Use of non-Conventional Material to Remove Cu^{+2} ions from Aqueous Solutions using Chemical Coagulation

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ABSTRACT

Coagulation - flocculation are basic chemical engineering method in the treatment of metal-bearing industrial wastewater because it removes colloidal particles, some soluble compounds and very fine solid suspensions initially present in the wastewater by destabilization and formation of flocs. This research was conducted to study the feasibility of using natural coagulant such as okra and mallow and chemical coagulant such as alum for removing Cu and increase the removal efficiency and reduce the turbidity of treated water. Fourier transform Infrared (FTIR) was carried out for okra and mallow before and after coagulant to determine their type of functional groups. Carbonyl and hydroxyl functional groups on the surface of okra and mallow were the major groups responsible for coagulation process. By using alum (conventional coagulants), okra and mallow (as a primary coagulant or in combination with the other two primary coagulants) and by the jar testing, the optimum pH-value and dose of the coagulants were determined. The results indicated that the optimal pH values were 6.7, 8 and 6 for alum, okra and mallow, respectively. Mathematical modeling show significant results (sig.<0.05) for the % Cu removal (dependent variable) with respect to coagulant dose (independent variable) for the okra as a primary coagulant, alum with okra and alum with mallow as binary coagulants and alum, okra and mallow as ternary coagulants .

Keywords: Heavy metal; coagulant; jar test; flocculation.

استخدام المواد غير التقليدية لإزالة ايونات النحاس من المحاليل المائية بطريقة التخثير الكيميائي

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الخلاصة

ان عمليتي التخثير والتلبيد تلعبان دورا رئيسين ومهمين في معالجة المياه الملوثة والمياه الصناعية الملوثة ايضا من حيث ازالة المعادن الثقيلة مثل (النحاس) والمواد العالقة الذائبة من هذه المياه لخطورتها وسميتها للبيئة والصحة العامة. ومن الاساس ان تكون نسبها ضمن المحددات البيئية العالمية والمحلية المسموح بها. في هذا البحث تم استخدام

مواد محلية ناتجة من النفايات الرخيصة الطبيعية والصديقة للبيئة مثل (مخلفات الباميا, اوراق الملوخية) كمخثرات لإزالة المعادن الثقيلة بطريقة **اختبار الجرة** .اضافة الى استخدام الشب الذي يعتبر من اكثر هذه المخثرات استخداما في هذه العمليات وقد استخدمت هذه المواد في هذه العملية لغرض زيادة وتحسين نسبة الازالة للعناصر الثقيلة وكذلك لتقليل نسبة العكورة الناتجة .حيث تم اجراء فحص التحليل الكيفي لورق الملوخية و مخلفات الباميا باستخدام جهاز الاشعة تحت الحمراء لغرض دراسة المركبات الكيميائية والمركبات المؤكسدة ومعرفة المجموعات الفعالة للمركبات العضوية مثل المجموعات الامينية الكربوكسيلية، الهيدروكسيل و الكربونيل على عملية التخثير والتلبيد .كما تمت دراسة العوامل المؤثرة على عملية التخثير مثل قيمة الدالة الحامضية وكمية المواد المخثرة .ومن خلال نتائج البحث تبين ان قيم الدالة الحامضية المثلى كانت6.7, 8, 6 لكل من الشب والباميا وورق الملوخية على التوالي. كما تم تطبيق موديل رياضي by SPSS (Multiple linear regression analysis) للمقارنة بين هذه المخثرات من حيث المعنوية واللامعنوية. هذا وتحتل عملية الفصل بالتخثير والتلبيد مكانة كبيرة باعتبارها تقنية واعدة في تكنولوجيا المياه النظيفة ومعالجة المياه الملوثة.

الكلمات الرئيسية: المعادن الثقيلة؛ المخثرات؛ جهاز فحص الجرة؛ التلبيد.

1. INTRODUCTION

As a result of industrial activities and technological development, the amount of heavy metal ions discharged into streams and rivers by industrial and municipal wastewater have been increased incessantly. Heavy metals are member of a loosely-defined subset of elements that exhibit metallic properties, which mainly includes the transition metals, some metalloids, lanthanides, and actinides. Heavy metals such as copper, lead and zinc are main toxic pollutants in industrial wastewater, and they also become major surface and ground water contaminants. Heavy metals are discharged by various industries such as metal purification, metal finishing, chemical manufacturing, mining operations, smelting, battery manufacturing, and electroplating **lssabayeva et al., 2010**. Removal of heavy metals from industrial wastewater is of primary importance because they are not only causing contamination of water bodies and are also toxic to many life forms. Most heavy metals are cations, carrying a positive charge, such as zinc, lead, copper, nickel and cadmium. Soil particles tend to have a variety of charged sites on their surfaces, some positive while some negative. The negative charges of these soil particles tend to attract and bind the positively charged metal cations, preventing them from becoming soluble and dissolve in water. The soluble form of metals is more dangerous because it is easily transported, hence more readily available to plants and animals. Metal behavior in the aquatic environment is surprisingly similar to that outside a water body. Sediments at the bed of streams, lakes and rivers exhibit the same binding characteristics as soil particles mentioned earlier. Hence, many heavy metals tend to be sequestered at the bottom of water bodies. The aquatic environment is more susceptible to the harmful effects of heavy metal pollution. Metal ions in the environment bioaccumulation and are biomagnified along the food chain. Therefore, their toxic effect is more pronounced in animals at higher trophic levels **Ahluwalia and Goyal, 2005**. During the last years, rapid growth of population, urbanization, and industrial as well as agricultural activities have increased water demand, particularly in recent decades. Water treatment industry is among the most important industries in many countries. Coagulation, flocculation, sedimentation, filtration and disinfection are the most common treatment processes used in the production of drinking water. Coagulation/flocculation processes are of great importance in solid-liquid separation practice **Yukselen and Gregory, 2004**.

1.1 Coagulation

Coagulation is the process by which colloidal particles and very fine solid suspensions initially present in water are combined into larger agglomerates that can be separated via sedimentation, flocculation, filtration, centrifugation or other separation methods. Coagulation is commonly achieved by adding different types of chemicals (coagulants) to the water to promote destabilization of the colloid dispersion and agglomeration of the resulting individual colloidal particles. The addition of some common coagulants to water not only produces coagulation of colloids but also typically results in the precipitation of soluble compounds, such as phosphates, that can be present in the water. In addition, coagulation can also produce the removal of particles larger than colloidal particles due to the entrapment of such particles in the flocks formed during coagulation **Metcalf and Eddy, 2003**. This is achieved by rapid mixing of a coagulant in solution for short durations in order to achieve complete and uniform coagulant dispersion. Insufficient coagulant mixing may result in uneven coagulant dispersion throughout the solution, resulting in the presence of too much coagulant in certain areas and too little in others thereby degrading the overall process. Coagulant over-mixing on the other hand is not believed to have an effect on coagulation performance **Horne, 2005; Bratby, 2006** .

2. EXPERIMENTAL

2.1 Materials

Analytical grade reagents were used in the experimental studies. Copper Sulfate pent hydrated ($CuSO_4.5H_2O$) from (E. MERK, Denmark) were used for preparing synthetic solutions. The properties of metal salts are given in **Table 1**. Adjustments of pH were carried out by using 0.1N HCl and 0.1N NaOH.

2.2 Coagulants

2.2.1 Alum

Alum was used as a coagulant for the removal of heavy metal. The alum was milled, sieved and particles sizes ≤ 0.6 mm were selected for the investigation.

2.2.2 Mallow

Mallow leaves were washed with tap water then distilled water, dried at 50°C for 24 hours in the oven to remove the moisture content until constant weight. The dried mallow was milled, sieved and particles size ≤ 0.6 mm were selected for the investigation.

2.2.3 Okra

Okra pods were washed with tap water then distilled water, dried at 50°C for 24 hours in the oven to remove the moisture content until constant weight. The dried okra was milled, sieved and particles size ≤ 0.6 mm were selected for the investigation.

2.3 General Description for the experimental procedure

Experiments had been carried out to find the optimum pH, and optimum dose. The procedure involved filling the beakers with 1 L of heavy metal ion solution of 0.47 mg/L. Primary doses of (0, 0.35, 0.7, 1.4, 2.1, 2.8) g/L for alum and (0, 0.2, 0.4, 0.5, 0.6, 0.7) g/L for okra or mallow, respectively were added into the beakers. The suspensions were stirred rapidly (300 rpm) for 1 minute at G (275 S^{-1}) to ensure adequate mixing. The rapid

mixing, then followed by slow mixing (50 rpm) for 15 minutes at G (16 S^{-1}) were performed to achieve opportunity for particle collisions and aggregate formation,
Sulaymon et al., 2009. Experiments were carried out at initial pH values (5, 6, 6.7, 7, 8 and 9). The suspension was then allowed to settle for 15 minutes, and the sample is drawn at 6 cm depth from the supernatant to measure % Cu removal, and % residual turbidity. For the binary coagulants combinations, the optimum dosages from the primary experiments, that are having the highest % Cu removal were selected. Combined binary doses of alum with okra or mallow of different percentages were used. The above procedure was repeated to estimate the optimum pH and dose for the highest %Cu removal. In the ternary coagulants combinations, the optimum doses and PH the binary experiments, that give the higher % Cu removal were selected. Combined ternary doses of alum, okra and mallow of different percentages were used. The procedure was repeated. Settling velocity, % residual turbidity, and conductivity for the selected optimum pH and coagulant dose combination were conducted and measured.

3. Results and Discussion

3.1 FTIR Result

In order to understand the possible coagulant- metal ion interactions, it is essential to identify the functional groups present in this process. The main effective binding sites can be identified by FTIR spectral comparison of the coagulant. Coagulants were examined using (Shimadzo FTIR, 800 series spectra- photometer). Two flasks were filled with 1000 ml of the metal solution and 1gm of (okra and mallow), then placed in the jar and agitated continuously (1 minute for rapid mixing and 15 minute for slow mixing). Samples of the coagulant materials were dried by sun for 48 hours before FTIR tests., from **Fig. 1**. The FTIR spectral indicate the presence of amino, carboxylic, hydroxyl and carbonyl groups. Contribution of each functional group in this process is summarized in Table 2. Mallow before test have greatest changes in the peak values of bands than okra before test, while the okra after test was the lowest one.

3.2 Primary Coagulant Experiments

3.2.1 Optimum pH Values

Samples of collected distilled water with Cu were placed in beakers and subjected repeatedly to a standard jar test using the following coagulants:-
1-Alum [$Al_2(SO_4)_3.18H_2O$] at a dose 1400 mg/L
2-Okra at a dose 500 mg/L
3-Mallow at a dose 500 mg/L
Each beaker in the set of the standard jar test apparatus had its pH adjusted to different values (5, 6, 6.7, 7, 8, and 9).
Fig. 2 shows the effect of pH on the % removal of Cu in which generally, the % removal of Cu for alum>Okra>mallow.

3.2.2 Optimum Coagulant Dose

Jar tests were conducted to find the optimum coagulants doses, at the optimum pH 6.7, 8.0, 6.0 for alum, okra, and mallow. The results are shown in **Figs. 3, 4 and 5** respectively.

3.2.3 Effect of Coagulant Dose

The effects of different dosages of alum, okra and mallow are shown in **Figs. 3, 4, and 5**. The % removal of Cu increased with the increasing doses of the coagulants. It is observed that when the doses of alum, okra and mallow were greater than 1400 mg/L, 500 mg/L and 500 mg/L, respectively, the removal increased slowly. Thus, the optimum doses of alum, okra and mallow were 1400, 500 and 500 mg/L for the highest removal of heavy metal each in its related optimum pH value. These results are mainly due to the fact that the optimum coagulant dosage produces flocs that have a good structure and consistency. But in dosages lower and higher than optimum dosages, the produced flocs are small and influence the settling velocity of the sludge. A comparison between alum, okra and mallow for the removal of Cu at the optimum conditions, then relative abundance of coagulants after treating distilled wastewater with Cu followed the order: mallow>okra>alum as shown in **Fig. 6.**

3.3 Binary Combination Coagulants Experiments

The combination of alum as a primary coagulant with another coagulant aid (okra or mallow) for removal Cu were carried out and tabulated in **Table 2**.

3.4 Ternary Combination Coagulants Experiments

The combination of alum as a primary coagulant with another two coagulant aids (okra and mallow) for removal Cu were carried out and tabulated in **Table 3**.

3.5 Variation of Turbidity with Dose

Figs. 7, 8, and 9 show the residual turbidity with dose for the primary, binary and ternary coagulants, in which the residual turbidity decreased as the dose of coagulant increased.

3.6 Variation of Conductivity with Dose

Fig. 10 shows the variation of the conductivity with dose for the optimal ternary combination coagulants of pH= 7 and dose 0.725 g/L, the conductivity decreased as the dose increased which indicates that the Cu concentration in the supernatant becomes lower by increasing the coagulant dose.

3.7 Settling velocity

In the **Fig.11** the settling velocity has been measured through the relation between time and height of interface for each successive points on the curve. **Fig. 12** shows the settling rate-concentration relationship for the optimal ternary combination coagulants of pH= 7 and dose 0.725 g/L by using alum, okra and mallow for Cu (0.47 mg/L).

3.8 Mathematical Modeling

Developing a mathematical model for the coagulation flocculation experiments, and generating quick decision-making information , using powerful statistics (multiple linear regression analysis MLR) by SPSS statistic software package (version 17.0), to understand and show an effective presentation for the results with a high quality of tabular and graphical modeling outputs. Equations of mathematical modeling for primary, binary and ternary coagulants shows in **Table 4**.

4. CONCLUSION:

The following results have been obtained:

1. The optimum coagulant doses in distilled water treatment with Cu concentration (0.47 mg/L) for alum, okra and mallow were 1400mg/L, 500mg/L and 500mg/L respectively.
2. The optimum pH values for coagulants (alum, okra and mallow) were 6.7, 8.0 and 6.0, respectively when used as primary coagulants.
3. Using okra and mallow as coagulant aids with alum (in binary and ternary combinations) cause quicker formation of flocs and that increases their rate of sedimentation.
4. Natural coagulants (when used as primary coagulants) seem to be more effective at higher turbidity levels.
5. Mathematical modeling show significant results (sig.<0.05) for the % Cu removal (dependent variable) with respect to coagulant dose (independent variable) for the okra as a primary coagulant, alum with okra, and alum with mallow as binary coagulants ,and alum, okra, and mallow as ternary coagulants .
6. Mathematical modeling show significant results (sig.<0.05) for the % residual turbidity (dependent variable) with respect to coagulant dose (independent variable) for the alum , okra ,and mallow as a primary coagulant, alum with mallow as binary coagulants ,and alum, okra, and mallow as ternary coagulants .

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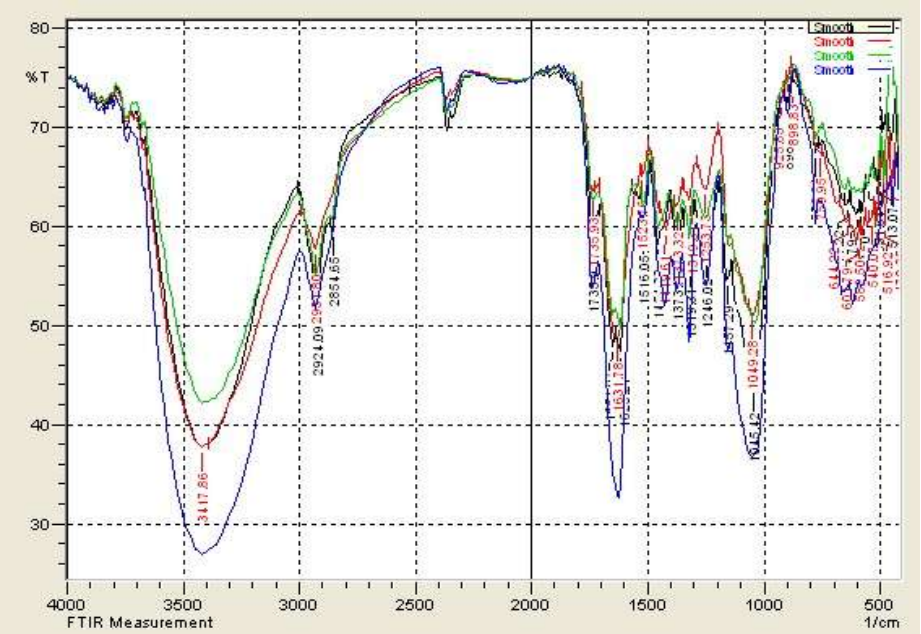

Figure 1. FTIR spectrum for Okra and Mallow before and after tests (• okra before test, • mallow before test•, okra after test, • mallow after test).

Table 1. Properties of metal salt.

Property	Copper sulfate $CuSO_4.5H_2O$
Molar mass g/mol	249.70
Atomic weight g/mol	63.546
Appearance	Blue
Density g/cm^3	2.284

Table 2. Function groups before and after okra and mallow coagulants with Copper ion.

Wave number (cm^{-1}) Okra before test	Assignment Groups	After Coagulation Of Cu	Wave number (cm^{-1}) Mallow before test	Assignment Groups	After Coagulation Of Cu
3417.86	Amides	3421.72	3417.86	Amides	3417.86
2931.80	Carboxylic acids	2927.94	2927.94	Carboxylic acids	2924.09
1735.93	Carboxylic acids, Aldehydes	1735.93	2854.65	Carboxylic acids	2854.65
1631.78	Amides	1624.06	1735.93	Carboxylic acids, Aldehydes	1735.93
1523.76	Nitro groups, Amides	1516.05	1651.07	Amides,lmines	1651.07

1419.61	Aromatics	1423.47	1616.35	Amides	1620.21
1373.32	Alkylhalides, Nitro groups	1373.32	1516.05	Nitro groups, Amides	1516.05
1319.31	Alkylhalides, Nitro groups	1319.31	1454.33	Aromatics	1454.33
1253.73	Alcohols Ketones Alkylhalides	1249.87	1369.46	Alkylhalides, Nitro groups	1373.32
1049.28	Alcohols, Alkylhalides, Phosphines	1053.13	1319.31	Alkylhalides, Nitro groups	1319.31
898.83	Phosphines, Sulfonates	898.83	898.83	Phosphines, Sulfonates	898.83

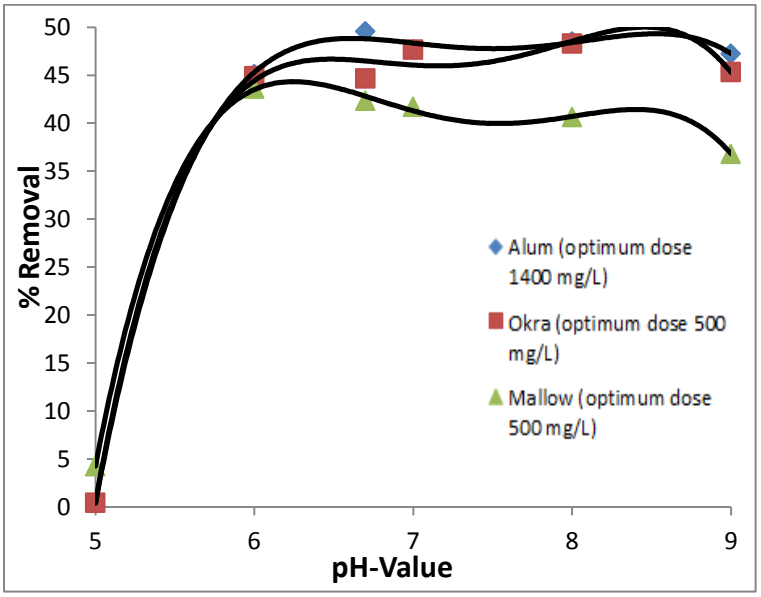

Figure 2. The effect of pH values on the % removal of Cu for the investigated coagulants.

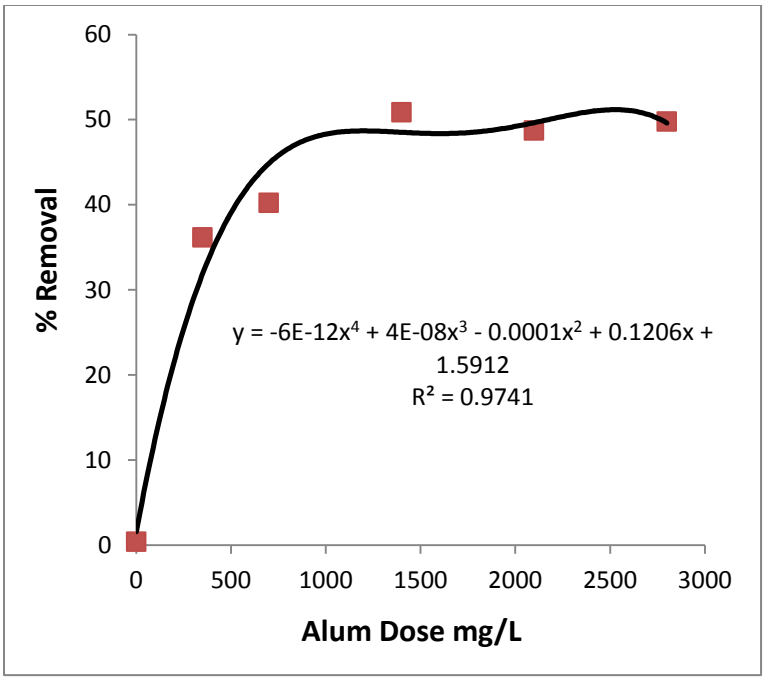

Figure 3. The effect of Alum coagulant dosages at optimum pH of 6.7 on Cu removal efficiencies of investigated coagulant.

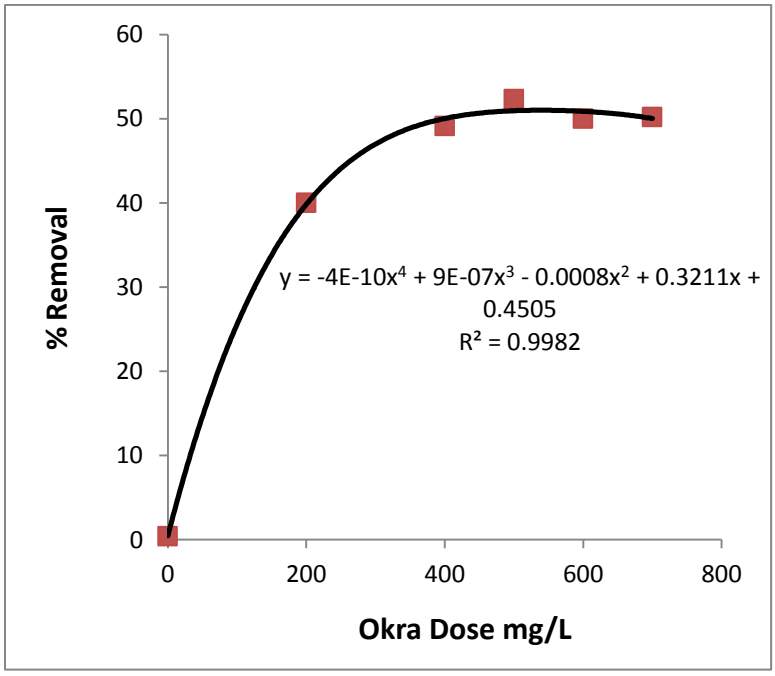

Figure 4. The effect of Okra coagulant dosages at optimum pH of 8.0 on Cu removal efficiencies of investigated coagulant.

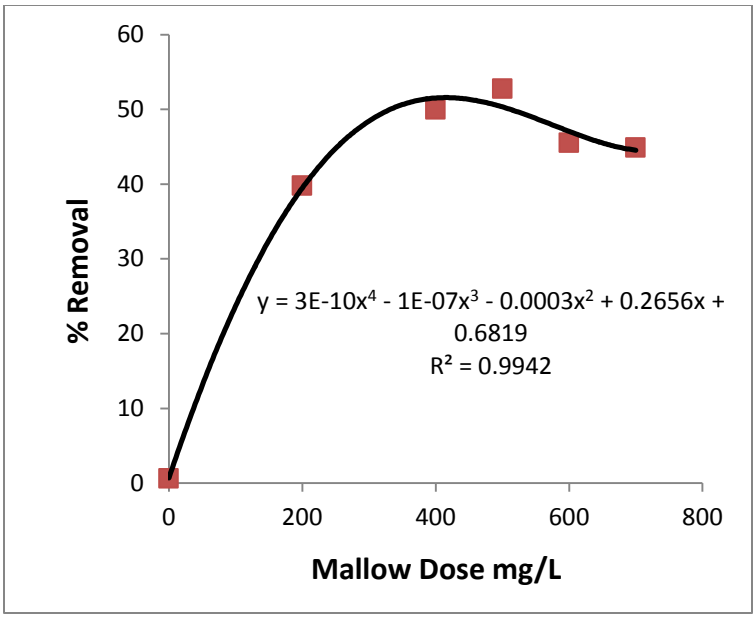

Figure 5. The effect of Mallow coagulant dosages at optimum pH of 6.0 on Cu removal efficiencies of investigated coagulant.

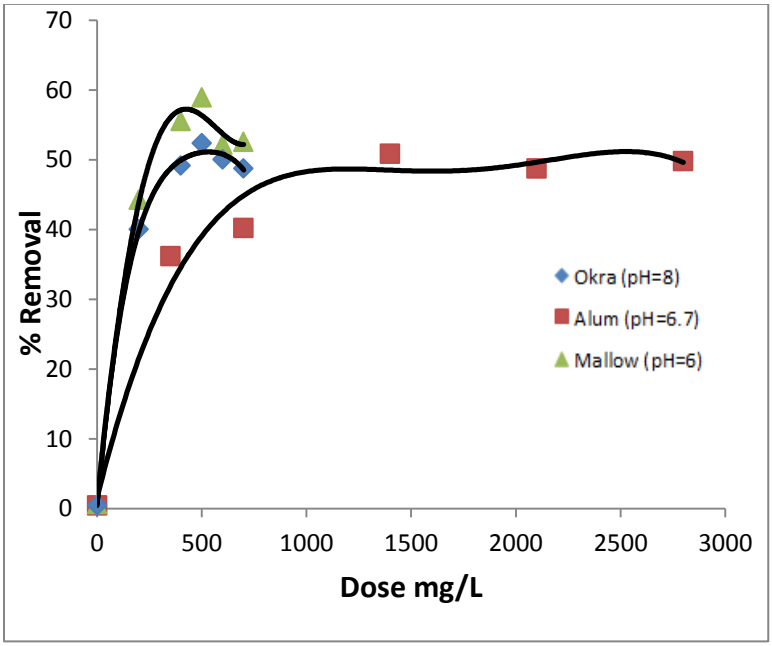

Figure 6. The effect of used coagulant and its dosages on the Cu removal efficiencies at their optimum pH.

Table 2. The percentages of the coagulant doses for binary coagulation .

Sample No.	1	2	3	4	5	6
Coagulants	85% of alum dose+15% one of (mallow or okra) dose (1.19g/L + 0.075g/L)	70% of alum dose+30% one of (mallow or okra) dose (0.98g/L + 0.15g/L)	55% of alum dose+45% one of (mallow or okra) dose (0.77g/L + 0.225g/L)	40% of alum dose+60% one of (mallow or okra) dose (0.56g/L + 0.3g/L)	25% of alum dose+75% one of (mallow or okra) dose (0.35g/L + 0.375g/L)	10% of alum dose+90% one of (mallow or okra) dose (0.14g/L + 0.45g/L)

Table 3. The percentage of the coagulant doses for ternary coagulation .

Sample No.	1	2	3	4	5	6
Coagulants	85% of alum dose+7.5% two of (mallow and okra) doses (1.19g/L + 0.0375g/L + 0.0375g/L)	70% of alum dose+15% two of (mallow and okra) doses (0.98g/L + 0.075g/L + 0.075g/L)	55% of alum dose+22.5% two of (mallow and okra) doses (0.77g/L + 0.1125g/L + 0.1125g/L)	40% of alum dose+30% two of (mallow and okra) doses (0.56g/L + 0.15g/L + 0.15g/L)	25% of alum dose+37.5% two of (mallow and okra) doses (0.35g/L + 0.1875g/L + 0.1875g/L)	10% of alum dose+45% two of (mallow and okra) doses (0.14g/L + 0.225g/L + 0.225g/L)

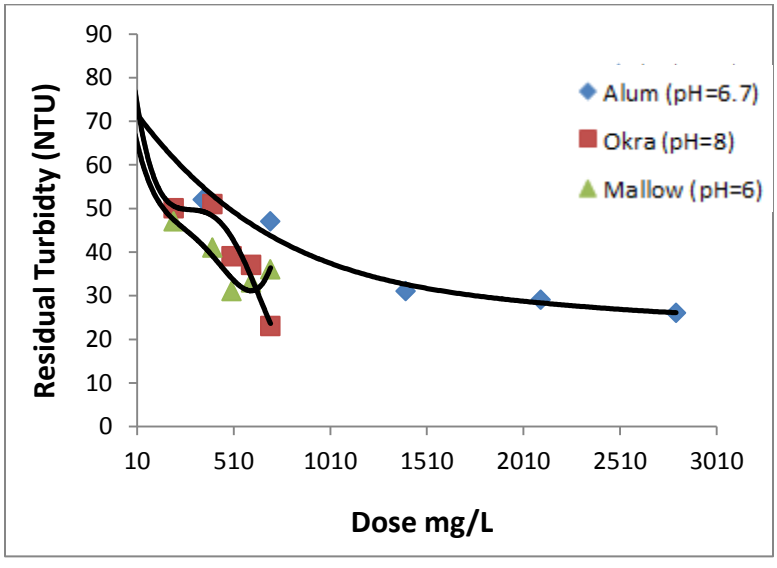

Figure 7. Residual turbidity vs. dose for primary coagulants

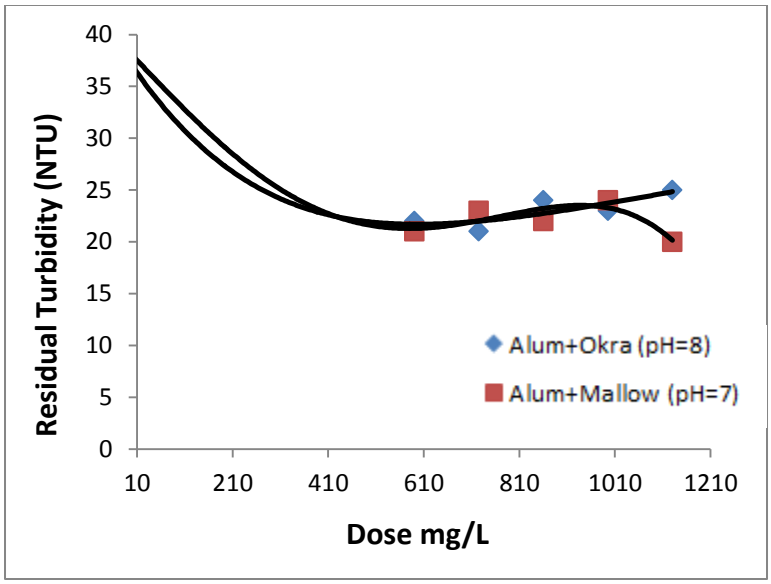

Figure 8. Residual turbidity vs. dose for binary combination coagulants.

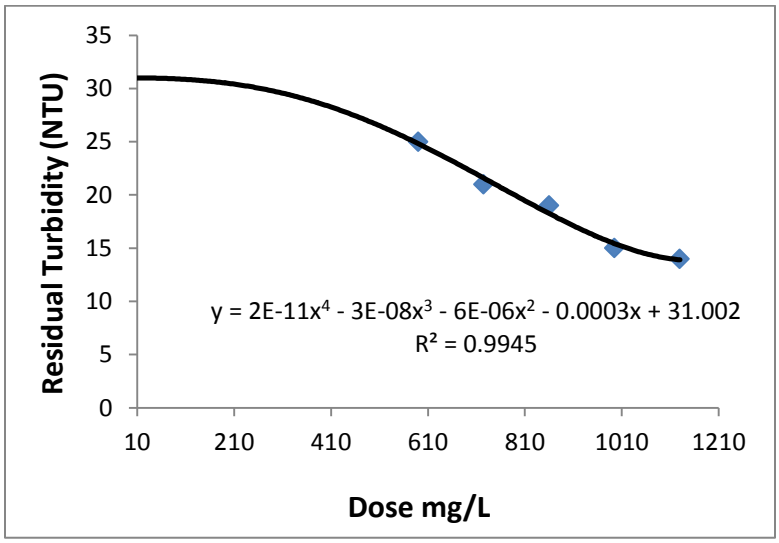

Figure 9. Residual turbidity vs. dose for ternary combination coagulants.

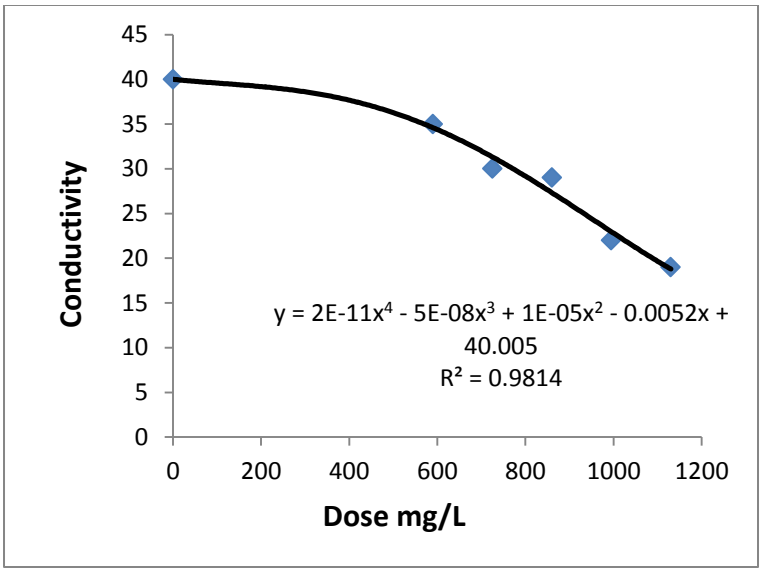

Figure 10. Conductivity vs. dose of alum in conjunction with okra and mallow for Cu (0.47mg/L) at pH= 7.

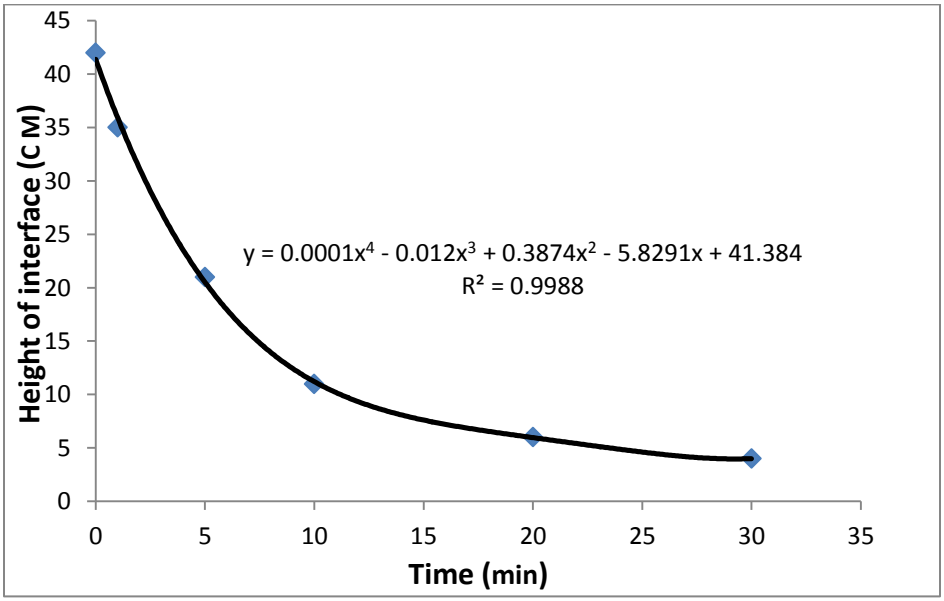

Figure 11. Height of interface vs. time for ternary combination coagulants .

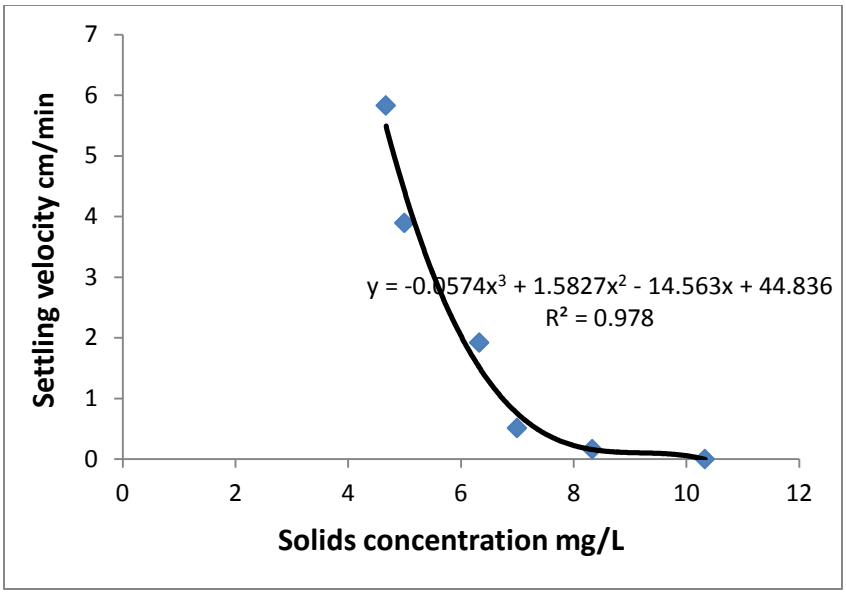

Figure 12. settling rate vs. solids concentration.

Table 4. Equations of mathematical modeling for primary, binary and ternary coagulants.

Stage	Coagulants	Equations	significant
primary	Alum	Y= 9.337x + (-25.14) for pH Y = 6.06x + 8.924 for dose	non significant (0.132) non significant (0.096)
	Okra	Y = 9.067x + (-24.47) for pH Y = 2.997x + 7.620 for dose	non significant (0.132) significant (0.046)
	Mallow	Y = 5.945x + (-6.42) for pH Y = 5.776x + 15.832 for dose	non significant (0.252) non significant (0.067)
Binary	Alum + Okra	Y = 10.93x + (-33.11) for pH Y = 4.603x + 11.55 for dose	non significant (0.093) significant (0.034)
	Alum + Mallow	Y = 10.22x + (-28.24) for pH Y = 4.604x + 11.084 for dose	non significant (0.124) Significant (0.029)

Ternary	Alum + Okra + Mallow	Y = 9.81x + (-21.878) for pH Y = 4.703x + 12.497 for dose	non significant (0.193) significant (0.039)