OPTIMIZATION STUDIES OF TURBIDITY REMOVAL IN ASA RIVER WATER USING C*ARICA PAPAYA* SEED AS COAGULANT

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ABSTRACT
This study evaluated the potential of Carica papaya Seed (CPS) as a coagulant for water treatment. Surface water samples from Asa River in Ilorin, Kwara State, Nigeria were collected for the study. The trace metal levels were determined using Inductively Coupled Plasma-Mass Spectroscopy (ICP- MS). Treated CPS was obtained from its seed using soxhlet extraction in ethanol .It was then applied for the removal of turbidity and trace metals in the surface water samples. The trace metal results showed the presence of Cu (6.07 ppb), Fe (394.16 ppb), Cr(21.50 ppm), Zn (6.69 ppb) and Ti (13.08 ppb) in the samples of the river water. Optimization studies was carried out for turbidity removal using Full Central Composite Design (FCCD) under the Response Surface Methodology (RSM). The results obtained showed that the maximum turbidity removal of 94.92% was achieved at optimum conditions; coagulant dose (0.47 g), contact time (15.17 min) and agitation speed (791.33 rpm). Also, all the trace metals were found to be below detection limit after contacting with the modified Carica papaya seed.

Key words: water, pollution, assessment, turbidity, trace metals

Introduction

Rapid industrialization, economic growth and increased population has made access to safe water to be limited and expensive especially in developing countries (Alam *et al*., 2007). The volumes of water used as well as the waste water generated in both domestic and industrial activities have increased significantly with little or no control on their discharge into ground and surface water bodies which has led to water pollution on many occasions (Simeonov *et al.*, 2003; Schwarzenbach *et al*., 2010; Dimitrovska *et al.*, 2012). Many industries are sited close to rivers for various reasons like availability of water for use in production processes and waste disposal (Onojake *et al*., 2015). Surface water has thus been reported polluted as a result of human activities, poor structured sewerage and drainage system, and discharge of both industrial and domestic wastes (Diaz *et al*., 1999; Alam *et al.,* 2007). The extent of contamination of surface water quality depends on factors such as, chemical composition of leachates, rainfall, depth and distance of the water from the source of pollution.

Trace metals, colour and turbidity have been known to be major water pollutants from industrial activities (Verma *et al.,* 2012). Some trace metals are essential, biologically reactive and have the profile of nutrients (Fe, Zn etc), others are considered toxic at concentrations above permissible levels (Cr, Cd, Pb e.t.c) while others are inert in nature and remain nearly constant from one point to the next relative to water salinity. The distribution of trace metals could be used to gain insight to the external sources of metals and identify effective processes for removing them (Alam *et al*., 2007; Duruibe *et al*., 2007; Pekey *et al*., 2004; Sharma and Agrawal, 2005).

The industries such as pulp, paper, rubber, textile and polymer are the mainly sources of surface and underground water pollutants (Ong *et al*., 2010) which affects the colour and turbidity of water (Verma, *et al.* 2012). Discharged wastewater into surface waters such as rivers and lakes reduces the transmission of light in the water which reduces photosynthesis and the amount of dissolved oxygen in the water (Ali and Singh, 2009). The turbidity is created due to the presence of suspended solids such as clay, mud, minerals, organic and water soluble particles. It is an important property used in characterizing water quality. Water with high turbidity are naturally repulsive to man even without determining the chemical properties.In addition to creating an unpleasant appearance for water, it is a safe haven for resistance of microorganisms against disinfection (Hao *et al.,* 2000).

The removal of turbidity has been done overtime using chemical salts such as Ferric chloride, Aluminum sulphate and polyaluminum chloride. In addition, some studies that have utilized plants for the removal of turbidity in water includes *Moringa oleifera, Cicer arietinum, and Dolichos lablab* (Asrafuzzaman *et al.*, 2011); *Nirmali, Okra, red bean, sugar and red maize(*Gunaratna *et al., 2007); Cactus latifera and seed powder of Prosopis juliflora (Diaz et al., 1999), Strychnos potatorum* (Babu and Chaudhuri, 2005). seed extract from seeds of *Phaseolus vulgaris, Robinia pseudoacacia, Ceratonia siliqua and Amorpha fruticosa (*Šćiban *et al., 2005),* cactus (Zhang *et al.*,

2006) , Enteromorpha extract (Zhao *et al.*, 2012) and other plant species (Megersa *et al.*, 2014) have been used as coagulants. The physical appearance of water is one of the first quality that is being observed in determining water quality and, a turbid water is generally and naturally considered as poor even without further studies. The use of chemical coagulants has been in existence for decades however, like most other activities of man, investigations are being continuously conducted to establish the use of natural / modified natural coagulants for the removal of perceived turbidity in water.

Asa River serves as the major source of water supply to Ilorin and its environs hence the need for a continuous monitoring to avert possible health implication. Also, monitoring the quality of surface water is essential to establish the suitability or otherwise for specific functions (Wang *et al.*, 2014). The aim of this study was to determine the physicochemical properties of a water body and to optimize the removal of turbidity using modified *Carica papaya* seeds.

Materials and Method

Water sample collection and characterisation

Water samples were collected in plastic bottles from different locations based on identified activities along Asa River, Ilorin, Kwara State. Two sets of water samples were collected in triplicates, the one for coagulation was immediately taken to the laboratory for analysis while the sample for trace metal analysis was preserved using a few drops of concentrated nitric acid. The presence of trace metals was established using Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and Atomic Absorption Spectroscopy (AAS). The Inductively Coupled Plasma Mass Spectrometer (ICP-OES iCAP6500 DUO, Thermo Scientific, UK) equipped with a charge injection device (CID) was used in the determination of all metal ions present in the wastewater sample.

Preparation and characterisation of pawpaw (Carica papaya) seeds.

The seeds of riped pawpaw were collected , washed and oven dried at 105ºC to constant weight and then pulverized. The oil component of the pulverized pawpaw seed was extracted by soxhlet extraction using ethanol as solvent and the residue was separated and washed , dried ans ready for use as coagulant (Verma *et al.*, 2012). The coagulant (*Carica papaya* seeds) was characterized using Fourier Transform Infrared (FTIR) spectroscopy using Shimadzu FT-IR-8400S spectrophotometer.

Turbidity Removal Efficiency

The produced natural coagulant was evaluated using jar test apparatus which is used to access the effect of various process factors to achieve optimum turbidity removal. Turbidity of the raw water was determined using a turbidimeter. Both the natural and modified natural coagulants were applied to the water samples in 100 ml beakers using the 5-level, 3-factor Full Central Composite Design (FCCD) as presented in Table 1 while the design matrix are as presented in Table 2 . The batch experiments were carried out by adding each dosage of the coagulant (0.1 - 0.5 g) to 100 ml of the water sample and agitated using the jar test apparatus for the duration of contact time (15 - 60 min) and agitation speed (500 - 1000 rpm). The mixture was filtered and the filtrate was analyzed for turbidity removal using a turbidimeter. The experiments were repeated three times, and the average value for the measured data was used.The turbidity removal efficiency was calculated using equation 1.

$$\%\, Turbidity\ Removal = \frac{(TB_o - TB_i)}{TB_o} * 100\% \quad (1)$$

Optimisation studies

Response surface methodology was applied to the results of the FCCD using Design expert version 6.0.8, (Stat – Ease, Inc., Minneapolis, MN 55413, USA) to evaluate the optimum process parameters .

Table 1: FCCD design values at various levels

Independent variables	Units	Codes	Levels of factors				
			(-α)	-1	0	1	(α)
Coagulant Dose	(g)	X_1	0.00	0.10	0.30	0.50	0.60
Contact Time	(min)	X_2	3.75	15.00	37.50	60.00	71.25
Agitation Speed	(rpm)	X_3	375	500	750	1000	1125

Table 2: FCCD design matrix for turbidity removal

Std. order	Type	X_1	X_2	X_3	% Turbidity Removal	
					Predicted	Experimental
1	Factorial	0.10	15.00	500.00	87.27	87.50
2	Factorial	0.50	15.00	500.00	78.69	81.25
3	Factorial	0.10	60.00	500.00	91.51	93.75
4	Factorial	0.50	60.00	500.00	57.07	55.53
5	Factorial	0.10	15.00	1000.00	67.29	70.71
6	Factorial	0.50	15.00	1000.00	90.82	90.46
7	Factorial	0.10	60.00	1000.00	63.18	62.50
8	Factorial	0.50	60.00	1000.00	60.85	62.50
9	Axial	0.00	37.50	750.00	90.13	87.50
10	Axial	0.60	37.50	750.00	81.95	81.25
11	Axial	0.30	3.75	750.00	92.56	89.50
12	Axial	0.30	71.25	750.00	73.27	73.00
13	Axial	0.30	37.50	375.00	70.24	68.75
14	Axial	0.30	37.50	1125.00	58.09	56.25
15	Center	0.30	37.50	750.00	87.07	87.50
16	Center	0.30	37.50	750.00	87.07	87.70
17	Center	0.30	37.50	750.00	87.07	88.00
18	Center	0.30	37.50	750.00	87.07	87.50
19	Center	0.30	37.50	750.00	87.07	87.25
20	Center	0.30	37.50	750.00	87.07	87.00

The general empirical model developed for 2^3 factorial design in coded values is given as equation (2):

$$\%TR = A + BX_1 + CX_2 + DX_3 + EX_1X_2 + FX_1X_3 + GX_2X_3 + HX_1X_2X_3 \quad (2)$$

Where TR is the predicted response, A is the global mean, A, B, C, D, E, F, G and H represents the other regression coefficients and X_1, X_2 and X_3 are the coded symbols for the studied factors.

Results and Discussion

Characterization of raw and treated pawpaw seed

The FTIR spectra of the pulverized, raw and treated pawpaw seed are as shown in Figure 1. Each sample was prepared with potassium bromide, (KBr pellets). The infrared spectral of both samples indicated a peak atν_{max}3300 cm^{-1} which corresponds to the stretching vibration of N-H, O-H bond of an alcohol or fatty acid (lipid). An aromatic C-H stretching was observed at 3002 cm^{-1} in both samples while the C-H stretching of aliphatic alkanes were observed at 2917, 2929 and 2853 cm^{-1}. The sharp peak at 1745 cm^{-1} corresponds to carbonyl stretching of ketone, aldehyde, carboxylic acid or esters. A prominent vibration was observed at 1707 cm^{-1} corresponding to the carbonyl stretching of carboxylic acid in the untreated sample. This may be due to the presence of some free fatty acids in the untreated sample. The fatty acids which would have been removed during the extraction process apparently accounted for loss of the peak in the treated sample. The weak peak observable at 1546 cm^{-1} correspondingto C=C stretching vibration of alkene in the untreated sample was also not present in the treated. The vibration of the N-H bending of amine was depicted at 1650 cm^{-1} while the C=C bending vibration was observed at 1463 cm^{-1} in both samples. C-O bending bands of the esters and carboxylics were observed as weak peaks at 1232 and 1163 cm^{-1}.

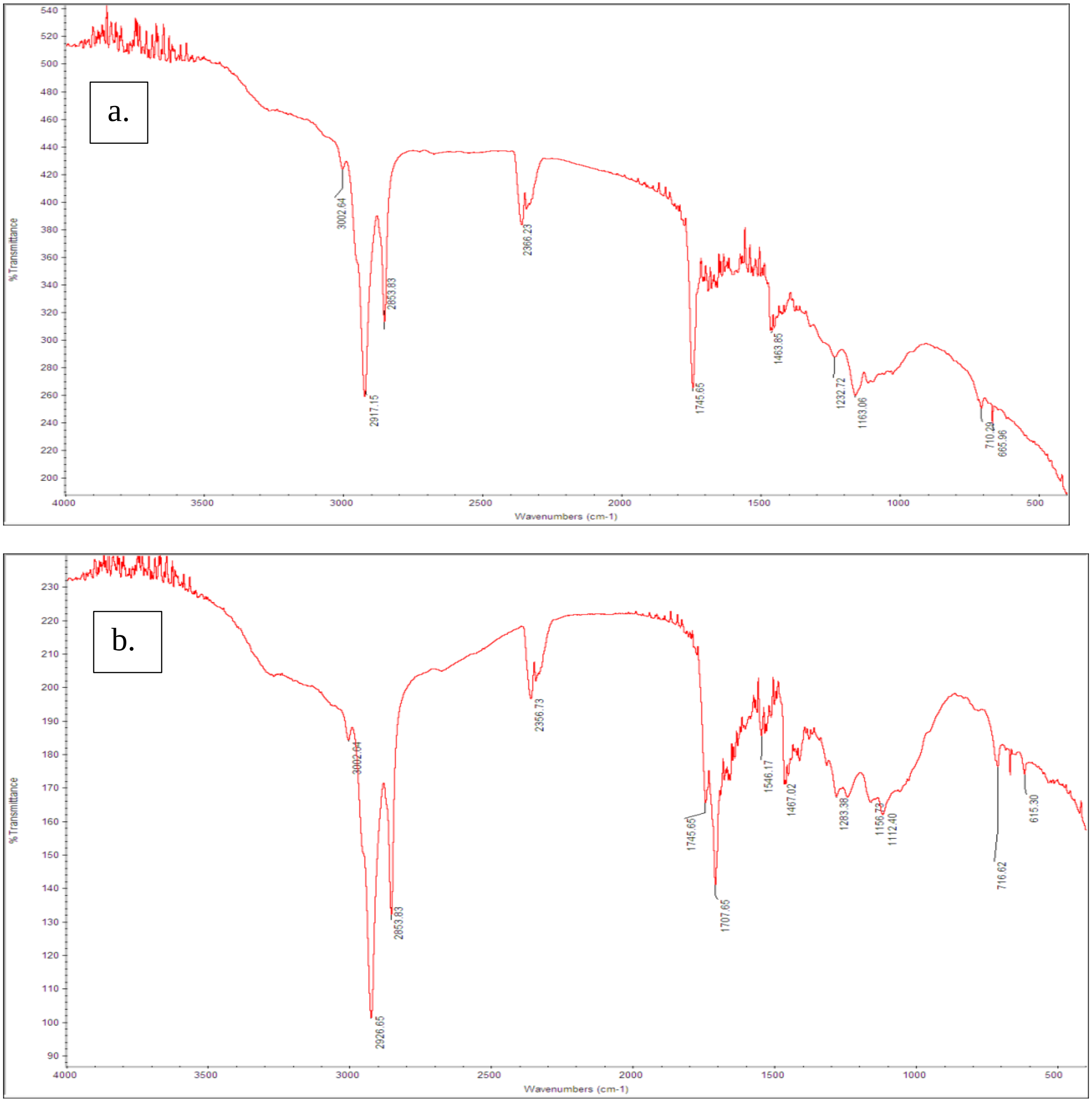


Figure 1: FTIR spectra of (a) raw pawpaw seed (b) treated pawpaw seed

Water sample characterization

The result of the Asa river water analysed is as presented in Table 3**.** After coagulation all the metals were found to be below detection limit suggesting that, apart from coagulation to remove turbidity, adsorption of metals had taken place.

Table 3: Result of river water analysis from ICP-MS

Trace metal	Value (ppb)
Cd	0
Co	0.0736
Cr	21.496
Cu	6.072
Fe	394.16
Pb	0
Mn	2.142
Ni	1.384
Ti	13.08
Zn	6.688

Optimization of process parameters

The experimental response in terms of turbidity removal efficiency was measured to be in the range of 56.25% to 93.75%. The measured data were analyzed using analysis of variance and the final empirical model equation developed is shown in equations 4.

$$TR = +25.76 - 73.29X_1 + 0.70X_2 + 0.19X_3 - 11.47{X_1}^2 - 0.004{X_2}^2 - 0.0002{X_3}^2 - 1.44X_1X_2 + 0.16X_1X_3 - 0.0004X_2X_3 \quad (4)$$

Where X_1, X_2 and X_3 represents coagulant dosage, contact time, and agitation speed respectively.

The equation (4) showed that among the main factors investigated, both the contact time and agitation speed have a positive influence on the turbidity removal efficiency while the coagulant dosage was found to have negative influence.The results also showed that coagulant dosage with coefficient (73.29) exert the greatest effect on the turbidity removal efficiency. The adequacy and significance of the developed model was evaluated using F and p-values as shown in Table 4. The Values of "Prob > F" less than 0.0500 indicates model terms are significant. From Table 4, all the terms except ${X_1}^2$ were found to be signficant in model terms for the turbidity removal. The P value of < 0.0001implies that the model is significantat 95% confidence level (Adewoye *et al.*, 2016). The suitability of the model was also evaluated using adjusted coefficient of determination (Adjusted R^2) and predicted residual sum of squares. The values of R^2 was found to be very high, which shows a good correlation existed between the experimental and predicted data.The Pred R-Squared of 0.8415 is in reasonable agreement with the Adjusted R-Squared of 0.9648.Adeq Precision measures the signal to noise ratio and a ratio greater than 4 is usually desirable. From Table 4, the developed model with ratio of 21.773 indicates an adequate signal and this shows that the developed model is reliable.

Table 4: ANOVA of Response Surface Quadratic Model for Turbidity Removal

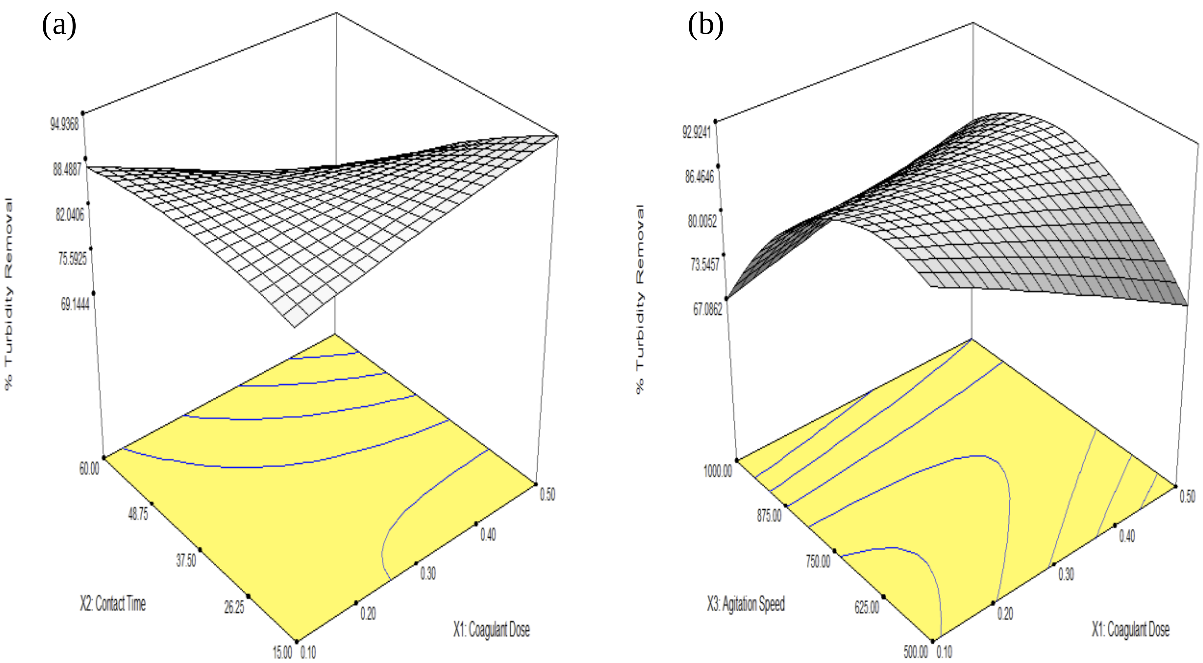
Source	**Mean Square**	**F-Value**	**P Value (Prob>F)**	**Remarks**
Model	312.79	58.86	< 0.0001	Significant
X_1	93.00	17.50	0.0019	Significant
X_2	517.00	97.29	< 0.0001	Significant
X_3	204.91	38.56	0.0001	Significant
${X_1}^2$	2.17	0.41	0.5372	Not Significant
${X_2}^2$	35.19	6.62	0.0277	Significant
${X_3}^2$	1068.24	201.02	< 0.0001	Significant
$X_1 X_2$	334.37	62.92	< 0.0001	Significant
$X_1 X_3$	515.53	97.01	< 0.0001	Significant
$X_2 X_3$	34.86	6.56	0.0283	Significant
Residual	5.31			
Lack of fit	10.51	87.26	< 0.0001	
Pure error	0.12			
R^2 = 0.982 ; Adj R^2 = 0.965				

The Design expert version 6.0.8 software was used to carry out the optimization of allprocess parameters for the turbidity removal onto the pawpaw seed extract. The objective function was to maximize turbidity removal within the experimental range of the studied independent variables. The solution of optimization is usually selected based on the highest desirability or its closeness to unity . The optimal conditions were found to be 0.47 g, 15.17 min, and 791.33 rpm for coagulant dose, contact time, and agitation speed, respectively. The turbidity removal efficiency at optimum conditions was found to be 94.92%. The model validation was carried out under optimum conditions by the developed model and the predicted values were found to agree satisfactorily with the experimental values, with an error of 1.78% as shown in Table 5.

Table 5: Model Validation

Coagulant Dosage, X_1 (g)	Contact Time, X_2 (min)	Agitation Speed, X_3 (rpm)	Turbidity Removal Efficiency, $Y_{turbidity\ removal}$(%)		
			Predicted	Experimental	Error (%)
0.47	15.17	791.33	94.92	96.70	1.78

Figure 2a demonstrates the effect of interaction between the coagulant dosage and contact time on the percentage turbidity removal. The combined effect of the increased coagulant dose and contact time results in the increment in percentage turbidity removal up to an optimum point (95.8%). The maximum turbidity removal was achieved at low contact time (15 min) and very high coagulant dosage (0.47 g). The combined effect of interaction between coagulant dose and agitation speed is shown in Figure 2b while the effect of interaction between contact time and agitation speed is shown in Figure 2c.



(c)

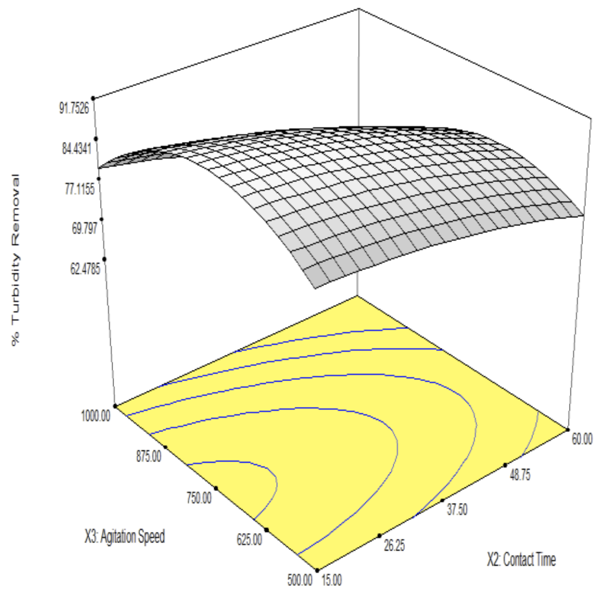


Figure 2: Three dimensional response surface plots: (a) effect of coagulant dosage and contact time on turbidity removal (b) effect of coagulant dosage and agitation speed on turbidity removal (c) effect of contact time and agitation speed on turbidity removal.

At the optimum conditions of adsorbent dose, contact time and agitation speed established, the treated water sample was analyzed before and after the adsorption studies. Trace metal analysis was carried out on the raw water sample and treated sample at optimum condition using the AAS. All the metals were found to be below detection limit of the AAS available, which confirms that, besidesturbidity removal, the pawpaw seed extract coagulant was very effective for the removal of trace metals from ASA river water investigated.

Conclusion

Coagulant prepared from pawpaw seeds was successfully used to reduce the turbidityof water samples obtained from ASA River. Central Composite Design under the Response Surface Methodology was used to determine the optimum process conditions for turbidity removal. Also, the pawpaw seed coagulant was found to be effective for the removal of trace metals from Asa river water. The effectiveness of the pawpaw seed as a coagulant gave a good result which helped in the coagulation of water for turbidity removal. Thus, this study has established that pawpaw seed is a potential natural coagulant for the removal of turbidity from surface river water.

References

Adewoye, L.T.; Mustapha, S.I.; Adeniyi, A.G.; Tijani, J.O.; Amoloye, M.A. and Ayinde, L.J. (2016). Optimization of nickel (II) and chromium (III) removal from contaminated water using sorghum bicolor. *Nigerian Journal of Technology, 36*(3): 960-972.

Alam, J. B., Hossain, A., Khan, S. K., Banik, B. K., Islam, M. R., Muyen, Z., and Habibur Rahman, M. (2007). Deterioration of water quality of Surma river. *Environmental Monitoring and Assessment, 134*: 233-242.

Ali, S. and Singh, R.P.(2009). Synthesis and characterization of a modified chitosan. *Macromolecular Symposium*, 1-7.

Asrafuzzaman, M., Fakhruddin, A. N. M., and AlamgirHossain, M. (2011). ReductionofTurbidityofWaterUsingLocally AvailableNaturalCoagulants. *International Scholarly Research Network, 2011*: 1-6.

Babu, R., and Chaudhuri, M. (2005). Home water treatment by direct filtration with natural coagulant *Journal of Water and Health, 3*(1): 27-30.

Diaz, A., Rincon, N., Escorihuela, A., Fernandez, N., Chacin, E., and Forster, C. F. (1999). A preliminary evaluation of turbidity removal by natural coagulants indigenous to Venezuela. *Process Biochemistry, 35*(3): 391-395.

Dimitrovska, O., Markoski, B., Toshevska, B. M., Milevski, I., and Gorin, S. (2012). Surface water pollution of major rivers in the Republic of Macedonia. *Procedia, 14*: 32-40.

Duruibe, J. O., Ogwuegbu, M.O.C., & Egwurugwu, J.N. (2007). Heavy metal pollution and human biotoxic effects *International Journal of Physical Sciences, 2*(5): 112-118.

Gunaratna, K. R., Garcia, B., Andersson, S., and Dalhammar, G. (2007). Screening and evaluation of natural coagulants for water treatment. *Water Science and Technology: Water Supply, 7*(5-6): 19-25.

Hao, O.J., Kim, H. and Chiang, P.C.(2000). Decolorization of wastewater. *Critical Review in. Environmental Science and. Technology*, 30: 449-505.

Megersa, M., Beyene, A., & Woldeab, B. (2014). The use of indigenous plant species for drinking water treatment in developing countries: a review *Journal of Biodiversity and Environmental Sciences, 5*(3): 269-281.

Ong, S.T., Lee, W.N., Keng, P.S., Lee, S.L., Hung, Y.T. and Ha, S.T.(2010). Equilibrium studies and kinetics mechanism for the removal of basic and reactive dyes in both single and binary systems using EDTA modified rice husk. *International Journal of Physical Sciences*, 5: 582- 595.

Onojake, M. C., Sikoki, F. D., D.D., B., Akpiri, R. U., Akpuloma, D., and Omokheyeke, O. (2015). Bioaccumulation of heavy metals in two matrices of the Bonny/New Calabar River Estuary in Niger Delta, Nigeria. *Ocean Science Journal, 50*(2): 203 - 208.

Pekey, H., Karakaş, D., Ayberk, S., Tolun, L., and Bakoğlu, M. (2004). Ecological risk assessment using trace elements from surface sediments of İzmit Bay (Northeastern Marmara Sea) Turkey. *Marine Pollution Bulletin, 48*(9): 946-953.

Schwarzenbach, R. P., Egli, T., Hofstetter, T. B., Gunten, U. V. and Wehrli, B. (2010). Global Water Pollution and Human Health. *Annual Review of Environment and Resources, 35*: 109-136.

Šćiban, M. B., Klašnja , M. T. and Stojimirović, J. L. (2005). Investigation of coagulation activity of natural coagulants from seeds of different leguminose species. *APTEFF 36*: 81-87.

Sharma, R. K. and Agrawal, M. (2005). Biological effects of heavy metals: An overview. *Journal of Environmental Biology, 26*(2): 301-313.

Simeonov, V., Stratis, J. A., Samara, C., Zachariadis, G., Voutsa, D., Anthemidis, A. and Kouimtzis, T. (2003). Assessment of the surface water quality in Northern Greece *Water Research, 37*: 4119-4124.

Verma, A.K., Dash, R.R. and Bhunia, P. (2012). A review on chemical coagulation/flocculation technologies for removal of colour from textile wastewaters. *Journal of Environmental Management*, 93: 154-168.

Wang, Y., Teng, E., Liu, T., Lv, Y., Jin, X., Giesy, J. P., and Hollert, H. (2014). A national pilot scheme for monitoring and assessment of ecological integrity of surface waters in China *Environmental Development, 10*: 104 - 107.

Zhang, J., Zhang, F., Luo, Y., and Yang, H. (2006). A preliminary study on cactus as coagulant in water treatment. *Process Biochemistry, 41*(3): 730-733.

Zhao, S., Gao, B., Li, X., and Dong, M. (2012). Influence of using Enteromorpha extract as a coagulant aid on coagulation behavior and floc characteristics of traditional coagulant in Yellow River water treatment. *Chemical Engineering Journal, 200-202*: 569-576.