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Study on the anionic natural coagulant aid for heavy metals and turbidity removal in water at *p*H 7.5 and alum concentration 25 mg/L-laboratory scale

Hamidi A. Aziz, Mohd. N. Adlan, Abdul M. D. Mohamed, Sujatha Raghavan, Mohd. Koflly Mohd. Isa & Mohd. Harmizi Abdullah

School of Civil Engineering, Universiti Sains Malaysia, Perak Branch Campus, 31750 Tronoh, Perak Darul Ridzuan, Malaysia

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This aims to search for an alternative natural polymer, which could be used as coagulant aids in water and wastewater treatment. The use of this polymer may save the amount of Alum (aluminium sulphate) dosed in water and wastewater treatments. An initial study conducted in laboratory to look at suitability of using sago (Metroxylon spp) starch as an alternative of coagulant aid as compared to the commercially applied synthetic polymer. Artificial pollutants consist of selected heavy metals, i.e., nickel (Ni), manganese (Mn), zinc (Zn), iron (Fe), cadmium (Cd) and turbidity have been used to stimulate the general real water and wastewater. Initial concentration of metals is set at 5 mg/L. Turbidity value at 300 NTU which, corresponds to the presence of colloids or suspended solids in water is also used in the experiment. Experiment has been conducted at optimum alum and *p*H values, predetermined beforehand. Jar test is conducted and results are obtained in terms of the removal percentage of each constituent, before and after the experiment. It could be concluded from the experiments that, at Alum concentration of 25 mg/L, the presence of sago starch improves the removal of selected heavy metals, i.e., nickel, manganese, zinc, iron, and cadmium. The improvements are obvious for Zn and Fe. However, there is no significant effect of turbidity removal in the presence of sago starch. This shows that the sago behaves as negatively charge polymer, which enhances the coagulation process of heavy metals. The study indicates that the use of sago starch as natural polymer is potential in wastewater industries for removing heavy metals.

Heavy metals such as cadmium, lead, zinc, nickel, copper and chromium (III) (Cr (III)) or their compounds are high-molecular-weight substances. They have been used extensively by various industries in recent years due to industrialization. Many of these metals are widely used, particularly by industries, which rely on solutions of the metallic ions. This leads to sharp increase in the contamination of water. Because of their toxicity, the presence of these metals in excessive quantities will interfere with many beneficial uses of the water. As a result, many water quality standards kept the value of these metals to a minimum. For example, the Standard B discharge limit of these metals under the Environmental Quality Act 1974 of Malaysia, (Sewage and Industrial Effluents), Regulation 1979 are kept below 1.0 mg/L in which the standard for Cd is 0.02 mg/L, 0.50 mg/L for Pb, 1.0 mg/L each for Zn, Ni, Cu and Cr (III)[1].

Current removals of heavy metals from solution are very much influenced by increasing the *p*H to allow the metals to precipitate into insoluble metal forms. The process requires addition of chemical agents in coagulation and flocculation processes, which is costly, and requires proper handling methods. The most likely used coagulants for water and wastewater treatment are aluminium and iron salts and lime is normally used to increase the *p*H. For some waters, cationic polymers are effective as a primary coagulant. It can be effective for coagulation, without hydrolysing metals, by producing destabilisation through charge neutralisation and inter-particle bridging. However, polymers are more commonly applied as coagulant aids. Other coagulant aids include *p*H adjusters, activated silica and clay[2]. Coagulant aids are necessary in some waters or effluents, when coagulation is poor, even with the best dose of coagulant. The addition of extra substances can often result in considerable improvement in coagulation and an increase in the settling velocity of the resulting floc. Coagulant aids may also be used to reduce coagulant consumption, shorter sedimentation periods and higher rates of filtration[3].

Synthetic polymers (normally called polyelectrolytes) are water-soluble high-molecular-weight organic[4,5] compounds that have multiple electrical charges along a molecular chain of carbon atoms. The basic chain is often a *polyacrylamide*.

Polyelectrolytes are either derived from natural sources or synthesised by chemical manufacturers. Polyelectrolyte can have a negative charge (anionic), positive charge (cationic), positive and negative charge (*polyamphotype*), or no charge (non-ionic). Polyelectrolyte is generally used to produce a tougher and denser floc, which grows to a larger size and settles more rapidly than is possible using a primary coagulant alone. This is due to the action of the long-chain molecules which, form bridges or cross-links between colloidal particles.

A wide variety of ampholytic polymers are derived from natural sources. A significant number of polyelectrolyte applications have been reported in literature[3]. Seeds of the nirmali tree (*Strychnos potatorum*) have been used to clarify turbid river water 4000 years ago in India. In Peru, water has been traditionally clarified with the *mucilaginuous* sap of *tuna* leaves obtained from certain species of *cacti*. Several villages in Chad, Nigeria, Sudan and Tunisia have also been using indigenous plants for turbidity, unpleasant taste and odour removal in drinking water. The British were among the first to use natural polyelectrolytes as coagulant aids (sodium alginate, a natural polymer extracted from brown seaweed) in urban water supplies. Other natural polymers that have been used successfully in England are *Hydroxyethyl cellulose* (HEC) and *wisprofloc*, a derivative of potato starch.

Polyelectrolytes are also commonly applied in water and wastewater industries in Malaysia in the coagulation and flocculation processes. It is normally dosed when Alum concentration needs to be reduced due to the unfavourable water condition. For example, polyelectrolyte could be dosed in turbid water and at the Dissolved Air Floatation plant. The use of *Chitin* and *Chitosan* (a natural polymer extracted from the processing waste of prawns, crabs and squids) for wide applications has been reported elsewhere[6]. However, the application of plant extracted polymer in water and wastewater industry in Malaysia has not been established so far.

As Malaysia is rich in natural polymer, the use of sago (*Metroxylon* spp) may be suitable as replacement agent of synthetic polymer. Current cost of synthetic polymers ranges from RM 5.10 to RM 16.70 per kilogram. This is compared to the current price per kilogram of sago starch, which is RM1.04.

This paper reviews some of the important results in the current research in the use of sago as coagulation aid for removing turbidity and heavy metals from water as opposed to the use of the synthetic chemicals. The results would be useful in developing the method for removing especially heavy metals, which could be of great use especially for the small and medium scale industries.

Materials and Methods

Starch of sago was prepared by peeling, crushing, filtering and washing the filtrate. The cleaned filtrate then was air dried for 24 h to form powder starch. The powder then was accurately weighed and dissolved to required concentration via moderate heating. For example, 1% solution of starch was prepared by dissolving 1 g of the powder into 100 mL distilled water. Dosing of this starch in the experiment was done by dilution principle.

Sample water that contains a significant amount of suspended solids or colloids (about 300 NTU) was prepared from clayey solids. Selected heavy metals, i.e., nickel, manganese, zinc, iron, and cadmium were prepared using commercially available standard solution. Initial concentration of these metals was set at 5 mg/L. Jar test was conducted to determine the *p*H and Alum optimum values, in the presence of turbidity and heavy metals. Optimum *p*H was determined by fixing the Alum concentration and ranging the *p*H. On the other hand, Alum optimum was determined by setting the *p*H value and ranging the Alum concentrations as detailed in the standard methods for the determination of water and wastewater[7]. These optimum values were used in the experiments that involved dosing of starch, with and without the presence of Alum. The concentration of each constituent, before and after the Jar Test was recorded and the removal percentage calculated.

Turbidity and *p*H were determined by 2020 Lamotte Turbidity meter, whilst heavy metals were determined by Shimadzu Atomic Absorption Spectrophotometer.

Results and Discussion

Figs 1 and 2 show the plot of turbidity against *p*H value, and turbidity against Alum concentration for determination of optimum *p*H and Alum values. Figs 3 and 4 show the plot of the removal of Ni, Mn and Zn at optimum *p*H and Alum values, with different sago starch concentrations. Finally, plot of the removal of Fe, Cd and turbidity against starch concentration is given in Fig. 4. The results are further summarised in Table 1.

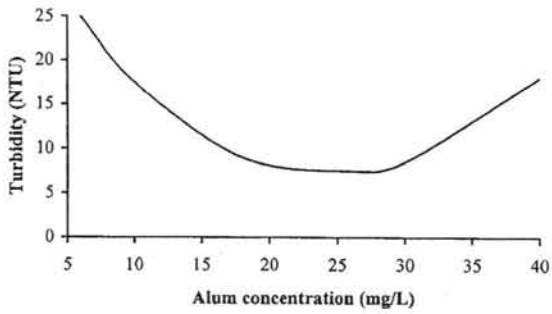

Fig. 1—Determination of optimum Alum concentration in the Jar Test

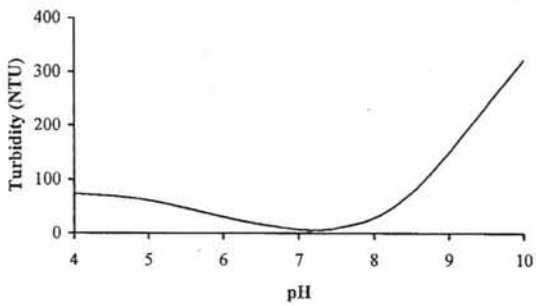

Fig. 2—Determination of optimum *p*H value in the Jar Test

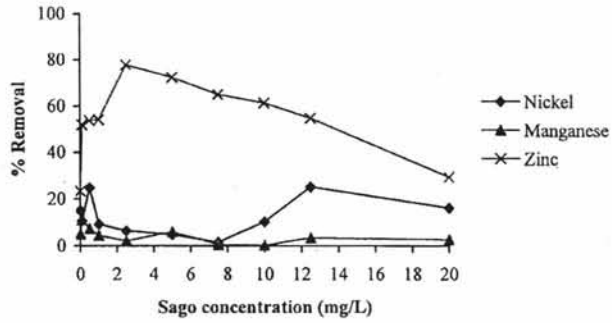

Fig 3—Influence of sago starch as coagulant aid in removing Ni, Mn and Zn from water at *p*H 7.5 and Alum concentration 25 mg/L

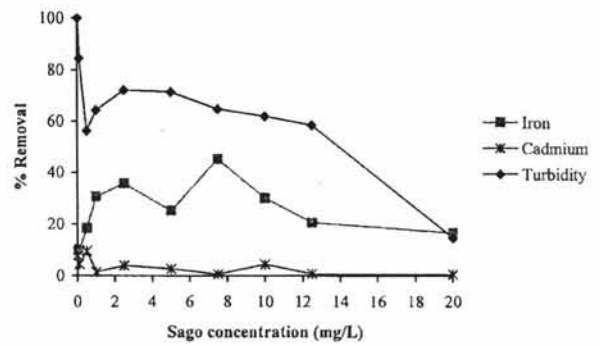

Fig. 4—Influence of sago starch as coagulant aid in removing Fe, Cd and turbidity from water at *p*H 7.5 and Alum concentration 25 mg/L

Table 1—Summary of experimental results on the use of sago starch as coagulation aid for removing heavy metals and turbidity in water

Experimental condition	Water quality parameter (mg/L)		% Removal without dosing of sago starch	Experiment With Dosing of Sago Starch				
				Dose range (mg/L)	% Removal	Optimum/ Economical Dose (mg/L)	% Removal	Comments
		Nickel	15	0.5	25	0.5	25	Positive Results
*p*H 7.5	Heavy	Manganese	5	0.5	11	0.5	11	Positive Results
Alum 25 mg/L	Metals	Zinc	24	0.1-8	65-80	0.1	50	Positive Results
		Iron	10	0.5-10	30-50	1	30	Positive Results
		Cadmium	8	0.5	13	0.5	13	Positive Results
	Turbidity		95	<90	<90	<90	<90	Negative Results

Results indicate that the optimum *p*H from the experiment is 7.5, which is the lowest point in Fig. 1. The optimum Alum concentration at this optimum *p*H is 25 mg/L, as shown in Fig. 2. This value is still within the range of an optimum *p*H as discussed by several researchers. For example, Eckenfelder[8] stipulates that at Alum dosage range of 75-250 mg/L, colloid coagulation and phosphorous removal for wastewater with high alkalinity and low stable phosphorous happens at *p*H 4.5-7.0. Davis and Cornwell[2] mention that, the optimal *p*H range for Alum is approximately 5.5 to 6.5 with adequate coagulation possible between *p*H 5 to 8 under some condition. Tebbutt[9] suggests that the solubility of Al $(OH)_3$ is *p*H dependent and is low between *p*H 5 and 7.5. Outside this range, coagulation with aluminium salts is not successful. Hammer and Hammer[10] report that Alum coagulation is generally effective with the

*p*H limits of 5.5 to 8.0. However, Schulz and Owen[3] mention that optimal floc formation using Alum occurs when the *p*H value of the water is between 6 and 8. Fig. 4 concludes that tapioca could react as coagulant aids. Furthermore, apart from behaving as a coagulant aid, tapioca starch could also reduce the amount of Alum from 25 mg/L to 15 mg/L with increased in the removal of anions and turbidity.

Figs 3 and 4 and data in Table 1 have shown that at Alum concentration 25 mg/L and *p*H value of 7.5, the removal of constituents are good in the presence of sago starch as coagulant aid, except for turbidity. Increased in the removal is significant for Zn and Fe. It can be noted from Fig. 3 and Table 1 that the removal of Zn without the presence of sago starch is 24%. The removal improves to above 50%, in the presence of 0.1 mg/L of sago starch. Similarly, the removal of Fe in the presence of 1 mg/L of sago starch is 30%, as compared to 10% removal without the starch. For other metals, improvements could also be noticed, even though their magnitude is rather small, as given in Table 1. Nevertheless, the experiment has generally shown an improvement on the metals removal in the presence of sago starch. Graphs in Figs 3 and 4 also show that positive improvements of metals removal starts at lower concentration of sago starch, i.e., at concentration lower than 1 mg/L. This is in line with previous research which say that dosage of coagulant aid is in the region of 0.1-1.0 mg/L and dosage of anionic polymer is normally in the region of 0.5-0.5 mg/L[10].

As sago starch significantly enhances the removal of positively charged heavy metals, it is expected that the starch was present in the form of an anionic polymer. By adding negative ions to water (sago starch for this case), heavy metals have undergone charge neutralisation, as mentioned previously[9]. In other words, the starch it attracts positively charge metals, destabilised and particle starts to agglomerate then precipitate. The claim that sago carries negative charge further supported by the findings of the turbidity removal in Fig. 4. It can be seen from the figure that the starch does not improve the removal of turbidity. This is due to the fact that most colloids are stable because they possess a negative charge that repels and collide with one another under *Brownian movement*[2]. By adding negative ions (sago) to water, it does not reduce the surface charge but rather improves the suspension of the colloids. Hence, the colloids remain repelling from each other, and further stabilised.

However, the exact starch composition, especially the charge composition is currently investigated. Its presence in the form of non-ionic polymer could not be ruled out as, previous report has stated that non-ionic polymers are more effective in water containing higher concentrations of divalent cations, i.e., Ca^{2+} and Mg^{2+} (ref. 10).

The research has highlighted the possibility of using sago as natural polymer in removing heavy metals in water. However, further research, especially the exact chemical reactions that bring the metals removal, the chemical properties of starch, the sludge characteristics, etc. need to be undertaken. The removal of each heavy metal at concentration of sago starch of less than 1 mg/L should also be intensified. Apart from that pilot plant experiments should also be conducted before the findings could be adapted in the field.

Conclusion

It could be concluded from the experiments that at Alum concentration of 25 mg/L, the presence of sago starch improves the removal of selected heavy metals, i.e., nickel, manganese, zinc, iron, and cadmium. The improvements are obvious for Zn and Fe. However, there is no significant effect of turbidity removal in the presence of sago starch. This shows that the sago possesses a negatively charge polymer which enhances the coagulation process of heavy metals.

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