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Heavy Metals Removal from Wastewater by Using Pomegranate Tannin with the Flocculants

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***Abstract*—Removal of heavy metals from wastewater is difficult and expensive. The use of methods such as reverse osmosis, ion exchange, activated carbon and adsorption is costly. The search of simpler and less expensive method becomes a main research focus. This study aims to adopt a new technique using pomegranate tannin with flocculant to remove heavy metals in urban wastewater .Removal of iron, cooper and zinc is performed. The tannin extracted from the skin of pomegranate is poured in wastewater to be treated .The flocculant is added after 30mn at 12h so that metals are combined with flocks that are removed by filtration. Experiments with synthetics solutions at concentrations between 20mg/l and 80mg/l showed the efficiency of method, proven by obtaining colored flocks. The taking of wastewater sample to add tannin and flocculant showed the difference in the amount of iron, copper, and zinc in wastewater, before and after treatment. Wastewaters between 0,54mg/l and 3,41mg/l of heavy metals are treated. Yields can reached up to 94.72%. At a high temperature with vigorous stirring, treatment can happen very quickly. This technique of wastewater treatment removes the metallic cations to a very low amount. It is a technique that preserves the environment; less expensive, durable and adapt to classical techniques of water treatment by the use of flocculants.**

***Index Terms*— Flocculant, Metals, Tannin, Wastewater**

I.INTRODUCTION

Water management is an essential project for most countries in the world. The presence of chemical industries and the evolution of current technology cause pollutions on groundwater and oceans. Population growth causes the increase in the volume of wastewater, while appropriate treatment techniques are expensive. Urban wastewater can contain lots of toxic substances that are dangerous for environment .Wastewater containing of a large amount of heavy metals entails risk to the environment and human health. [1]_[2] . Treatment of contaminated wastewater with chemicals substances such as hydroxides and sulphates is expensive. It is performed by precipitation or by chelation. The precipitations need the variation of pH of wastewater to be treated to match the pH of precipitation. It requires other products and chooses the type of wastewater to be treated. The use of chelators such as trimercaptotriazine and sodiumthiocarbonate causes serious impacts on the environment [3]. Other methods such as reverse osmosis, ion exchange, activated carbon, or membrane are expensive. The search of simpler and less expensive method becomes a main research focus [3].The use of low-cost adsorbents such as kaolinite [4], ,zeolites [5], and shells of aragonite [6] is performed but the search of products to use, the method and waste management are still difficult. It is very interesting to find a method of simple and less expensive by use of vegetable extracts .The technique using tannin of pomegranate is invented for the resolution of this problem.

Technique of removal of Fe, Cu, and Zn by using tannin of *Punica granatum* (pomegranate) is to eliminate these toxic and unwanted minerals in wastewater by a simple and less expensive method. Tannins of pomegranate are water soluble; which can decompose gallic and ellagic acid in aqueous solution [7].These tannins or tannic acids are able to fix metallic cations to be coagulated or flocculated by the flocculant. The objective of this study is to adopt a new technique for wastewater treatment, using pomegranate tannin with the flocculant.

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II. METHODS

A. Principle of the Method

The tannin solution is poured into the processed water sample. After stirring, the sample is left standing about 30 minutes at 12h. The flocculant is then poured and followed by stirring. Metals eliminated combine with flock; the filtration separates treated water and flock (Fig.1).The treatment may be carried out for all pH of water to be treated chosen (pH= 6, pH =7, pH=8).

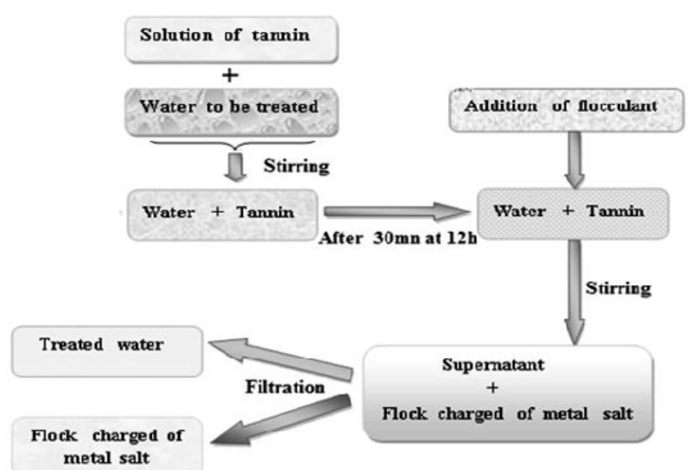


Fig. 1. Principle of the method

The pomegranate tannins , punicalin, punicalagin and pedunculagin [8] _ [9] can be decomposed into gallic acid and ellagic acid by hydrolysis. These acids and tannins fix metallic cations and become colloids, in aqueous solution.

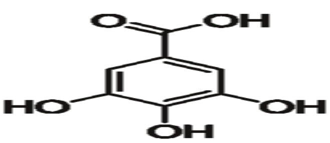


Fig. 2*:* Gallic acid

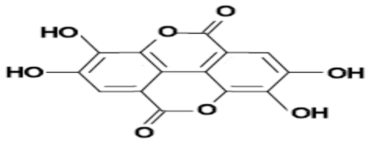


Fig. 3: Ellagic acid

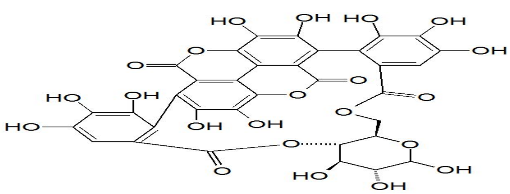


Fig. 4: Punicalin

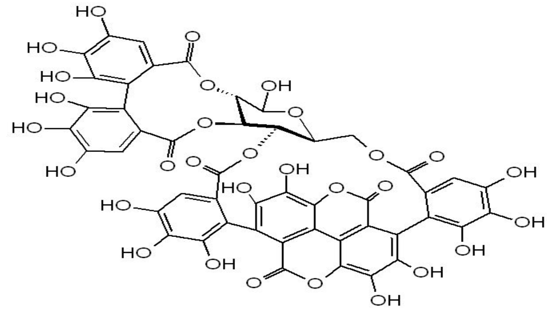


Fig.5: Punicalagin

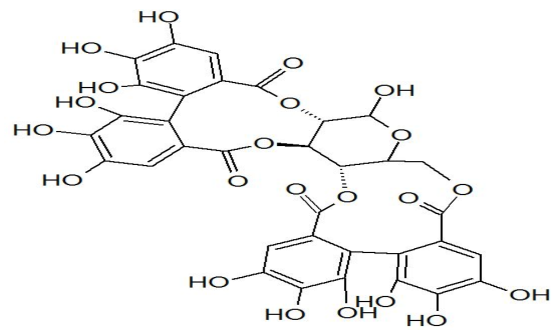


Fig. ***6:*** Pedunculagin

Following Krekel hypothesis [7] , gallic acid fix Fe^{2+} according to the reactions *:*

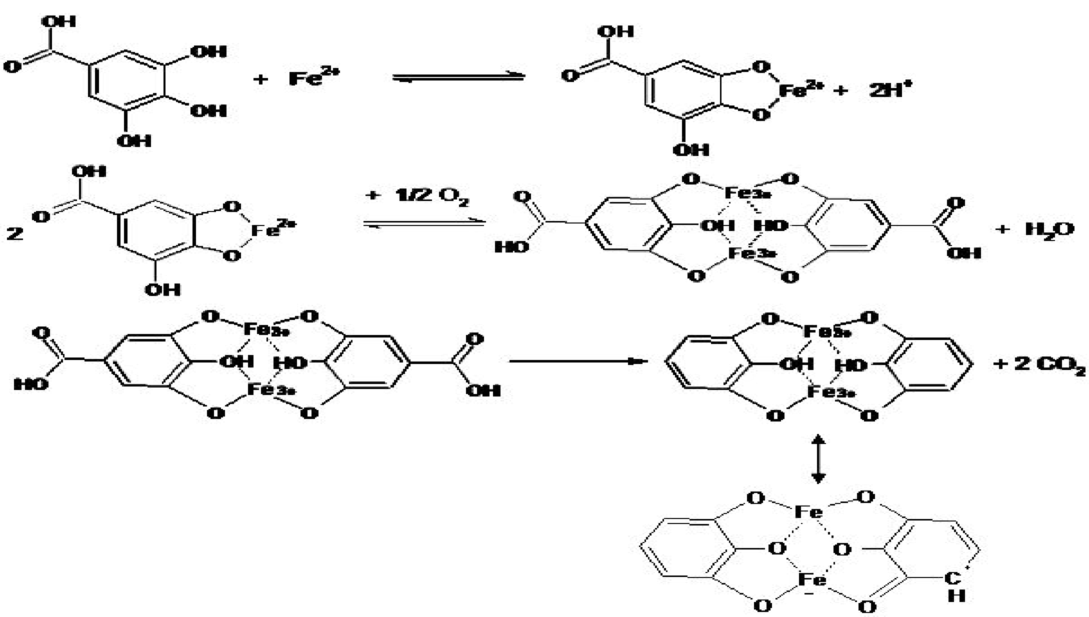
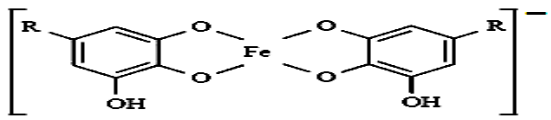


Fig. 7. Fixation reaction of Fe^{2+} by gallic acid according to Krekel

For the fixing of Fe^{3+} by tannins ;according to Afidah and Jain [10] the reactions are :

$$\text{Tannin-2OH} + Fe^{3+} \rightarrow (\text{Tannin-2O-}Fe^{3+})^{+} + 2H^{+}$$

$$\text{Tannin-2OH} + (\text{Tannin-2O-}Fe^{3+})^{+} \rightarrow (\text{2Tannin-4O-}Fe^{3+})^{-} + 2H^{+}$$



R: The other part of the tannin molecule

Fig. 8. Iron-tannate bis-complexes, according to Afidah and Jain

The same reactions are also possible for zinc and copper. These reactions show the obtaining of complex negatively charged or neutral charge with charge transfer. The color of complex is obtained according to the nature of fixed cation. These complexes have different properties compared with tannins and its hydrolysis products. Their charge leads them to the same property with colloids of suspended matter of raw water which become flock under the action of flocculants.

The steps of reaction and the property of the molecules of tannin and its hydrolysis products entail a low speed of fixing reaction for obtaining colloids.

B. Effect of Temperature and Agitation

The temperature and agitation have a very important role for chemical reactions. These two parameters have a relation to the rate of reaction; they determine the rate of wastewater treatment in this method. In the absence of agitation and at ambient temperature (25°C), the formation of complex reached up to 12hours in water.

The increasing in temperature leads to a high mobility of ions in solution and promotes chemical reactions. Also, agitation is important for contact between metallic cations and tannins proceeds rapidly. The low temperature and stirrings slow down chemical reactions and cause a loss of time for water treatment.

C. Sampling

- *Preparation of Tannin Solution*

Tannin used is an extract from the skin of pomegranate fruit grown in the highlands of Madagascar. It is extracted by maceration. The skin of fruit is cleaned; cutting into pieces by steel knife and weighing. Then, pieces are macerated in distilled water [11] for three days .The tannin solution was obtained after stirring and filtration. This solution is relatively stable; it can retain its chemical properties for several days without any preservative system.

- *Preparations of Flocculants*

In this work, aluminium sulphate ,*Opuntia dillenii* sap and *Moringa oleifera* seed are used as flocculants. The solid grains of aluminium sulphate are used to dissolve in wastewater to be treated. *Opuntia sap* is prepared by milling, extraction by pressing and filtering. The resulting solution can maintain its characteristics in a few days [12]_[13] . For the *Moringa* seeds , it passed by grinding , sieving and weighing to be fine powders . This powder is introduced in water to be treated. The protein is the molecule responsible of flocculation for this flocculant [14]_[15].

- *Preparations of Distilled Water Charged of Metals Salt*

The solutions are prepared by dissolving metals salt (2+ and 3+) in distilled water. Salts of Fe, Cu, and Zn are chosen, since they are almost the same reactions on fixing with tannins. The 3+ metal salts are prepared from solid rusts metal [16]. Rusts metals sprayed for purposes powders. The obtained powders are then prepared in distilled water after weighing. Stirring is carried out for about 30 minutes so that the metal powder becomes 3+ ions soluble in distilled water. After the centrifuge, sediments are weighed after separation with water and drying. The mass of soluble metal is obtained by the difference in mass of metal salt added and the mass of residue sediment. The mass of added metal and the volume of distilled water are varied for the desired mass of soluble metal. The powders are taken separately according to the nature of metal. The distilled water containing a well-defined mass of metal is used in the experiments.

Metal salts 2+ are obtained from samples of $FeCl_2$, $CuCl_2$, and $ZnCl_2$. They are dissolved in distilled water [17] by stirring after weighing. After the passage of solution to the centrifuge, the residual sediment is weighed after separation with water and drying .The mass of soluble metal is obtained by the difference in mass of metal salt added and the mass of residue sediment .The distilled water containing a well-defined mass of metal is used in the experiments. The mass of added metal and the volume of distilled water are varied for the desired mass of soluble metal.

- *Mixture of Metals*

The technique of atomic absorption by flame emission is used for the determination of metals concentration in water [18]. In this technique, the water sample was sprayed into a flame .The lamp light source delivers radiation characteristic lines consisting of the analyte. The light beam then falls on the flame in which the atoms are “target”. In addition, the monochromator is used to select a band of wavelength or energy corresponding to the analyte .The absorbance of the atoms is obtained from transmitted intensity measured by the detector. Absorbance and concentration are related by etalonage curve.

Taking wastewater samples was made in different places: Evacuation channels of a big city, paint industry discharges and rejection of electric battery factory. The samples are filtered before being used in the experiment.

The materials used are: Thermometer, precision balance, conductivity meter, shaker, centrifuge and systems jar-test.

III. RESULTS AND DISCUSSION

In this section, experiments are carried out with tannin solution at 3.55 ms /cm of conductivity, extracted from 100g of pomegranate skin in 300ml of distilled water. *Opuntia* sap at 1,984 ms /cm of conductivity is used. All experiments and measurements were carried out at the ambient temperature (25 ° C).

A. Study of the Action of Flocculant to the Colloidal Solution of Pomegranate Tannin

At the beginning of the experiment, tests were performed for the action of flocculant to the tannin in water. 100 ml of distilled water is taken to add tannin and flocculant, the results are given in Table 1 below.

Table 1. Tests results of flocculation of a tannin colloidal solution

Flocculant used	Tannin added (ml)	Observation
Aluminium sulphate (2g)	0.5	No flock
	2	No flock
	4	No flock
Opuntia sap (3ml)	0.5	No flock
	2	No flock
	4	No flock
Moringa seed (2g)	0.5	No flock
	2	No flock
	4	No flock

From this experiment (Table1), the flocculants can not coagulate or flocculate the tannin solution. They can not flocculate tannin in aqueous solution.

Tannins and its hydrolysis products are neutral charge molecules (no charge). In aqueous solution, the presence of cations, protein or long molecular chains of flocculants can not group or agglomerate molecules dispersed in solution. The flocculation is not possible for the tannins and its hydrolysis products in aqueous solution.

B. Power Rating of Flocculant to the Colloidal Solution of Tannin with Metallic Salts in Aqueous Solution

In the rest of the experiment, metallic salts (2+and 3+) were used. They are introduced into 100 ml of distilled water so that water contains metallic ions. Solutions of concentrations at 20mg/l to 80mg/l are taken. The experiment was carried out by addition of tannin (2ml), followed by addition of flocculant after agitation (following the principle of the method).The results are shown in the tables below.

Table 2. Effects of the addition of tannin followed by flocculant for distilled water added of iron salts

	Flocculant used														
	Aluminium sulphate (1g)					***Opuntia* sap (2ml)**					***Moringa* seed (2g)**				
Soluble Fe^{2+} salt added (mg)	2	3	5	6	8	2	3	5	6	8	2	3	5	6	8
Amount of flock observed	++	+++	++++	+++++	++++++	+	++	+++	++++	+++++	+	++	+++	++++	+++++
Flock color	Green					Green					Green				
Soluble Fe^{3+} salt added (mg)	2	3	5	6	8	2	3	5	6	8	2	3	5	6	8
Amount of flock observed	++	+++	++++	+++++	++++++	+	++	+++	++++	+++++	+	++	+++	++++	+++++
Flock color	Blue black					Blue black					Blue black				

Table 3. Effects of the addition of tannin followed by flocculant for distilled water added of copper salts

	Flocculant used														
	Aluminium sulphate (1g)					***Opuntia* sap (2ml)**					***Moringa* seed (2g)**				
Soluble Cu^{2+} salt added (mg)	2	3	5	6	8	2	3	5	6	8	2	3	5	6	8
Amount of flock observed	++	+++	+++ +	++++ +	+++++ +	+	++	+++	+++ +	++++ +	+	++	+++	+++ +	++++ +
Flock color	Blue yellow					Blue yellow					Blue yellow				

Soluble Cu^{3+} salt added (mg)	2	3	5	6	8	2	3	5	6	8	2	3	5	6	8
Amount of flock observed	++	+++	+++ +	++++ +	+++++ +	+	++	+++	+++ +	++++ +	+	++	+++	+++ +	++++ +
Flock color	yellow					yellow					yellow				

Table 4. Effects of the addition of tannin followed by flocculant for distilled water added of zinc salts

	Floculant used														
	Aluminium sulphate (1g)					***Opuntia* sap (2ml)**					***Moringa* seed (2g)**				
Soluble Zn^{2+} salt added (mg)	2	3	5	6	8	2	3	5	6	8	2	3	5	6	8
Amount of flock observed	++	+++	+++ +	++++ +	+++++ +	+	++	+++	+++ +	++++ +	+	++	+++	+++ +	+++++ +
Flock color	yellow					yellow					yellow				
Soluble Zn^{3+} salt added (mg)	2	3	5	6	8	2	3	5	6	8	2	3	5	6	8
Amount of flock observed	++	+++	+++ +	++++ +	+++++ +	+	++	+++	+++ +	++++ +	+	++	+++	+++ +	+++++ +
Flock color	yellow					yellow					Yellow				

$^{+}$: Little flock
$^{++++++}$: Big splat

From Tables 2, 3**,** and 4, the presence of metallic cations in distilled water causes formations of colored colloids by the action of tannin. These colloids are tannates metals; they are flocculated by the flocculant. The amount of flock obtained depends on the quantity of metallic cations soluble in the distilled water. When the amount of soluble metallic salts increases, the volume of resulting flock also increases. So the metallic cations become flocks by addition of tannin and flocculant.

The fixing of metallic cations transforms the property of tannins and its hydrolysis products in aqueous solution. The final complexes obtained are negative or neutral charge with charge transfer. These complexes with charge transfer are identified for the fixing of Fe^{3+} and Fe^{2+} by the blue-black and green color of colloids. Under the action of cations, proteins,or long molecular chains of flocculants, complexes agglomerate to form flocks.

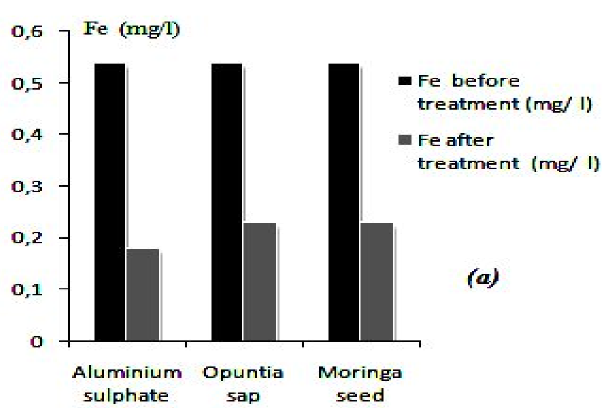
C. *Taking Water Samples*

In the last step, water samples are taken .The treatments are performed by using the following flocculant: aluminium sulphate , *Opuntia* sap and *Moringa* seed. The mineral content is measured before and after treatments. Yields are calculated by the formula:

$$\text{yield}\ (\%) = \left[1 - \frac{\text{Concentration after treatment (mg/l)}}{\text{Concentration before treatment (mg/l)}} \right] \times 100$$

Table 5: Treatments of water discharge of channels responsible of 0.54mg / l of iron

Flocculant	Fe before treatment (mg/ l)	Fe after treatment (mg/l)	*Yield (%)*
Aluminium sulphate	0.54	0.18	**66.6**
Opuntia sap	0.54	0.23	**57.40**
Moringa seed	0.54	0.23	**57.40**



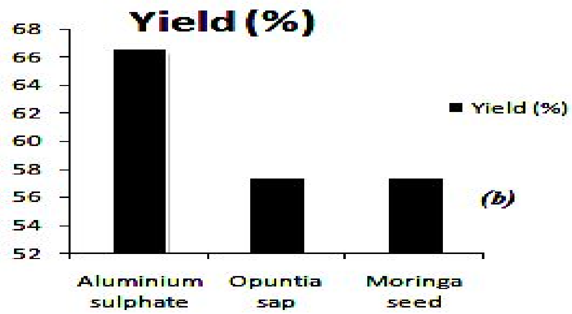
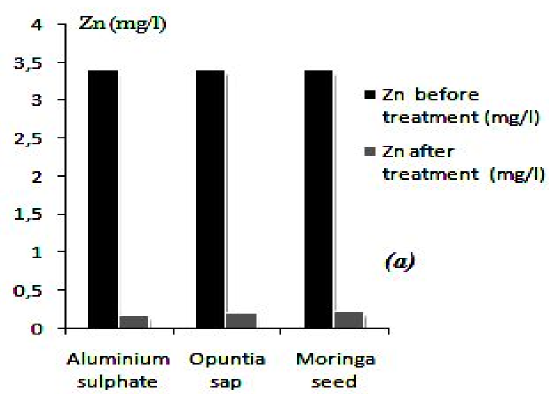


Fig. 9: Variations of iron 0.54mg / l after treatment (a) and yields for three flocculants used (b)

Table 6: Industrial wastewater responsible of 3.41mg / l of zinc treated by use of aluminum sulphate, *Opuntia* sap and *Moringa* seeds

Flocculant	Zn before treatment (mg/ l)	Zn after treatment (mg/l)	*Yield (%)*
Aluminium sulphate	3.41	0.18	**94.72**
Opuntia sap	3.41	0.21	**93.84**
Moringa seed	3.41	0.22	**93.54**



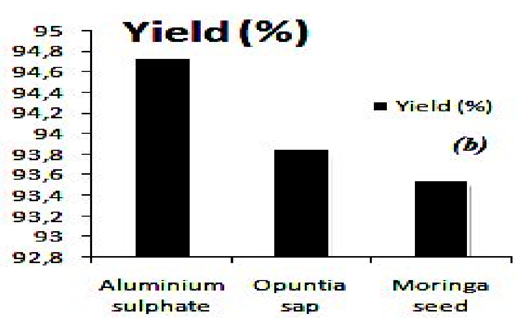
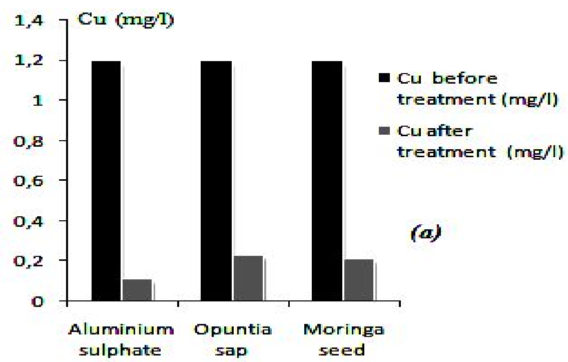


Fig. 10: Lowering of the amount of Zn 3.4mg / l after treatment (a) and yields for three flocculants used (b)

Table 7: Treatment of wastewater discharge of factory 1.20 mg / l of copper

Flocculant	Cu before treatment (mg/ l)	Cu after treatment (mg/l)	*Yield (%)*
Aluminium sulphate	1.20	0.11	**90.83**
Opuntia sap	1.20	0.23	**80.83**
Moringa seed	1.20	0.21	**82.50**



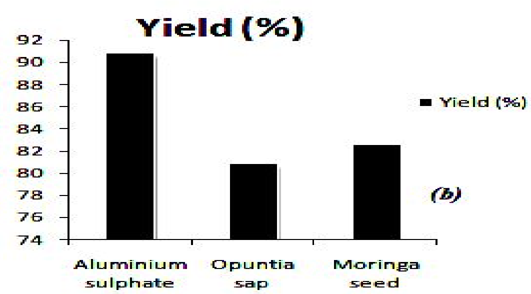


Fig. 11: Effects of treatment for water sample 1.20mg /l of Cu (a) and yields for three flocculants used (b)

The concentration of metal in wastewater decreases after treatment. The iron at 0,54 mg / l in water drainage channels decreases to 0,18 mg / l; the zinc at 3.41mg / l varies to 0.18mg /l for industrial wastewater and copper at 1.20 mg / l decreases to 0.11 mg / l for discharge factory. There was a decreasing in the rates of metals for all wastewater samples after treatment; this decreasing was dependent on the nature of flocculant used. Major reduction is achieved in the use of aluminium sulphate.

About the yields obtained, their variation depends on the initial concentration of metal cation in water and the type of flocculant used. Residuals are due to different factors: low agitation, effect of temperature, chemical composition and nature of flocculant used. The aluminium sulphate which is a better flocculant results in better performance than other two which are organic flocculants.

The results of processing obtained by taking wastewater samples proved the characteristics of complex (tannin-metal) able to flocculate by the flocculant. Other ionic compositions in wastewater and the pH value did not prevent the fixing reaction of cations (Fe, Cu and Zn) to form colloids. These colloids are flocculated by the flocculant.

The use of distilled water containing metal cations (water of high concentration of cation) and the taking of wastewater samples (water of low cation concentration) justify that the method is applicable for various metal concentrations of wastewater. It is effective for the removal of iron, copper and zinc in any type of wastewater.

To identify processing efficiency, the conductivity is measured for 100ml of two clear wastewater samples, added with flocculants and 0.5ml of tannin.

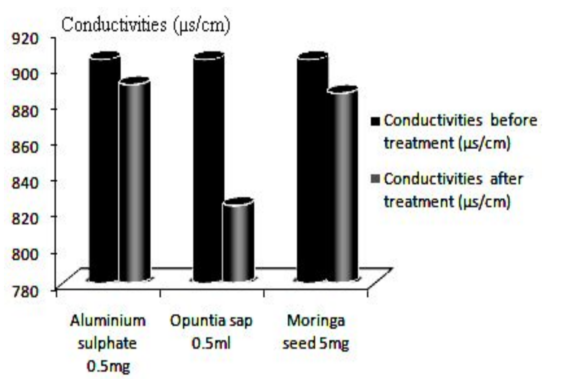


Fig. 12: Conductivities change in 904.3µs/cm of water

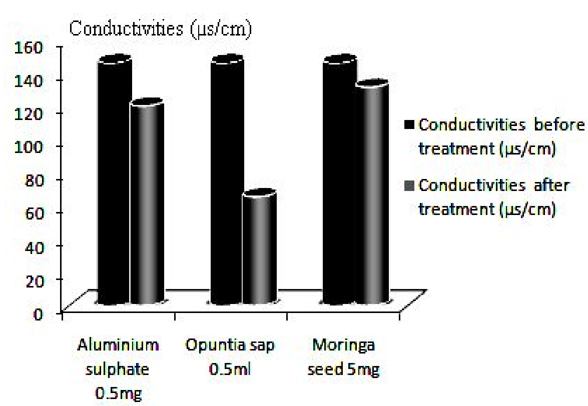


Fig. 13: Conductivities change in 146.2 µs/cm of water

After treatment, the conductivities of wastewater samples decrease, even if flocculant was added with tannin. Metal cations are trapped by the action of tannin and flocculant. Some part of ions in wastewater sample remains in the flocks. This decreasing in conductivity has a relationship to the variation rate of minerals Fe , Cu and Zn in wastewater samples. It marks the decreasing in the amount of components dissolved in water. Then the method with tannin is very effective. It is applicable to any type of water without varying pH or property of water to be treated.

Comparing to technical using chemicals such as precipitation (CaO, H_2S, $Ca(OH)_2$, trimercaptotriazine, potassiumethyl xanthate, ...), this technique is simple and less expensive. The techniques by chemical precipitation (CaO, H_2S, Ca $(OH)_2$) require a pH range for precipitation. The precipitates obtained are treated in great difficulty. Other techniques (trimercaptotriazine, sodiumthiocarbonate ...) causes environmental risks and others (zeolites , kaolinite ...) are difficult for application and the search of product. The technique with granada tannins offers the ability to treat wastewater charged of Cu, Zn and Fe has a very low-cost without pH change of water by exploiting the natural resources. It is a technique that preserves the environment. It is durable and adapts to classical techniques of water treatment by the use of flocculants .The flocks obtained are exploitable in other use (ink, paint ...).

IV. CONCLUSION

In this work the method of treatment used tannins extracted from the skin of pomegranate to trap metals Cu, Zn, and Fe in wastewater .Flocculants are used to flocculate the resulting complexes and easy separation of water.

The new technique with tannin of pomegranate can easily remove salts of iron, copper, and zinc in wastewater. It is simpler, less expensive, durable and preserves the environment, compared to other techniques like chemical precipitation, reverse osmosis, ion exchange, adsorption and activated carbon technique. For stations of water treatment that perform the steps of screening, coagulation flocculation, sedimentation, filtration and disinfection; the method can be carried out by addition of tannin before coagulation flocculation.

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