mg/L, MOCE 50mg/L and settling time of 15 hours (900 minutes). Coagulant dosage vs turbidity removal (d.), absorbance removal (e.) and final pH (f.). Experimental conditions, neutral pH (7.8) and settling time of 15 hours (900 minutes)

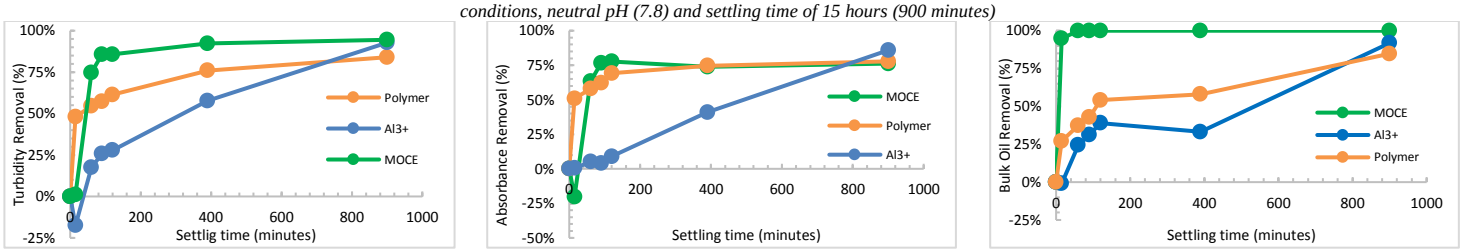

Figure 2: Settling time vs turbidity removal (a.), absorbance removal (b.) and oil removal (c.). Experimental conditions coagulant dosage Al^{3+} 10mg/L, polymer 2.5mg/L, MOCE 50mg/L and initial pH of 7.8

Purification of MOCE using membrane filtration and characterisation with SDS-PAGE - One of the limitation to natural coagulants such as MOCE is that it can increase the organic load on the target wastewater therefore purification is desirable and has been completed by other researchers using ion exchange Sanchez-Martin (2010). Membrane filtration is a more practical and applicable for large scale processing and is selected as an alternative for the purification studies.

Figure 3: De-fatted moringa seed cake

Figure 4: Moringa extracted coagulant (MOCE)

Figure 5: Purified and freeze dried moringa proteins

Table 2: Molecular weights of MOCE and freeze dried protein

MOCE	Freeze dried protein
74.45	-
51.55	-
39.12	-
28.36	28.74
27.09	25.83
18.75	16.84
13.59	13.59

SDS-PAGE results (Table. 2) show that the proteins in MOCE vary in molecular mass from 74.5 to 13.5kDa and that after membrane purification the range is reduced to 14.5-28.75kDa. Jar test results have also shown that the freeze dried protein is comparable to MOCE in removal efficiencies and more effective at removing organics as indicated by the absorbance, TOC and COD removal data.

Conclusion - Overall, this study has shown that MOCE is an effective coagulant-flocculent for stabilised oil-water emulsions. This natural coagulant showed high removal efficiencies regardless of pH conditions and does not require pH adjustment that would be needed in alum and polymer dosing. MOCE also breaks the emulsion much more rapidly than alum or the polymer as shown by the settling time experiments. Purification of MOCE is possible and produces a solid protein material (13-28.75kDa) which has comparable coagulation capability to the unpurified MOCE.

Acknowledgements – The authors would like to thank the materials and manufacturing academy (M2A) for their financial support which has been provided from the European Social Fund via the Welsh Government, the Engineering and Physical Sciences Research Council (EPSRC), and Tata Steel.

References

Bhatia, S., Othman, Z., Ahmad, A. L. (2006). Journal of Chemical Technology and Biotechnology **81**(12): 1852-1858.
Bhatia, S., Othman, Z., Ahmad, A. L. (2007). Chemical Engineering Journal **133**(1-3): 205-212.
Bhatia, S., Othman, Z., Ahmad, A. L. (2007). Journal of Hazardous Materials **145**(1-2): 120-126.
Bratby, J. (2006). Coagulation and Flocculation in Water and Wastewater Treatment. London, Seattle, IWA.
Gopalakrishnan, L., Doriya, K., Kuma, D. S. (2016). Food Science and Human Waste **5**(2): 49-56.
Jagaba, A. H., Kutty, S. R. M., Hayder, G., Latiff, A. A. A., Aziz, N. A. A., Umaru, I., Ghaleb, A. A. S., Abubakar, S., Lawal, I. M., Nasara, M. A. (2020). Ain Shams Engineering Journal **11**(4): 951-960.
Rondeau, V., Commenges, D., Jacqmin-Gadda, H., Dartigues, J-F. (2008). Am J Epidemiol **152**(1): 59-66.
Sanchez-Martin, J., Ghebremichael, K., Beltran-Heredia, J. (2010). Bioresour Technol **101**(15): 6259-6261.