Nature Environment and Pollution Technology
An International Quarterly Scientific Journal

p-ISSN: 0972-6268
e-ISSN: 2395-3454

Vol. 16 | No. 2 | pp. 509-514 | 2017

Original Research Paper

Open Access

Hybrid Method of Coagulation-Flocculation and Adsorption-Filtration Processes for the Removal of Hexavalent Chromium from the Aqueous Systems

K. Ravikumar*(**)† and J. Udayakumar***

*Environmental Resources Research Centre (ERRC) of M.G. University, Trivandrum, India
**Kerala Water Authority, Trivandrum, India
***Department of Civil Engineering, TKM College of Engineering, Kollam, India
†Corresponding author: K. Ravikumar

Nat. Env. & Poll. Tech.
Website: www.neptjournal.com

Received: 23-05-2016
Accepted: 16-07-2016

Key Words:
Moringa oleifera
Kaolinite clay
Heavy metals
Chromium removal

ABSTRACT

Hexavalent chromium is one the most important water pollutants. There are a number of available technologies used for the remediation of chromium, but none of them is applicable to all situations. In this study a hybrid method of coagulation-flocculation uses *Moringa oleifera* seed coagulant polymer and adsorption-fine filtration with composite of kaolinite clay and sand media for removing chromium ions present in aqueous systems. 98% of chromium ions were removed from the water by this novel technique of coagulation-flocculation and adsorption-filtration process.

INTRODUCTION

Heavy metals are introduced into water bodies mainly by industrial, agricultural, mining and many other activities carried out by man. A number of methods have been developed for the removal of heavy metals from water, namely reverse osmosis, chemical precipitation, ion exchange, solvent extraction, etc. However, these methods have several disadvantages such as unpredictable metal ion removal, high reagent requirement, generation of toxic sludge, etc. (Das et al. 2008). Adsorption, ion exchange and coagulation-flocculation processes have become preferred methods for removal of toxic heavy metals from aqueous systems due to their cost effectiveness.

Natural clay and its composites are capable of removing contaminants ranging from metals to priority pollutants from contaminated drinking water. In most of the cases, they proved to be better or comparable with the existing commercial filter materials, adsorbents, and materials in conventional methods used for decontamination of drinking water. Being natural and due to their abundant presence they become low-cost, green and nontoxic adsorbents, which can be used for removal of different contaminants from water and for making clean and pure drinking water available for developed and developing nations (Srinivasan 2011).

The *Moringa oleifera* (Fig. 1) plant is a natural biosorbent which is used for a wide range of applications utilizing its water coagulation, nutritional and pharmacological properties. The plant is chemically composed of a large protein molecule with a molecular mass of 6.5 kDa and has an isoelectric point above pI 10. The active sites responsible for the adsorptive capability of *M. oleifera* contain functional groups such as hydroxyl, carboxyl, amines, phenolic, methoxyl and hydroxyl-aliphatic groups (Ndibewu 2011).

The use of native cassava starch grafted poly (acrylonitrile) for heavy metal ion removal is technically feasible, eco-friendly and with high efficiency. Besides that, being composed of natural polysaccharides, it helps in the reduction of environmental pollution and safe disposal of heavy metals (Ekebafe 2012).

Adsorbent can be assumed as “low cost” if it requires little processing, or abundant in nature, or if it is by-product or waste material from industry. Some of the reported low-cost adsorbents include bark, tannin-rich materials, lignin, chitin, chitosan, peat moss, moss, modified wool and cotton. Insoluble starch xanthates have been found to be very useful to remove heavy metal ions from solutions. Agricultural waste materials such as spent grain, polymerized onion skin, rice husks, bark and sawdust, maize cobs, wheat etc. are used as bio-adsorbents for the removal of heavy metals from aqueous systems. The adsorption of heavy metals by these materials might be attributed to their proteins, carbohydrates and phenolic compounds, which have carboxyl, hydroxyl, sulphate, phosphate and amino groups that can bind metal ions (Bulut & Tez 2007).

One of the most common unconventional methods being considered for the removal of heavy metals from water is the use of various plant seeds for their biosorption properties, and they seem to hold great potential as an alternative low cost adsorbents. They are readily available, cheap and ecofriendly (Edogbanya et al. 2013).

The ability and efficiency of the adsorption technologies in water treatment depend on the characteristics and functions of adsorbents. Therefore, to transfer the species of pollutants for promoting the adsorption rate, we can design and prepare some special composite adsorbents with the redox, catalytic and adsorptive functions, which can carry out the processes of oxidation/reduction and adsorption of pollutants synchronously (Jiuhui 2008).

Health problems caused by aluminium salts used as adsorbents have been recently reported. Various reports have mentioned the direct and indirect toxic effects of metals to cause tumours, cancers and allergies. In order to replace aluminium salts used as adsorbents and coagulants, the capability of bentonite and combination of bentonite used as coagulants in wastewater treatment via adsorption, ion exchange and coagulation-flocculation processes make this good coagulant which can absorb chemical oxygen demand (COD) for 90.5% of removal (Syafalni et al. 2013).

Use of Al-based coagulants especially $Al_2(SO_4)_3$ (alum) often leads to an increase in treated water Al concentrations. A high (3.6 to 6 mg/L) concentration of Al will lead to precipitate as aluminium hydroxide, giving rise to consumer complaints. Al is also a suspected causative agent of neurological disorders such as Alzheimer's disease and presenile dementia. During conventional water treatment processes, Al undergoes various transformations (also called 'speciation' of Al) which are influenced by factors such as pH, turbidity, temperature of water source and the organic and inorganic legends present in water (Srinivasan et al. 1999).

Chitosan is an important additive in the filtration process. Sand filtration apparently can remove up to 50% of the turbidity alone, while the chitosan with sand filtration removes up to 99% turbidity. Chitosan removes phosphorus, heavy metals and oils from the water (Gavhane et al. 2013).

Aygun & Yilmaz (2010) reported that, coagulation-flocculation process was used to treat detergent wastewater with ferric chloride as coagulant. The improvement of the process by using polyelectrolytes and clay minerals (montmorillonite and bentonite) as coagulant aids was also investigated. Addition of coagulant aids provided higher removal efficiencies. The maximum removal efficiency was obtained with the addition of polyelectrolyte and it was found that the ferric chloride combination with coagulant aids, at certain pH and agitation speed, provided higher removal efficiencies compared to coagulation with ferric chloride alone.

Study of the effectiveness of the locally sourced coagulants show that the combined coagulants of chitosan/clay give better results when compared to conventional/synthetic coagulants and with locally sourced coagulants used independently. By implication, the synergistic effects were evident in the removal of the colloidal particles and consequently the pollution level was significantly reduced in the treated sludge (Ize-Iyamu et al. 2013).

Sole use of clay coagulants showed limited efficiency in removal of pollutants from wastewater, whereas, the combined use showed high removal efficiency comparable to that one achieved by poly aluminium chloride (PAC). Use of these clays as a coagulant aid with PAC is beneficial and economical and can reduce the cost of the treatment considerably depending on the characteristics of the wastewaters (Awad 2013).

Previous studies (Ravikumar et al. 2012, 2013a,b,c,d, 2014) show the potential of *Moringa oleifera* as a coagulant, clarifier, adsorbent and for other uses. This is due to the presence of some functional groups such as hydroxyl, carboxyl, amines, phenolic, methoxyl and hydroxyl aliphatic groups. Ravikumar et al. (2014) reported that when composite coagulant, prepared by adding alum and starch with *Moringa oleifera,* was used for coagulation of fluoridated water, the fluoride concentration reduced below 1mg/L and the turbidity was within the standard limit of drinking water. Ravikumar et al. (2013d) conducted the analysis of the heavy metals cadmium, copper, chromium and lead, before and after treatment of water with *Moringa oleifera* seed coagulant. The results showed that the percentage removal by *Moringa* seeds was 95 % for copper, 93 % for lead, 76 % for cadmium and 70 % for chromium.

The present study is an attempt to treat water and wastewater containing hexavalent chromium using hybrid method of coagulation/flocculation using *Moringa oleifera* seed coagulants and adsorption/filtration using kaolinite clay. Objectives of the study are (1) to identify a sustainable, low cost, locally available, simple, reliable, acceptable, eco-friendly water treatment technology for removing hexavalent chromium ions from the aqueous systems, (2) to design clay-polymer composites for removal of hexavalent chromium ions based on the sorption of cationic polymer of *Moringa oleifera* (MO) seed coagulant on a commercial kaolinite clay.

MATERIALS AND METHODS

Preparation of MO seed powder: Dry MO pods were collected, pod shells removed manually, kernels (Fig. 2) grounded in a domestic blender and sieved through 600 micrometer stainless steel sieve.

Oil extraction and biodiesel production: Oil was removed by mixing the seed powder (Fig. 3) in ethanol. This was mixed with a magnetic stirrer for 30-45 min and subsequently, separation of the residue from the supernatant was done by centrifuging for 45 min at 3000 rpm. The supernatant was decanted and the residual solid was dried (seed cake Fig. 4) at room temperature. The supernatant containing oil and ethanol when mixed with potassium hydroxide catalyst, the chemical reaction produces biodiesel (Fig. 5) and glycerol.

Aqueous extract: Aqueous extract was prepared by using 200 mL of distilled water and 25 g of MO seed cake powder, mixed by a magnetic stirrer for 60 minutes and settled for 20 minutes. *Moringa oleifera* aqueous extract was finally filtered through 20 μm paper filter.

Preparation of crude extract: Crude extract was prepared by using 200 mL of 1 mole of NaCl solution and 25 g of MO seed cake powder, mixed by a magnetic stirrer for 60 minutes and settled for 20 minutes. *Moringa* crude extract was finally filtered through 20 μm paper filter (Fig. 6).

Preparation of synthetic solution of chromium (VI): In a clean beaker 100 mL distilled water was boiled and 0.6131 g of cadmium chloride was added with constant stirring. Then the solution shaken well and cooled to make 1000 ppm stock solution. From this various concentrations (2, 4, 6, 10, 12, 14, 16, 18, 20 mg/L) were prepared with appropriate dilutions.

Preparation of clay materials: Kaolinite clay was collected locally from Kollam, Kerala and its characteristics are given in Table 1.

Smaller particles of the medium are more effective than larger ones because of greater availability of surface area and consequently higher adsorption capacity. The kaolinite was stored in a plastic container for the ready use.

Coagulation of MO: The standard procedure was 45 min of rapid mixing (100 rpm) followed by 15 minutes of slow mixing (50 rpm) for flocculation.

Adsorption media: Kaolinite clay was used as the adsorption media for removal of chromium from the aqueous systems after coagulation-flocculation with various *Moringa oleifera* coagulants.

Hybrid method of coagulation using MO and adsorption using kaolinite column: Three PVC columns with an inner diameter of 110 mm and a length 100cm were used. The

Table 1: Characteristics of kaolinite clay.

Appearance	White Powder
Brightness	85.0%
Grit on 300 mesh (max)	0.05% (max)
Loss on ignition	14% max
pH of 20% aqueous solution	4 to 6
Particles less than 2 microns	82% (min)
Bulk density	0.8 g/cc
Moisture	1-2% (max)
Iron as ferric oxide	0.5%
Silica	45.17%
Alumina	37.59%

Fig. 1: *Moringa oleifera* plant.

Fig. 2: *Moringa oleifera* de-husked seed kernel.

Fig. 3: *Moringa oleifera* seed powder.

Fig. 4: *Moringa oleifera* seed cake.

Fig. 5: *Moringa oleifera* biodiesel.

Fig. 6: *Moringa oleifera* crude extract.

bottom of the column was sealed off with a plastic cap to prevent the loss of adsorbent during the process. Four different outlets were provided at different heights with 20 cm height from the bottom of the column. Water reservoir (bucket) with facilities for coagulation with optimum quantity (2.5 g/L) of *Moringa oleifera* seed coagulants for first stage coagulation-flocculation processes (the standard procedure was 45 min of rapid mixing at 120 rpm and 15 min of slow mixing at 50 rpm) was kept at a certain height above the column to allow coagulated water to flow under the action on gravity into the column for second stage adsorption-filtration processes.

A clinical drip was attached from the coagulated water reservoir to the column to maintain a constant flow rate of water. The medium (mixture of kaolinite clay and sand in the ratio 2:3) is compacted tightly inside the column through which the sample water flows downward. Head loss is constantly maintained for the proper functioning of the apparatus. Finally, the water passing through the composite medium was collected from one of the outlets into a collecting device (beaker). The flow rate was kept in the range of 50 mL/min to 150 mL/min. The outlets were kept at gaps of 20 cm height from the bottom. At one point of time, treated water was collected through a single outlet only, while the others were closed using clips. A synthetic solution of chromium was used for testing of the adsorption column.

RESULTS AND DISCUSSION

When an optimum flow rate of 50 mL/ min was maintained, in the treated water collected from 20 cm height from the bottom of the column, the percentage removal of chromium was more than 98% for MO crude extract, 97% for MO aqueous extract and 96% for *Moringa oleifera* seed cake coagulation-flocculation and composite media of kaolinite and sand column adsorption-filtration. It was also observed that the crude extract has a tendency to adsorb a greater amount of chromium ions within a short period compared to MO aqueous extract and MO seed cake coagulants in the hybrid processes of coagulation/flocculation and adsorption/filtration as shown in Fig. 7.

Considering a particular flow rate (50 mL/min), the maximum removal efficiency of chromium was 99.5% at a height of 20 cm from the base of the column and 99%, 97.5% and 95.5% for the heights 40 cm, 60 cm and 80 cm respectively in the case of MO crude extract coagulation-flocculation and composite media of kaolinite and sand adsorption-filtration.

From Fig. 7, it is clear that the MO crude extract coagulation/flocculation followed by composite media of kaolinite and sand adsorption-filtration has a tendency to

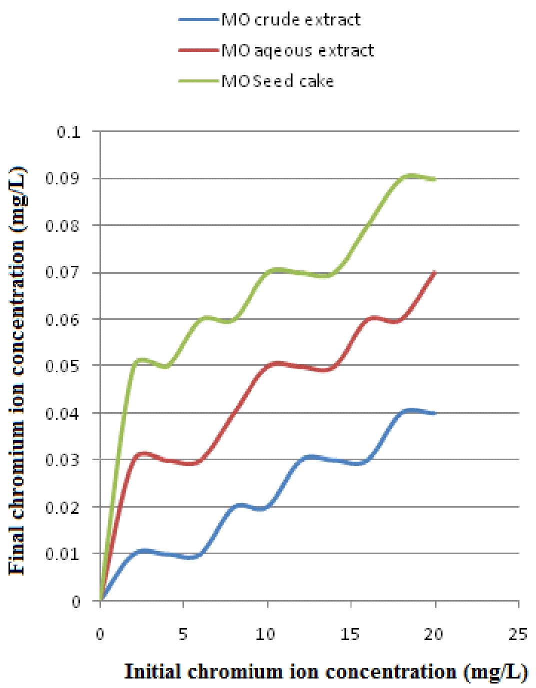

Fig. 7: Final chromium concentrations based on various initial concentrations of chromium with optimum dosage of 2.5 g/L of various MO coagulants and optimum flow rate of 50 mL/min though the composite media of kaolinite clay and sand column adsorption/ filtration.

adsorb greater amount of chromium ions than the aqueous extract or seed cake as coagulant. The hybrid method made of polymer-clay interactions may be used for adsorption of cations, like chromium from the aqueous systems, owing to the large specific surface area of the clay crystallites and the exchangeable ions on the surface provided by the polymer. Polymer interacts physico-chemically with the clays to form the composite. This novel composite action of kaolinite clay and *Moringa oleifera* seed cake polymer increases the removal of chromium ions due to the improved cation exchange capacity during the adsorption process. The process reduced the chromium ion concentrations below 0.05 mg/L in all the cases (2-20 mg/L of initial chromium ion concentrations) and the turbidity after treatment was within the standard limit (<5 NTU).

The use of clay materials with natural polymer (*Moringa oleifera*) coating holds great promise for water treatment. The adsorption capacity of natural and modified clay minerals increases with an increase in the coating of polymer on them. The composite action of clay and polymeric materials in the coagulation/flocculation-adsorption/filtration processes, removes the chromium ions present in the aqueous systems, promise the use of natural materials for emerging contaminant treatment without undesired toxic effects to the ecosystem.

The performance of the clay-polymer complexes in removal of chromium ions was strongly dependent on the conformation adopted by the polycation on the clay surface, the charge density of the polycation itself and the ratio between the concentrations of clay and polymer used during the sorption process. The chromium ion removal by the clay-polymer system was due to the cationic monomers adsorbed on the clay surface, which resulted in a positive surface potential of the complexes and charge reversal.

CONCLUSIONS

The coagulation-flocculation using different *Moringa oleifera* seed coagulant polymers followed by adsorption-filtration through composite media of kaolinite clay and sand column is an environment friendly hybrid method most suitable for the treatment of water containing undesirable chromium ion concentrations. Based on the experimental test results, the following conclusion can be drawn.

The optimum dosage of *Moringa oleifera* coagulants was 2.5 g/L of crude extract for coagulation-flocculation and 50 mL/min flow rate through composite media of kaolinite and sand column adsorption-filtration. It removed maximum concentrations of chromium ions. The removal efficiencies vary between 99.95 and 99.97% and depend on the initial chromium ion concentrations. Final chromium ion concentrations in all the cases were within the limits.

It is an eco-friendly technology which is economically more advantageous than other treatment alternatives. In accordance with the above conclusions, it can be suggested that *Moringa oleifera* coagulation-flocculation and composite media of kaolinite clay and sand media adsorption-filtration process is most suitable for construction of small scale waterworks.

REFERENCES

Awad, Mohammed, Fengting Li and Wang Hongtao 2013. Application of natural clays and poly aluminium chloride for waste water treatment. College of Environmental Sciences and Engineering, 15(2): 287-291.

Aygun, A. and Yilmaz, T. 2010 Improvement of coagulation-flocculation process for treatment of detergent wastewaters using coagulant aids. International Journal of Chemical and Environmental Engineering, 1(2):97-101.

Bulut, Yasemin and Tez, Zek 2007. Removal of heavy metals from aqueous solution by sawdust adsorption. Science Direct/Journal of Environmental Sciences, 19: 160-166.

Das, Nilanjana, Vimala, R. and Karthika, P. 2008. Biosorption of heavy metals-an overview. Indian Journal of Biotechnology, 7: 159-169.

Edogbanya, P.R.O., Ocholi, O.J. and Apeji, Y.A. 2013. Review on the use of plant's seeds as biosorbents in the removal of heavy metals from water. Advances in Agriculture, Sciences and Engineering Research, 3(8): 1036-1044.

Ekebafe, L.O., Ogbeifun, D.E. and Okieimen, F.E. 2012. Removal of heavy metals from aqueous media using native cassava starch hydrogel. African Journal of Environmental Science and Technology, 6(7): 275-282.

Gavhane, Y. N., Gurav, A. S., and Yadav, A. V. 2013. Chitosan and its applications: a review of literature. International Journal of Research in Pharmaceutical and Biomedical Sciences, 4(1): 312-331.

Ize-Iyamu, O.K., Eguavoen, I.O., Egbon, E.E., Ize-Iyamu, O.C., Azih, M.C. and Ibizugbe, O.O. 2013. Physicochemical treatment of brewery sludge with locally sourced coagulants (chitosan and clay). Nigerian Annals of Natural Sciences, 13(1): 008-016.

Jiuhui, Q.U. 2008. Research progress of novel adsorption processes in water purification: a review. Journal of Environmental Sciences, 20: 1-13.

Ndibewu, P. P., Mnisi, R. L., Mokgalaka, S. N., and McCrindle, R. I. 2011. Heavy metal removal in aqueous systems using *Moringa oleifera*: a review. Journal of Materials Science and Engineering, B1(6B): 843-853.

Ravikumar, K. and Sheeja, A.K. 2012. Water clarification using Moringa oleifera seed coagulant. International Conference on Green Technologies(ICGT), Mar Baselios College of Engineering and Technology, Trivandrum, 064-070.

Ravikumar, K. and Sheeja, A.K. 2013a. *Moringa oleifera*: the 2nd generation biodiesel feedstock-prospects for profitable sustainability. National Seminar on Development, Disparity and Social Research, 29-31 January 2013, Christ University Nodal Office, Trivandrum.

Ravikumar, K. and Sheeja, A.K. 2013b. *Moringa oleifera*: A sustainable resource for combating global warming. Proceedings of the National Seminar on 'Impact of Global Warming and Climate Change' jointly organized by Christ University Bangalore and Department of Environment and Climate Change, Government of Kerala, 22-23 February 2013 at Christ University Nodal Office, Trivandrum.

Ravikumar, K. and Sheeja, A.K. 2013c. Fluoride removal from water using *Moringa oleifera* seed coagulation and double filtration. International Journal of Scientific & Engineering Research, 4(8).

Ravikumar, K. and Sheeja, A.K. 2013d. Heavy metal removal from water using *Moringa oleifera* seed coagulant and double filtration. International Journal of Scientific & Engineering Research, 4(5).

Ravikumar, K. and Sheeja, A.K. 2014. Removal of fluoride from aqueous system using *Moringa oleifera* seed cake and its composite coagulants. International Journal of Current Engineering and Technology, 4(3).

Srinivasan, P.T., Viraraghavan, T. and Subramanian, K.S. 1999. Aluminium in drinking water: an overview. Water SA, 25(1): 47-55.

Srinivasan, Rajani 2011. Advances in application of natural clay and its composites in removal of biological, organic, and inorganic contaminants from drinking water. Advances in Materials Science and Engineering.

Syafalni, Rohana Abdullah, Ismail Abustan and Aimi Nadiah Mohd Ibrahim 2013. Wastewater treatment using bentonite, the combinations of bentonite-zeolite, bentonite-alum, and bentonite-limestone as adsorbent and coagulant. International Journal of Environmental Sciences, 4(3): 379.