Research Square

Preprints are preliminary reports that have not undergone peer review.
They should not be considered conclusive, used to inform clinical practice,
or referenced by the media as validated information.

# Suspended matter and heavy metals (Cu and Zn) removal from water by coagulation/flocculation process using a new Bio-flocculant: Lepidium sativum

**Asmae Skotta**
Ibn Zohr University Faculty of Science Agadir: Universite Ibn Zohr Faculte des Sciences Agadir
**Jmiai Aaziz** ( aziz.jmiai@edu.uiz.ac.ma )
Ibn Zohr University Faculty of Science Agadir: Universite Ibn Zohr Faculte des Sciences Agadir
https://orcid.org/0000-0003-2310-5940
**Widad Elhayaoui**
Ibn Zohr University Faculty of Science Agadir: Universite Ibn Zohr Faculte des Sciences Agadir
**Abdallah El-Asri**
Ibn Zohr University Faculty of Science Agadir: Universite Ibn Zohr Faculte des Sciences Agadir
**Malika Tamimi**
Ibn Zohr University Faculty of Science Agadir: Universite Ibn Zohr Faculte des Sciences Agadir
**Ali Assabbane**
Ibn Zohr University Faculty of Science Agadir: Universite Ibn Zohr Faculte des Sciences Agadir
**Souad El Issami**
Ibn Zohr University Faculty of Science Agadir: Universite Ibn Zohr Faculte des Sciences Agadir

**Research Article**

**Keywords:** Lepidium Sativum, Marl limestone, Water treatment, Bioflocculent, mucilage, heavy metals and suspended matter

**Posted Date:** August 4th, 2022

**DOI:** https://doi.org/10.21203/rs.3.rs-1792666/v1

**License:** This work is licensed under a Creative Commons Attribution 4.0 International License.
Read Full License

# Abstract

In this work we used a new organic bio flocculant (BF), which we extracted from natural seeds of Lepidium Sativum (LS). This extract is known for it's performance in various fields such as cosmetology, pharmacology and food products. Moreover, it does not present any danger to human health. The main purpose of our study is the exploitation of a new natural supports, as bio polymers in the treatment of water loaded with marl limestone suspended solids (SS) and trace elements, including Copper and zinc. We studied the effectiveness of this extract in comparison with other products usually used in the treatment and depollution of water; the preliminary tests were carried out on pseudo samples prepared at the laboratory level. The comparative study with a synthetic flocculant (Anionic polyacrylamide: APA), usually used in water treatment, provided a good competitiveness with an important flocculation power. The combination of the two steps of neutralization and coagulation by aluminum sulfate (AS), followed by a flocculation step by the new flocculant (LS), then a natural decantation, gave significant results, in the abatement of $Cu^{2+}$, $Zn^{2+}$ and (SS). For the solution rich in marl limestone, the turbidity passes from an average of 600 NTU to values close to 1 NTU. The sludge thus produced after treatment is submitted to an analysis by (SEM) and (XRD) and the retained chemical elements are detected. The study generally enters as a sustainable development strategy capable of improving long-term global water security and protecting the environment from synthetic products used excessively in water treatment.


# Highlights

- Turbidity lower than 1 NTU at 0.1 mL of LS.
- L.S reduce 10 mg/L of coagulant

# 1. Introduction

Water treatment (potabilization and purification) is an essential way to protect natural water resources, ecosystems and human health, which has improved with the evolution of science and technology. The economic development and the demographic growth have imposed more severe treatment methods. The classical treatment process by coagulation and flocculation allows to improve the physicochemical quality of the treated water (Aouba 2017).This technique uses several chemical treatment agents, in particular, coagulants and flocculants of inorganic nature, although they allow achievement of the treatment objective, they present more or less intense disadvantages But unfortunately most of these synthetic compounds are expensive and toxic for human health, safety and also for the environment. hence the need to adopt new alternative products, leading to more in-depth scientific research on natural flocculants (Belbahloul et al. 2014). Our study is part of a context that takes into account health and environmental requirements, allowing integrating a new natural and biodegradable product in the process of water treatment. For this reason, we are working on the valorization of mucilage from cress seed (Lepidium Sativum).The latter has mucilaginous, emulsifying (Behrouzian et al. 2014a, Behrouzian et al. 2014b), and gelatinous characteristics (Naji et al. 2013, Razmkhah et al. 2017),also known for it's diuretic,

anti-diarrheal, anti-diabetic and healing activities (Doke &Guha 2014).In the traditional system of medicine, Lepidium Sativum (LS) seeds are an effective medicinal remedy for respiratory disorders such as bronchitis and asthma (Gaouji 2016),thus for the treatment of asthma, jaundice, liver problems, gastrointestinal disorders, fractures and other inflammatory conditions (Hussein 2016). The valorization of (LS) extract is applied for the depollution and treatment of waters loaded with marl limestone (SS) and metallic elements, in Particular $Cu^{2+}$ and $Zn^{2+}$ ions. Although these two elements are essential for the living organisms, but an exposure to high concentrations, and for a long time causes a bioaccumulation in the human body, This then causes many diseases more or less serious such as Wilson's disease, due to the exposure to the high contents of Cu (Salvarredy Aranguren 2008),stomach cramps, skin irritation, vomiting, nausea, anemia...etc. The progressive and continuous accumulation of these metals can also have harmful consequences on the biogeochemical processes (Belbahloul et al. 2014). For this purpose, various works have been performed, in order to eliminate certain metals as well as (SS) present in natural, industrial and waste waters (Khider et al. 2015, Pallier 2008). The processes followed by these researchers required several treatment steps, using synthetic polymers as flocculation aids in combination with chemical coagulants (neutralizing salt). The objective of our study consists in the substitution of synthetic polymers, using purely natural products. In this sense we have used (AS) as a neutralizing agent, which we reduced in the present work in combination with the natural product extracted from the gum of Lepidium Sativum (LS) seeds, the latter is exploited as a co-flocculant to improve the formation of colloidal, organic and mineral matter conglomerates during the flocculation process. The comparative experimental study and all the treatment analyzes were performed according to physicochemical analysis protocols (Turbidity measurement, Flame atomic absorption (FAA), X-ray diffraction spectroscopy (XRD) and (SEM) microanalysis coupled with (EDS)).

## 2. Materials And Methods

# 2.1 LS extract Preparation

The seeds cress (LS), were purchased in a local market in the city of Agadir, which is located in the southwest of Morocco. The cleaning of the seeds is done manually, to eliminate all impure matters such as stones, dust, dirt and broken seeds (Behrouzian et al. 2013). Seed juice was extracted from whole seeds emerged in distilled water at 308 K (with an extraction ratio (V/M) = 30/1). The seeds absorb water rapidly and produce a sticky, colorless liquid around the seed surface (Karazhiyan et al. 2011).To separate the gum from swollen grains, we ground the mixture using an elises blender, and then are filtered through a porous tissue. The extracted product in it’s natural state is a mucilaginous liquid; miscible with water; it’s color is light yellow (Fig. 1); it’s density is about 0.997 $\simeq$ 1Kg/L and it’s pH is 7.44. The mucilage obtained is relatively stable, it can keep it’s flocculation capacity for several days, without any preservation system and for several months stored at a temperature below 277 K.

The analysis performed by UV-visible spectroscopy of the juice gave the absorption spectrum below (Fig. 1) with a dilution percentage in distilled water of 12.5%. The absorbance spectrum as a function of (LS)

wavelength, show an intense peak with an absorbance of 2.675 corresponding to the dilution of 12.5% in mucilage, with a maximum in wavelength around 325 nm. The grains contain a large amount of mucilaginous substances as well as compounds with a high molecular weight (Karazhiyan et al. 2011), such as : Cinnamic acid,4-hydroxy-3-methoxy-(5-hydroxy-2-hydroxymethyl) and Methyl (1-O-retinyl-2,3,4-triacetyl-ß-D-glucopyran) urinate, with molecular weight M = 652 g/mol and 602 g/mol, respectively (Hussein 2016).

# 2.2 Materials

The experimental study and all the analyses were carried out using the following equipment according to the physicochemical analysis methods followed by Rodier (Rodier et al. 2009).

- Turbidimeter (HACH Company, Model 2100N detection at 4000 NTU), for turbidity measurement; in nephelometric turbidity unit (NTU).
- UV-visible spectrophotometer (JENWAY 6705 UV / Vis) to determine the absorbance spectrum of mucilage.
- Atomic absorption spectrophotometer with air-acetylene flame (SHIMADZU AA-7000) for the analysis of Cu and Zn elements.
- Jar-test system (VELP Scientifica, JLT6 Flocculation tester) to perform the coagulation-flocculation treatment.
- pH-meter (WTW, GmbH pH 340i) for the measurement of the hydrogen potential (pH).
- Scanning Electron Microscopy “SEM” (JEOL JSM IT-100) coupled with energy dispersive X-ray spectrometry “EDS” detector for the surface analysis of the sludge formed after treatment.
- X-Ray Detector “DRX”, Burker D8 Advance Twin, for the obtaining of the chemical molecules spectrum (organic and inorganic) present in the sludge.

The chemical products used during our experiments are:

- Products tested for coagulation, initially prepared at 10 g/L and are Aluminum sulfate [$Al_2$ $(SO_4)_3$, 18 $H_2O$], Iron chloride [$FeCl_3$, 15 $H_2O$] and Barium chloride ($BaCl_2$) respectively.
- Synthetic polymer: Anionic polyacrylamide (APA), initially prepared at 1 g/L, for comparison to (LS) mucilage.
- Solutions prepared for pH adjustment: Sulfuric acid ($H_2SO_4$) at 1.83 M, Sodium hydroxide (NaOH) at 2 M.
- Copper and zinc sulfate salt initially prepared at 5 mg/L; [$CuSO_4$, $5H_2O$] and [$ZnSO_4$, $7H_2O$] respectively.

# 2.3 Treatment process description

Our tests are performed at 298 K, on synthetic samples that we prepared in the laboratory, whose (SS) load was prepared from a suspension of marly limestone (ML) from the region of klaa sraghna

(Morocco). The contents of 1 ppm in $Cu^{2+}$ and $Zn^{2+}$ are prepared respectively from stock solution. The treatment steps followed are performed on a volume of 500 mL of sample and are described as follows:

- **Coagulation**: It was performed by (AS), with a fast agitation at the speed of 120 turns / min for 2 min duration.
- **Flocculation**: It is made by a slow agitation at 45 rpm for 20 min. This step allows associating the fine flocs between them, by forming agglomerates that can be easily decanted.
- **Decantation**: The solution is left to settle for a 30 minutes, in the same enclosure where the coagulation-flocculation is performed. The physico-chemical analyses of the water were carried out according to the methods described by Rodier (Rodier et al. 2009) and focused on the following parameters; Turbidity, pH, Conductivity, [Cu] and [Zn]. The reduction efficiency of the parameters; Turbidity and the mass concentration of the metallic elements Cu and Zn are expressed as a percentage, the latter are calculated by the following formula (Abid et al. 2009, Mohan 2014):

$$\%\mathrm{Efficiency of} X = \frac{(\mathrm{Ci}\,(\mathrm{X}) - \mathrm{Cf}\,(\mathrm{X}))}{\mathrm{Ci}\,(\mathrm{X})} \times 100$$

**Ci:**Initial concentration of X in the raw water.

**Cf:**Final concentration of X in the treated water.

## 3. Results And Discussions

A natural sedimentation test of (ML) is performed to evaluate it's tendency to settle without any treatment, then the same content of this suspension is subjected to the treatment by the new biopolymer based on (LS), which is tested in combination with chemical coagulants (aluminum, iron and barium salt), for the depollution of waters loaded with (SS) and trace elements in particular Cu and Zn. We have determined the adequate working combination (coagulant/bioflocculent), then we have optimized the treatment with this pair of products, and we have performed a comparative study with the synthetic polymer.

# 3.1 Treatment of water loaded with (SS)

# 3.1.1 Natural settling test

We performed a natural settling test, with the initial (SS) content of the (ML) powder is 1 g/L, in water without any treatment system.

The follow-up of the turbidity variations according to the settling time during 6 hours (Fig. 2 **(a)**), allowed us to note that after 90 min, the settling of the solution keeps a turbidity going from 100 NTU equivalent to 78.77% in the abatement of the prepared suspension, the decrease continues slowly until values approaching 38 NTU which is equivalent to 92.29% after 6 hours of. The settling difficult part corresponds to the fine solid particles of (ML) in the colloids state in the water. The latter have a very low and almost negligible weight, their generally negative charges; generate repulsive forces between them that prevent them from being easily decanted.

## 3.1.2 Evaluation of the mucilage flocculating power: Physicochemical treatment

The (LS) mucilage prepared is tested in combination with three commercial coagulants, in order to optimize the strong exploitation used in these reagents (high concentration), on the other hand to improve the decantation of the water polluting load, by the use of bioflocculent.

## 3.1.2.1 Suitable treatment combination

In order to find the appropriate combination of the protocol (Coagulant / (LS) mucilage) to succeed the treatment by coagulation flocculation, we carried out tests with three chemical coagulants, it's the aluminum sulphate ($Al_2(SO_4)_3$), ferric chloride ($FeCl_3$) and barium chloride ($BaCl_2$) The treatment by coagulation flocculation was performed on synthetic samples initially prepared at 1 g/L (ML) with an average turbidity of 620 NTU The three combinations(aluminum sulfate / (LS) mucilage), (ferric chloride / (LS) mucilage) and (barium chloride / (LS) mucilage) will be noted combination 1, combination 2 and combination 3 respectively.

In each combination, the pH influence of the medium is studied in order to specify the pH range where the metal cation of each coagulant salt forms precipitates with the $OH^-$ hydroxides present in the medium.

The dose of coagulants used in the three combinations is 40 mg/L, it is chosen according to the results of many research works performed for the treatment of waters with turbid load (Abid et al. 2009, Diaz et al. 1999). The addition of coagulant is followed by 0.1 mL of (LS) mucilage to improve flocculation. The suitable coagulant will be optimized in turn in the further work.

**Combination 1: Aluminum Sulfate/(LS) Mucilage**

According to the results of our tests, it is observed that (AS) provides a good neutralization of the suspended particles loads, at slightly basic pH. Thus we observe that pH between 7 and 9 the turbidity of the settled water is less than 1 NTU (Fig. 2 **(b)**). The turbidities recorded are: 0.92 NTU, 0.64 NTU and 0.61 NTU, which is suitable for 99.9% in abatement for the three pH values 7, 8 and 9, respectively.

The abatement observed in this pH range could be attributed to the presence of the flocculant form of the coagulant: $Al(OH)_3$, which traps the neutralized species (Achak et al. 2008). Beyond this pH range, coagulation slows down, giving 4.71 NTU at pH = 10 and 56.8 NTU at pH = 11, and the floc conglomerates

formed become very fine and give a slight opalescence, making them difficult to settle. The pH of the water to be treated must then be in a range of the optimum pH; where there is coexistence between the coagulating forms and the floc form.

The ion $Al^{3+}$ form, undergoes a very rapid hydrolysis reaction to give mononuclear species and oxide/hydroxide salts (diagram of the Aluminum hydrolyzed species as a pH function (Achak et al. 2008)) according to the below reactions (Guseva et al. 2009, Kuo &Tsai 2001):

At predominant pH [4.5 to 5.5] $Al^{3+} + H_2O \rightarrow Al(OH)^{2+} + H^+$ **(1)**

At predominant pH [5 to 5.5] $2\ Al^{3+} + 4\ H_2O \rightarrow 2\ Al(OH)_2^{+} + 4\ H^+$ **(2)**

At predominant pH [5.5 to 8.5] $Al^{3+} + 3\ H_2O \rightarrow Al(OH)_3 + 3\ H^+$ **(3)**

The $Al(OH)_3$ precipitate which forms as a function of the pH, constitutes the fluculant form of the coagulant, generally having interesting adsorption properties, and subsequently comes into contact with the negatively charged particles and traps them. Trapping and adsorption of colloids on aluminum flocs occurs when sufficient amounts of coagulant are added (Achak et al. 2008). The mechanisms leading to the destabilization of loads have been widely studied (Amirtharajah 1988) and can be summarized as follows; Charge neutralization relies on the addition of sufficient cation, to neutralize the negative charge of stable particles. On the other hand, an overdose of coagulant can cause too much adsorption of cation and reverse the charge of particles which then become positive. The particles would thus be re-stabilized (Achak et al. 2008).

**Combination 2: Ferric chloride/ (L.S) mucilage**

The treatment is applied in a basic pH range, where ferric cations are complexed with $OH^-$ anions, giving a precipitate of ferric hydroxide, easy to be decanted by adsorbing on the surface of the flocs formed, after their neutralization by $Fe^{3+}$. The turbidities recorded for pH = 7 and 8 start to stabilize after 15 min of settling (Fig. 2 **(c)**), and the values reached are respectively: 1.47 NTU and 1.39 NTU with corresponding abatement equal to 99.7%. $FeCl_3$ is known for it's effectiveness in coagulating suspended particles. In the solution, it gives an hydrate in the form of $Fe(H_2O)_6^{3+}$, then hydrolyses to form different monomer, dimer or trimer complexes, as a function of the reaction pH. Mostly the complexes are positively charged (Duan &Gregory 2003, Lefebvre &Legube 1990), according to the forms: $Fe(OH)^{2+}$, $Fe(OH)_2^{+}$, $Fe_2(OH)_4^{2+}$ and $Fe_3(OH)_4^{5+}$. Increasing the pH leads to the presence of monomeric divalent and then monovalent species and finally uncharged iron hydroxide $Fe(OH)_3$. The solubility of this hydroxide is low and an amorphous precipitate forms at neutral pH values (Duan &Gregory 2003).

$$Fe^{3+} \rightarrow Fe(OH)^{2+} \rightarrow Fe(OH)_2^{+} \rightarrow Fe(OH)_3 \quad (4)$$

Generally the dissolution reaction of the $Fe^{3+}$ ion leads to the formation of the iron hydroxide precipitate $Fe(OH)_3$ (reaction 5) (Ching et al. 1994). The released acidity can then react with species usually in solution, such as bicarbonate ions (reaction 6):

$$Fe^{3+} + 3H_2O \rightleftarrows Fe(OH)_3 + 3H^+ \quad (5)$$

$$HCO_3^- + H^+ \rightleftarrows H_2O + CO_2 \quad (6)$$

$$Fe^{3+} + 3HCO_3^- \rightarrow Fe(OH)_3 + 3CO_2 \quad (7)$$

The two main parameters regulating flocculation coagulation are therefore the pH of the treated suspension and the dose of iron used (Pallier 2008).The optimal coagulation flocculation conditions for iron are theoretically determined using the coagulation zone distribution diagram or Amirtharajah diagram (Amirtharajah 1988, Amirtharajah &Mills 1982).

It is at (pH = 6.5 to 10.5) where the coagulation of colloids is achieved by trapping in less soluble iron hydroxides ($Fe(OH)_3$). The colloids are then generally eliminated, but less efficiently than at (pH < 6); where the flocculation is by neutralization, destabilization, adsorption and precipitation of colloids. In this pH zone, the cationic species of iron predominate and neutralization becomes effective.

For this purpose, we notice that $Al_2(SO_4)_3$ is more powerful for this type of suspension coming from (ML) at slightly basic pH, in comparison with $FeCl_3$.

**Combination 3: Barium chloride / (LS) mucilage**

$BaCl_2$ showed it's performance in abatement of the pollutant load in (SS). The monitoring of T (NTU) as a function of time for each pH value, allowed us to observe that after 10 minutes of decantation at a pH of 7 and 8, a level of turbidity stabilizes as a function of time (Fig. 2 **(d)**), at values close to 9 and 23 NTU respectively with yields of 98.2% and 95.6%. These percentages recorded for $BaCl_2$ are lower than those obtained in the case of $Al_2(SO_4)_3$ and $FeCl_3$. This is caused by difference of the metal cation charge in solution, where $Al^{3+}$ and $Fe^{3+}$ are much more electropositive than $Ba^{2+}$. Although the observed flocs are of medium shape, above this pH, the turbidity values start to increase, towards too high values corresponding to removal efficiency around 65%, subsequently the flocculation process by $BaCl_2$ in basic medium is low.

# 3.1.2.2 Comparative study

The choice of the adequate combination is focused on the (AS), which will be considered as a good charge neutralizer for the continuation of our tests; valorization and optimization of the flocculating power (LS) mucilage. On the one hand, the turbidity values obtained by combining with mucilage are the lowest, On the other hand, the flocs obtained have a large shapes, which increase the speed of their precipitation and therefore reduces the time of their settling. At pH 8 (Fig. 3 **(a))** the turbidity in NTU recorded for the three combinations: 1, 2 and 3 after 30 min of settling is respectively 0.64 < 1.39 < 23.1 NTU. The settling time starts to stabilize from 15 min (Fig. 3 **(b)**) for combination 2 and 3 which makes the choice of using the first combination; where (AS) is more advantageous with the new bioflocculent by it's stability in turbidity obtained after 5 min compared to the others. Thus, neutralizing power of coagulating salts used with respect to the abatement of the (ML) suspension, can be classified as follows: $Al_2(SO_4)_3 > FeCl_3 > BaCl_2$.

The coagulation flocculation operation allowed increases the size of the colloidal particles, by destabilization of the particles in suspension, then formation of the flocs by adsorption and aggregation with the bioflocculent. Colloidal particles in solution are negatively charged and the addition of cationic coagulant, leads to the neutralization of their repulsive charges that keeping them in suspension. To choose a coagulant, it is then necessary to take into account it's valence. Indeed, coagulation is more efficient as the valence of an ion is higher. (AS) is the preferred coagulant based on it's valence (trivalent cation), a less expensive salt which can be minimized by coupling with a natural flocculant. It's reaction takes place in two main steps:

$$Al_2(SO_4)_3 \rightarrow Al(OH)_y(SO_4)_x \rightarrow Al(OH)_3 \quad \textbf{(8)}$$

Generally, the addition of coagulation reagents gives rise to hydroxides which are largely separated at the stage of decantation by gravity (Dahhou et al. 2012).

# 3.1.3 Flocculating pH

According to the results obtained in the (AS) treatment test, with pH adjustment (**Table. 1**), it appears that at slightly basic range, the flocculation is perfect. Then, turbidity is less than 1 NTU, from 7 to 9 pH value, which is suitable for 99.9% in abatement. However, our (ML) solution prepared is characterized by a basic pH close to 9. That last is lowered by the addition of (AS), to slightly basic value, where the shape of the generated flocs is medium. Indeed, a good flocculation is observed at pH = 8 for the (ML) suspension. This means that it is not necessary to adjust it. In the continuation of the treatment tests, the normal pH of the prepared solutions was kept, since it represents a raw surface water pH.

Table 1
Turbidity variation as a function of time and reaction pH (using (AS) combined with (BF) at 0.1 mL)

| Time (min) | T (NTU) | | | | |
|---|---|---|---|---|---|
| | pH = 7 | pH = 8 | pH = 9 | pH = 10 | pH = 11 |
| 5 | 0.88 | 0.84 | 0.77 | 5.48 | 75.9 |
| 10 | 1.08 | 0.91 | 0.81 | 5.33 | 69.8 |
| 15 | 0.94 | 0.96 | 0.71 | 5.25 | 68.8 |
| 20 | 0.84 | 0.67 | 0.63 | 5.05 | 65.3 |
| 25 | 0.87 | 0.72 | 0.69 | 5.95 | 59.3 |
| 30 | 0.92 | 0.64 | 0.61 | 4.71 | 56.8 |
| Efficiency (30 min) | 99.85 | 99.90 | 99.90 | 99.24 | 90.84 |

# 3.1.4 (AS) coagulant optimization

(AS) has been shown an effective treatment for colloidal suspension from (ML), we have optimized the latter, in the following work, by testing (AS) alone without combination with a flocculating agent, thus in coupling with a fixed content of (BF) compared with (APA) as mentioned in (**Table. 2**).

Table 2
Turbidity as a function of (AS) alone, then coupled with (BF) and (APA), after 30 min of settling time

| (AS) (mg/L) | T (NTU) | | |
|---|---|---|---|
| | (AS) alone | (AS) + 0.1 mL (BF) | AS + 0.1 mL (APA) |
| 10 | 2.54 | 1.57 | 1.35 |
| 20 | 1.02 | 0.48 | 0.49 |
| 30 | 0.77 | 0.47 | 0.39 |
| 40 | 0.89 | 0.46 | 0.53 |
| 50 | 0.86 | 0.59 | 0.49 |

The primary effectiveness of (AS) in the treatment of water loaded with (SS), through it's neutralizing effect, is inevitable. (LS) mucilage is used as a bioflocculent to optimize the (AS) dosage by reducing the concentrations of this chemical product during the treatment process, thus minimizing the settling time of the formed flocs.

From the curve (**Figure 3 (c)**), it is obvious that the higher the (AS) content, the water becomes more clarified. At 10 mg/L there is a shift about 1 NTU, between the two curves resulting from turbidity abatement by (AS) alone and combined with (LS) extract, where the best performance is recorded in the case of the combination with the natural extract. At the rate of 20 mg/L and in the presence of 0.1 mL of (BF), we observe the beginning of turbidity stabilization level and reaches it's optimum 0.48 NTU. In the absence of the mucilaginous juice, the coagulant content rises to 30 mg/L to reach 0.77 NTU in turbidity (**Table. 2**). The (BF) allowed us to reduce 10 mg/L of coagulant and to improve the shape of the flocs obtained. The comparison between (APA) and (BF) showed that the two curves generated by those two flocculants are overlapping, and the results obtained are almost comparable. This result can be justified by the polymeric effect, which the mucilaginous (LS) gel has, in the agglomeration of very fine flocs (which are in the slight opalescence form), generated by the neutralizing effect of the coagulant. The (BF) then facilitates the approach of the flocs between them and the increase of their weight, hence the improvement of their sedimentation speed, as well as the reduction of the settling time. It allowed to lower the high content of coagulant and to reduce it's harmful effect, in addition to it's capacity flocculent comparable to synthetic flocculants (APA).

Generally, the ability of a suspended solid or colloidal material to be decanted from water, by such a treatment, depends on certain criteria; specific to this material such as the particle size, their specific surface, electrostatic charges and capillary forces that retain water (Dahhou et al. 2012).

## 3.1.5 (LS) mucilage Optimization and comparison with industrial flocculant (APA)

We propose to compare the flocculent capacity of (LS) mucilage with the synthetic polymer (APA) prepared at 1 g/L, then to determine the optimum of the treatment by two flocculants in the abatement of the turbidity in both cases.

From the curve (Fig. 3 **(d)**), it's observed that the coupling with (BF) gave comparable results with (APA) with a difference in removal efficiency not exceeding 0.5% between (BF) and (APA).

For (LS), the optimum in mucilage is observed at 0.1 mL equivalent to 99.92% of turbidity removal correspond to a value of 0.30 NTU. For (APA) the curve shows a stabilization level of Turbidity (NTU), it slightly lowered and stabilized for 0.1 mL in (APA), and which is equivalent to 99.96%.

This can be explained by the viscosity and gelatinous properties, distinct to each, of the two polymers, In addition, the tendency of the polymer to agglomerate the fine flocs thanks to it's molecular structure containing carbon chains, whose ramifications contain functional groups (acetyl, acetone, carboxyl...), having a more or less electronegative anionic character, allowing attraction of neutralized colloids, then giving an enlarging floc (Fig. 4).

## 3.2 Evaluation of the (LS) mucilage purifying power in Copper and Zinc removal

## 3.2.1 $Zn^{2+}$ and $Cu^{2+}$ abatement in synthetic samples

We prepared a series of 1 g/L (SS) samples based on (ML) loaded with $Cu^{2+}$ and $Zn^{2+}$ at two different concentrations: 0.5 and 1 ppm. A control containing the metals alone in distilled water (DW) is prepared to draw the influence of the prepared (SS) load on the metals removal, on the other hand to detect the contribution of the bio flocculant to trap the metal cation in the conditions previously chosen as optimum of (SS) treatment at 1 g/L in (ML) (Fig. 4).

The removal efficiency of $Cu^{2+}$ and $Zn^{2+}$ at the initial concentration of 1 ppm is much higher than initial concentration of 0.5 ppm. We see that in the presence of the (ML) (SS), a small part is retained by the latter, and this in comparison with the control loaded with metals under the same conditions.

In water loaded with (ML), the $Zn^{2+}$ ion with an initial content of 1 ppm reaches 87% in abatement compared to the control including 84.6% (Fig. 4. **(a')**). Similarly, when we start with 0.5 ppm, we note a difference of 7% between (ML) and the control. This implies the adsorptive effect of (ML) on the presence of Zn metal cations. For Cu, from an initial concentration of 1 ppm we have 71.21% in efficiency, compared to 56.54% in the control, with 14% difference (Fig. 4. **(b')**). The large decrease in $Cu^{2+}$ and $Zn^{2+}$ can be justified by the polymeric effect that (LS) mucilage has on the flocs formed and therefore to facilitate their entrapment in the agglomerates of these flocs.

We can deduce that a part of the studied metals is adsorbed by the (ML) material in colloidal state, considering the marked difference between the control and the water loaded with (SS) of (ML). Another part is either trapped in the agglomerates formed by using (BF), called macro-flocs, under the effect of a mechanism governed by physisorption, or by adsorption effect obtained under the affinity action of the amino, carboxyl and hydroxyl groups, present in the (BF) mucilage (Abu Tawila et al. 2019) and then decanted during sedimentation, in this case we can report it to chemisorptions phenomenon.

## 3.3 Mineralogical characterization of (ML) sludge treated with (LS) mucilage

Surface characterization and mineralogical analysis, after drying sludge at 323 K resulting from the treatment of 1 g/L (ML) suspension with (AS) 20 mg/L alone and combined with two different contents of bio-polymer extracted from (LS) (in particular 0.1 and 0.5 mL), were evaluated by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) and X-ray diffraction spectroscopy (XRD).

## 3.3.1 Scanning electron microscopy (SEM) analysis

SEM analysis is a powerful tool that uses a focused beam of electron to produce complex, high magnification image of a sample's surface topography.

In this part of work, (SEM) microanalysis coupled with (EDS), allowed us to observe the topography of the formed sludge and to visualize the flocs morphology (Fig. 5), constructed by coupling (AS) 20 mg/L with the (BF), as well as carry out the elemental chemical analysis of the components contained in this sludge (Fig. 5).

Flocculation with (AS) alone resulted in sludge imagery with very fine floc sizes. The addition of the bioflocculent contributes to the floc growing and thus, to the compaction of the sludge formed, as shown by the expansion at 10 µm (Fig. 5. **c**). We thus observe crystalline structures of amorphous forms at 5 µm. The precipitation of these structures remains very easy, by effect of their molecular weight, which reduces the time spent on settling.

The analysis of the elements characteristic emissions by (EDS) allowed us to determine the local quantitative elemental composition of each sludge sample. It is to be noted that from the micrograph (Fig. 5) of the chemical elements distributed in their pure states, on the surface of the flocs; formed after treatment with the combination ((AS) + 0.1 mL in (BF) mucilage), that the elements Cu and Zn are distributed in a homogeneous way on the surface of the flocs, this is due to their low initial content of 1 ppm as well as their direct adsorption on the surface of the flocs, which can be considered homogeneous through the (BF) intermediary with the flocs formed. Aluminum on the flocs surface is distributed in a heterogeneous and concentrated way, this can be due to it's presence in it's precipitated states, especially the form $Al(OH)_3$ predominating at pH 5.5 to 8 according to the distribution diagram of the Aluminum hydroxide species (Achak et al. 2008).

The quantitative analysis is given as a mass percentage of the elements (C, O, Ca, Cu, Zn, Al). It is observed that the percentages of the elements Cu, Zn and Al in their pure state (Fig. 5) and in their oxide state undergo a slight increase as a function of the (LS) gel volume.

The (EDS) spectrum shows the pure chemical elements contained in the (ML) sludge after treatment by combining (BF) 0.1 mL, the presence of various elements like Ca, Si, Fe and O, represent the main components of the (ML) suspension in the form of calcite, silica. For the elements Al, Cu and Zn, these undergo an increase according to the (BF) volume added for flocculation, where the content of organics carbonaceous elements in the sludge increases. A relationship between these organics structures and cations or metal oxides could be established. The Al has the tendency to complex with the natural water-soluble organic matter (especially humic or fulvic substances, protein...) contrary to the inorganic anions (Cherifi 2013), a comparable phenomenon can be observed in the Cu and Zn case at the presence of (BF).

After destabilization of the particles by the hydrolysis of $Al_2(SO_4)_3$ and their agglomeration by the (LS) gel, the particles form conglomerates; where the oxides of the cationic elements present in solution are

trapped. Aluminum oxide ($Al_2O_3$) has a higher mass percentage than Cu and Zn (Fig. 6 **(a)**), given it's initial content injected for the (ML) coagulation and neutralization. For the element CuO the percentage is 1.94% in the sludge from the treatment with (BF) 0.5 mL, compared to 1.36% in the absence of (BF). ZnO recorded an elevation of 1.81% compared to 0.88% without the (BF) addition. The results obtained confirm the trapping of these oxide elements in the conglomerates, subsequently; the presence of (BF) improves and facilitates this phenomenon of metal oxides retention through the macro-flocs.

## 3.3.2 X-ray diffraction (XRD) analysis

A comparison between the absence and presence of (BF) at 0.1 mL content, allowed us to obtain the results by (XRD) of the elements present in the dried sludge as shown in the spectrum at (BF) 0.1 mL. The data processing by the software "High score" allowed us to define the chemical structures suitable for the obtained peaks and to detect the Zn, Cu and Al oxides, in their most predominant forms $Zn_2O_2$, $Cu_4O_2$ and $Al(O\ H)_3$ respectively, as illustrated in (Table 3).

Table 3
Illustration of the main compounds from treatment with and without (BF)

| N° | Ref. Code | Score (BF = 0,0) | Score (BF = 0,1) | Compound Name | Chemical formula |
|---|---|---|---|---|---|
| **1** | 96-901-6707 | 89 | 75 | Calcite | $Ca_6C_6O_{18}$ |
| **2** | 96-500-0036 | 46 | 46 | Quartz | $Si_3O_6$ |
| **3** | 96-100-0064 | 17 | 35 | Cuprite | $Cu_4O_2$ |
| **4** | 96-101-1259 | 9 | 13 | Zincite | $Zn_2O_2$ |
| **5** | 00-037-1377 | 6 | 6 | Aluminum Hydroxide | $Al(OH)_3$ |
| **6** | 96-201-8646 | 0 | 3 | poly[(\m ~ 4~-benzene-1,2-dicarboxylato)zinc(II)] | $Zn_4O_{16}C_{32}H_{16}$ |

From the spectrum (Fig. 6 **(b)**), Calcite and quartz are major peaks. They are the basic components of the (ML) (SS). The presence of Cu and Zn oxide; ($Cu_4O_2$), ($Zn_2O_2$) respectively, shows that they are trapped more in the sludge while presence of (BF), than in it's absence. Aluminum hydroxide $Al(OH)_3$ has almost the same value because of it's optimal content injected in both cases is unchanging. Thus it should be noted that $Cu^{2+}$ and

$Zn^{2+}$ are associated with polymeric molecules, as the case of poly [(m-4-benzene-1,2-dicarboxylato) zinc(II)]. The (LS) mucilage is characterized by the presence of various molecular structures, including functional groups more or less electronegative (ester, acetyl, carboxyl and phenolic groups) (Fan et al. 2014, Sakran et al. 2014). These organic structures can react with the metal cation as the case of the structure ($Zn_4$ $O_{16}$ $C_{32}$ $H_{16}$) (Table 3), that contains two carboxyl groups attached to the benzene ring. These groups improves the coagulation capacity by leading to the inter-particle bridging effect of the coagulant (Mohan 2014). It is reported that these molecular structures are very effective as a coagulation aid. This property is attributed, due to the presence of poly-electrolyte proteins, lipids, carbohydrate and alkaloids containing COOH and $OH^-$ groups in the (LS) seed (Karazhiyan et al. 2011). For this purpose as a whole adsorption and charge neutralization, adsorption and inter-particle bridging can be responsible for the removal of trace elements in particular $Cu^{2+}$ and $Zn^{2+}$.

# 4. Conclusion

Lepidium Sativum mucilage is a possible alternative to chemical flocculants. However, it's extract, known for a long time in the pharmaceutical field, is not used on an industrial scale in the field of water treatment. Indeed, our results show that the combination of Lepidium Sativum with $Al_2(SO_4)_3$ coagulant can be a substitute for synthetic flocculants in the treatment of water loaded with marl limestone suspended solid, where coagulation is more effective as the valence of the coagulant ion is higher. For a solution rich in marl limestone, the turbidity goes from an average of 600 NTU to values lower than 1 NTU, under optimum conditions of (AS) 20 mg/L and (BF) 0.1 mL. Thus, this coupling is profitable for the treatment of water containing certain metals, in particular copper and zinc. The sludge thus produced in the optimum conditions of (AS) and (BF), showed after analysis by (EDS) and (XRD) that the chemical elements Cu, Zn and Al retained in the sludge, increases according to the (BF) content by adsorbing effect in this last and/or inter-particulate bridging on the flocs formed, which reduces the intense risk of these metals in natural waters, in particular those intended for human consumption.

# Declarations

**Acknowledgments** Not Applicable

**Supplementary Materials** Not Applicable

**Data availability statement** Not Applicable

**Ethics approval and consent to participate** Not Applicable

**Consent for publication** Not Applicable

**Funding:** This research received no external funding

### Authors Contributions

*Asmae Skotta*: Conceptualization, Methodology, Original Draft & Writing

*Aaziz Jmiai*: Conceptualization, Original Draft, Writing - Review & Editing

*Widad Elhayaoui, Abdallah El-Asri* and *Malika Tamimi* : Visualization, data analysis, review & editing

*Ali Assabbane* and *Souad El Issami* : Supervision, Validation, data analysis, critical feedback & revision,

All authors have read and agreed to the published version of the manuscript.

### Conflict of interest

We confirmed that this work is original and has not been published elsewhere nor is it currently under consideration for publication elsewhere. This article has been written by the stated authors who are all aware of its content and approve its submission. In case of acceptation, we commit that the article will not be published elsewhere in the same form (in any language) without the written consent of the publisher. We assigned that there are not any conflict of interest about this work.

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

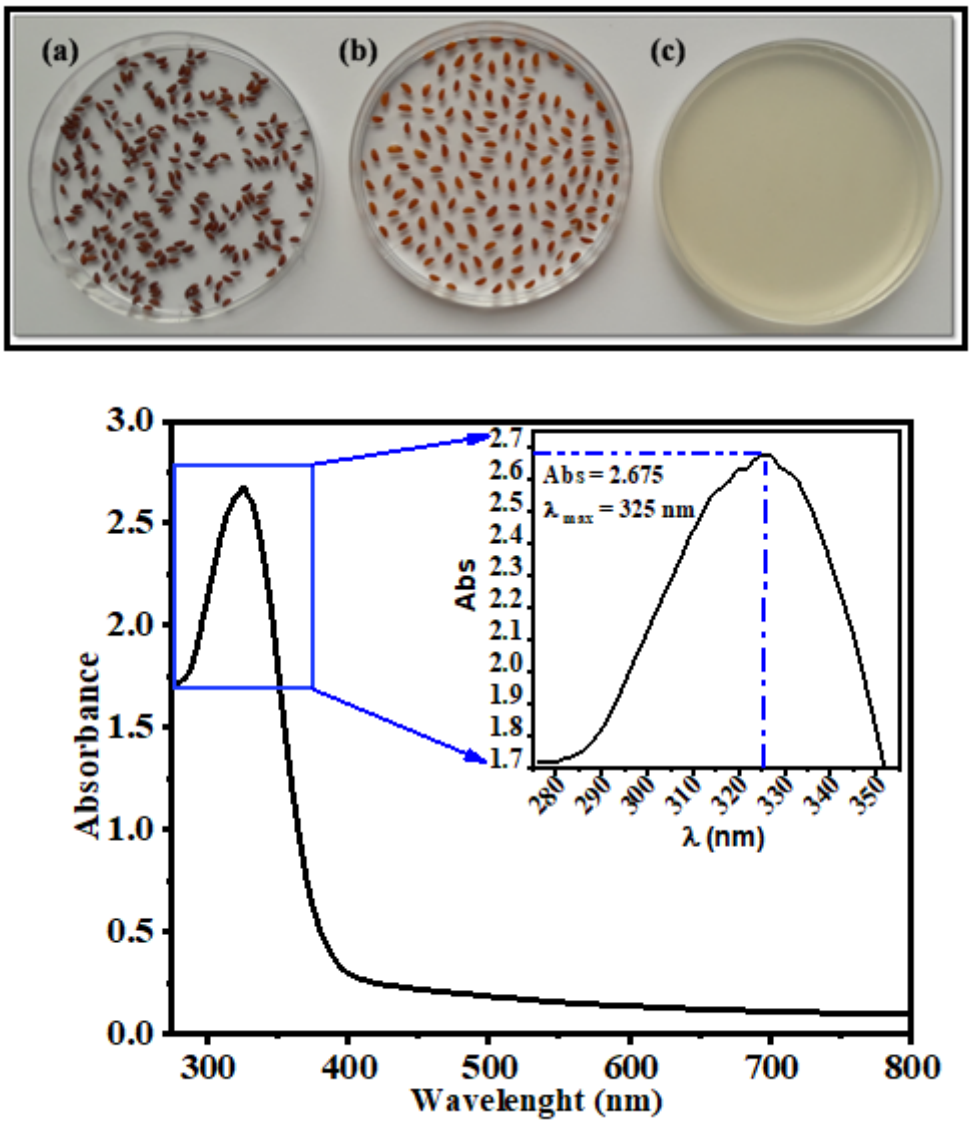
## References


1. Abid a, Zouhri A, Kholtei aIS (2009): Valorization of a new bio flocculant (cactus extract) in the physico-chemical treatment of liquid discharges loaded with copper, zinc and suspended matter. , Rev. Renewable Energies. 12, 321-330
2. Abu Tawila ZMM, Ismail S, Abu Amr SS, Abou Elkhair EK (2019): A novel efficient bioflocculant QZ-7 for the removal of heavy metals from industrial wastewater. RSC Advances 9, 27825-27834
3. Achak M, Ouazzani N, Yaacoubi A, Mandi L (2008): Modern olive mill effluent characterization and their treatment by coagulation-floculation using lime and aluminium sulphate. Journal of Water Science 21, 53-67
4. Amirtharajah A, Mills KM (1982): Rapid-Mix Design for Mechanisms of Alum Coagulation. Journal / American Water Works Association 74, 210-216
5. Amirtharajah A (1988): Some theoretical and conceptual views of filtration. Journal / American Water Works Association 80, 36-46
6. Aouba N (2017): Study of a natural organic coagulant for the treatment of drinking and waste water: Tanfloc. Québec, Canada, 1-1
7. Behrouzian F, Razavi SMA, Karazhiyan H (2013): The effect of pH, salts and sugars on the rheological properties of cress seed (Lepidium sativum) gum. International Journal of Food Science and Technology 48, 2506-2513

8. Behrouzian F, Razavi SMA, Karazhiyan H (2014a): Intrinsic viscosity of cress (Lepidium sativum) seed gum: Effect of salts and sugars. Food Hydrocolloids 35, 100-105
9. Behrouzian F, Razavi SMA, Phillips GO (2014b): Cress seed (Lepidium sativum) mucilage, an overview. Bioactive Carbohydrates and Dietary Fibre 3, 17-28
10. Belbahloul M, Zouhri A, Anouar A (2014): Cactus opuntia ficus indica: A solution against métal pollution and suspended solids. Journal of Materials and Environmental Science 5, 2381-2384
11. Cherifi M (2013): Electrokinetic decontamination of drinking water sludge containing aluminum. Universite Badji Mokhtar
12. Ching HW, Tanaka TS, Elimelech M (1994): Dynamics of coagulation of kaolin particles with ferric chloride. Water Research 28, 559-569
13. Dahhou M, El Moussaouiti M, Khachani N, Assafi M, Hsain LA, Mostahsine S, Bouqallaba K (2012): Physico-chemical characterization of sludge from a unit water drinking production. MATEC Web of Conferences compagne 2
14. Diaz A, Rincon N, Escorihuela A, Fernandez N, Chacin E, Forster CF (1999): A preliminary evaluation of turbidity removal by natural coagulants indigenous to Venezuela. Process Biochemistry 35, 391-395
15. Doke S, Guha M (2014): Scholars Research Library Garden cress ( Lepidium sativum L . ) Seed - An Important Medicinal Source : A Review. J . Nat . Prod . Plant Resour 4, 69-80
16. Duan J, Gregory J (2003): Coagulation by hydrolysing metal salts. Advances in Colloid and Interface Science 100-102, 475-502
17. Fan QL, Zhu YD, Huang WH, Qi Y, Guo BL (2014): Two new acylated flavonol glycosides from the seeds of Lepidium sativum. Molecules 19, 11341-11349
18. Gaouji (2016): Synthetic study of the mechanisms action of medicinal plants used in the treatment of asthma. UNIVERSITE MOHAMMED V DE RABAT
19. Guseva O, Schmutz P, Suter T, von Trzebiatowski O (2009): Modelling of anodic dissolution of pure aluminium in sodium chloride. Electrochimica Acta 54, 4514-4524
20. Hussein HM (2016): Analysis of trace heavy metals and volatile chemical compounds of Lepidium sativum using atomic absorption spectroscopy, gas chromatography-mass spectrometric and fourier-transform infrared spectroscopy. Research Journal of Pharmaceutical, Biological and Chemical Sciences 7, 2529-2555
21. Karazhiyan H, Razavi SMA, Phillips GO, Fang Y, Al-Assaf S, Nishinari K (2011): Physicochemical aspects of hydrocolloid extract from the seeds of Lepidium sativum. International Journal of Food Science and Technology 46, 1066-1072
22. Khider M, Facult B, Sa G, Pr YL, Pr BA, Larbi H, Biskra UMK (2015): Elimination of zinc by adsorption and by coagulation-flocculation Larakeb Manal.
23. Kuo H-s, Tsai W-t (2001): Effects of alumina and hydrogen peroxide on the chemical-mechanical polishing of aluminum in phosphoric acid base slurry. Materials Chemistry and Physics 69, 53-61

24. Lefebvre E, Legube B (1990): Iron(iii) coagulation of humic substances extracted from surface waters: Effect of pH and humic substances concentration. War. Res 24, 591-597
25. Mohan SM (2014): Use of naturalized coagulants in removing laundry waste surfactant using various unit processes in lab-scale. Journal of Environmental Management 136, 103-111
26. Naji S, Razavi SMA, Karazhiyan H (2013): Effect of freezing on functional and textural attributes of cress seed gum and xanthan gum. Food Bioprocess Technol 6, 1302-1311
27. Pallier V (2008): Elimination of Arsenic by coagulation flocculation and electrocoagulation of weakly mineralized waters. Doctoral school science - Technology. WCM. UNIVERSITE DE LIMOGES N°73
28. Razmkhah S, Razavi SMA, Mohammadifar MA (2017): Dilute solution, flow behavior, thixotropy and viscoelastic characterization of cress seed (Lepidium sativum) gum fractions. Food Hydrocolloids 63, 404-413
29. Rodier J, Legube B, Merle N (2009): Water analysis. 9th edition, pp. 1600-1600
30. Sakran M, Selim Y, Zidan N (2014): A new isoflavonoid from seeds of Lepidium sativum L. and its protective effect on hepatotoxicity induced by paracetamol in male rats. Molecules 19, 15440-15451
31. Salvarredy Aranguren MM (2008): Heavy metal contamination of surface waters and sediments of Val de Milluni (Bolivian Andes) by mining waste. Geochemical, mineralogical and hydrochemical approaches. 489-489

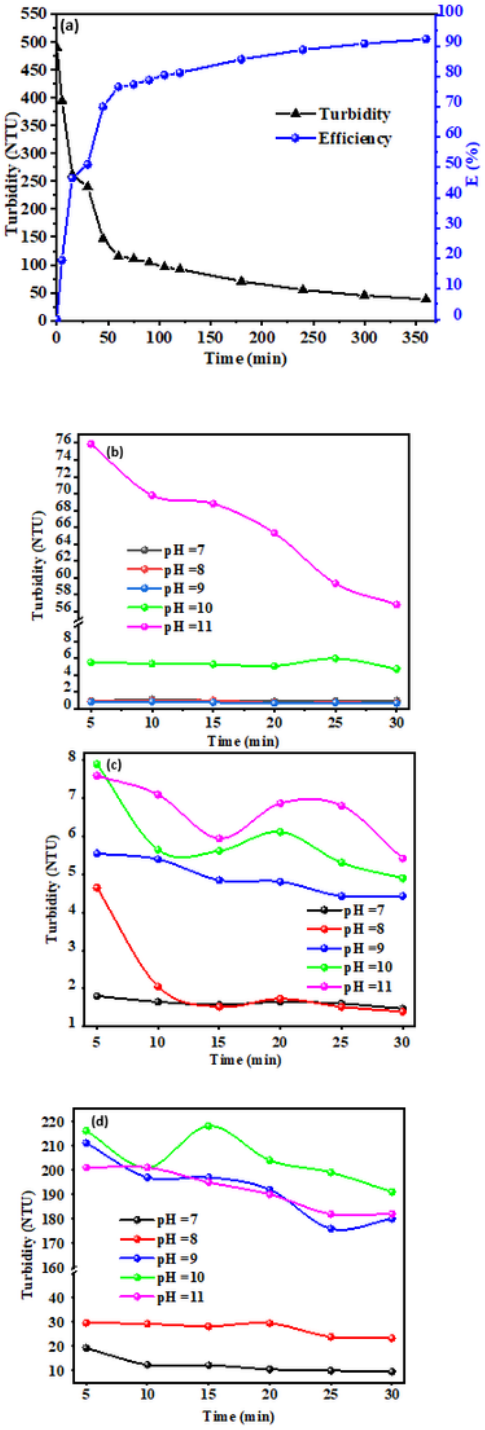
# Figures




## Figure 1

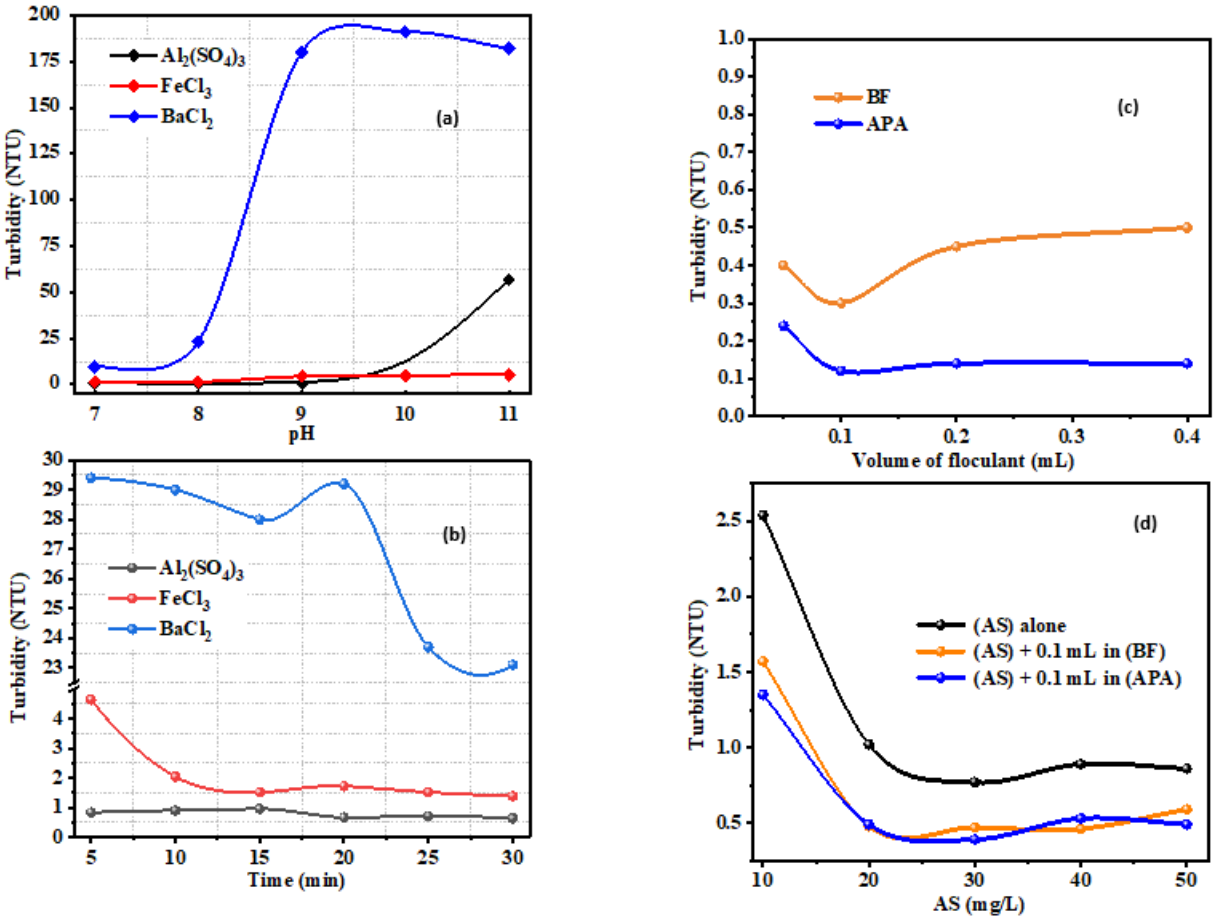
Photographic image of (LS) mucilage preparation; **(a)** Dry seeds, **(b)** Swollen seeds after immersion in water and **(c)** Mucilaginous seed juice. **And** UV absorbance spectrum of (LS) seed mucilage

diluted to 12.5 % in distilled water



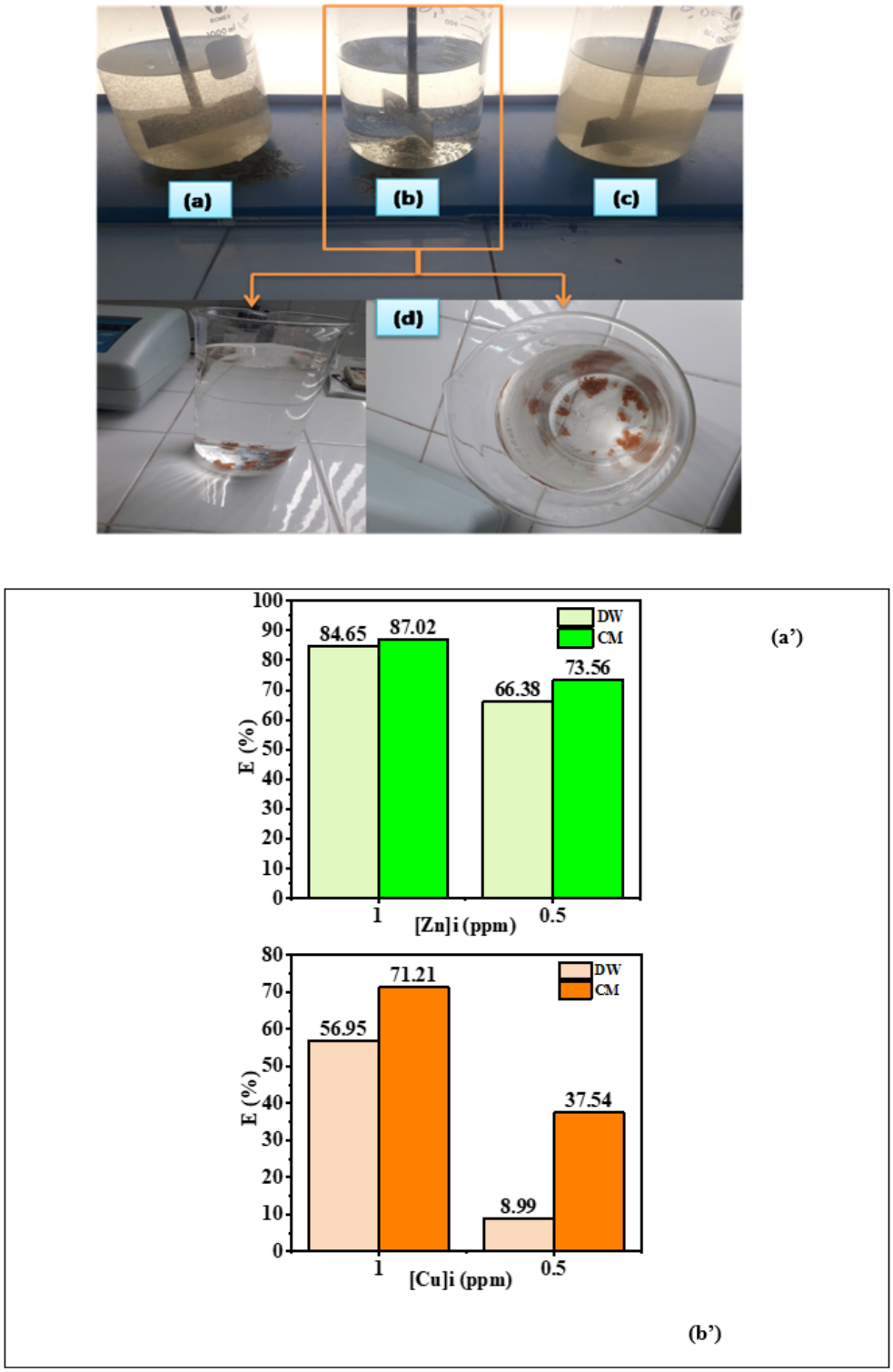

## Figure 2

**(a)**Turbidity variation (NTU) during natural settling of ML (1 g/L), Turbidity variation as a function of time and reaction pH (**(b)** case of combination 1), (**(c)** case of combination 2) and (**(d)** case of combination 3)



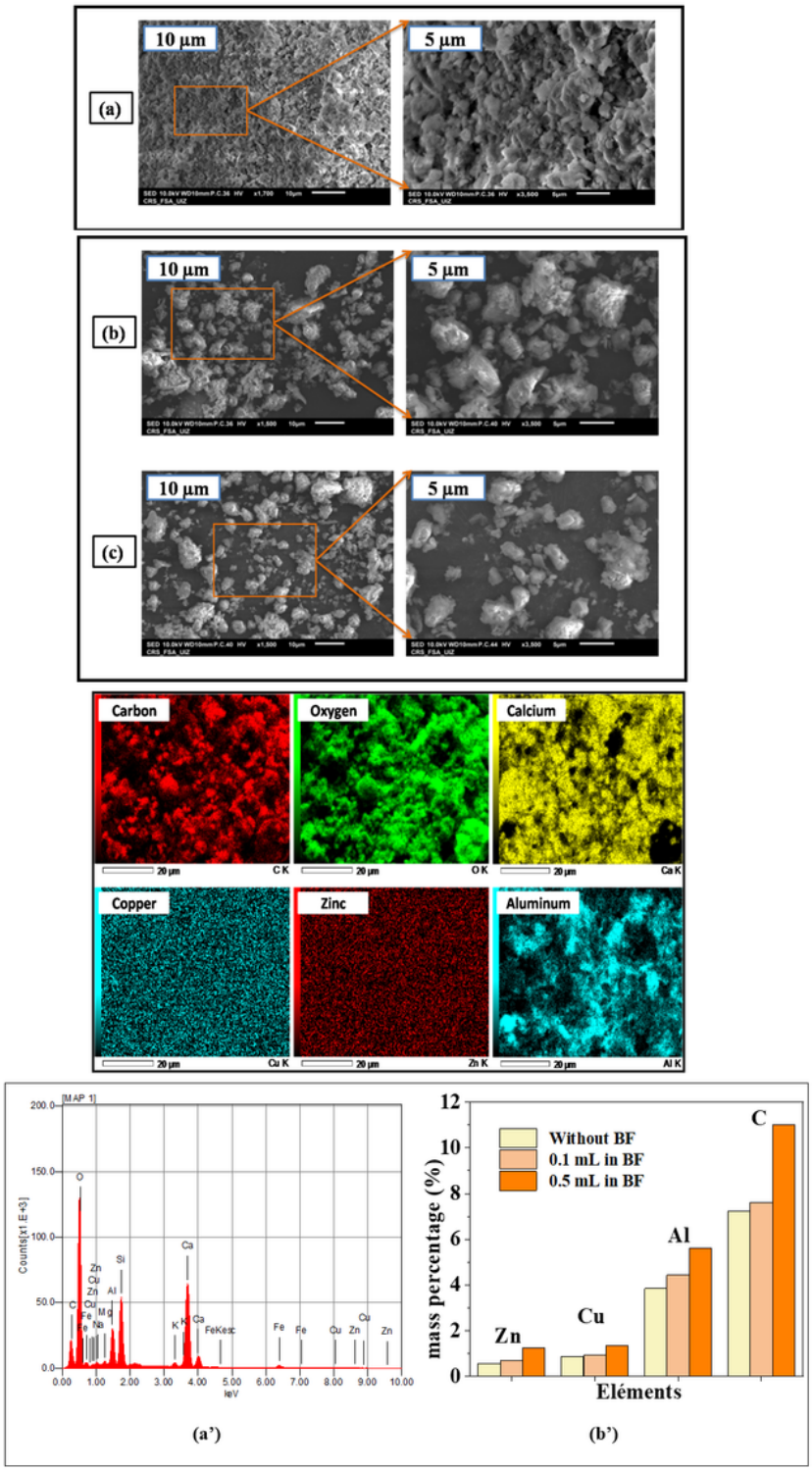

## Figure 3

**(a)** Variation of turbidity after 30 min of settling as a function of pH for the three combinations, **(b)** Turbidity variation as a function of time at pH = 8, **(c)** Turbidity reduction after treatment as a function of progressive doses in (AS) alone and coupled with (BF) and (APA) and **(d)** Variation of turbidity as a function of flocculant volume (APA) and (BF)




## Figure 4

Photographic image of flocs from coagulation by 20 mg/L (AS) with and without polymer **(a)** (AS)+(LS) 0.1 mL, **(b)** (AS)+ (LS) 0.5 mL, **(c)** (AS) alone, **(d)** settled flocs, And Abatement of $Cu^{2+}$ and $Zn^{2+}$ by using (LS) mucilage as bioflocculent (at pH= 8, [AS]= 20 mg/L, (BF)= 0.1 mL). Zinc and Copper removal efficiency; **(a')** and **(b')** respectively




## Figure 5

(SEM) image of a sludge floc formed after treatment with expansion 10 µm and 5 µm respectively. (**a**) $Al_2(SO_4)_3$ alone, (**b**) $Al_2(SO_4)_3$ combined with (BF) 0.1 mL, (**c**) $Al_2(SO_4)_3$ combined with (BF) 0.5 mL , Micrograph of chemical elements distribution by mapping to (BF) 0.1 mL. And Main chemical elements in pure state in the formed sludge; **(a')** (EDS) spectra of main chemical elements in pure state (at (BF) 0.1 mL), **(b')** Variation of Zn, Cu, Al and C as a function of (BF)

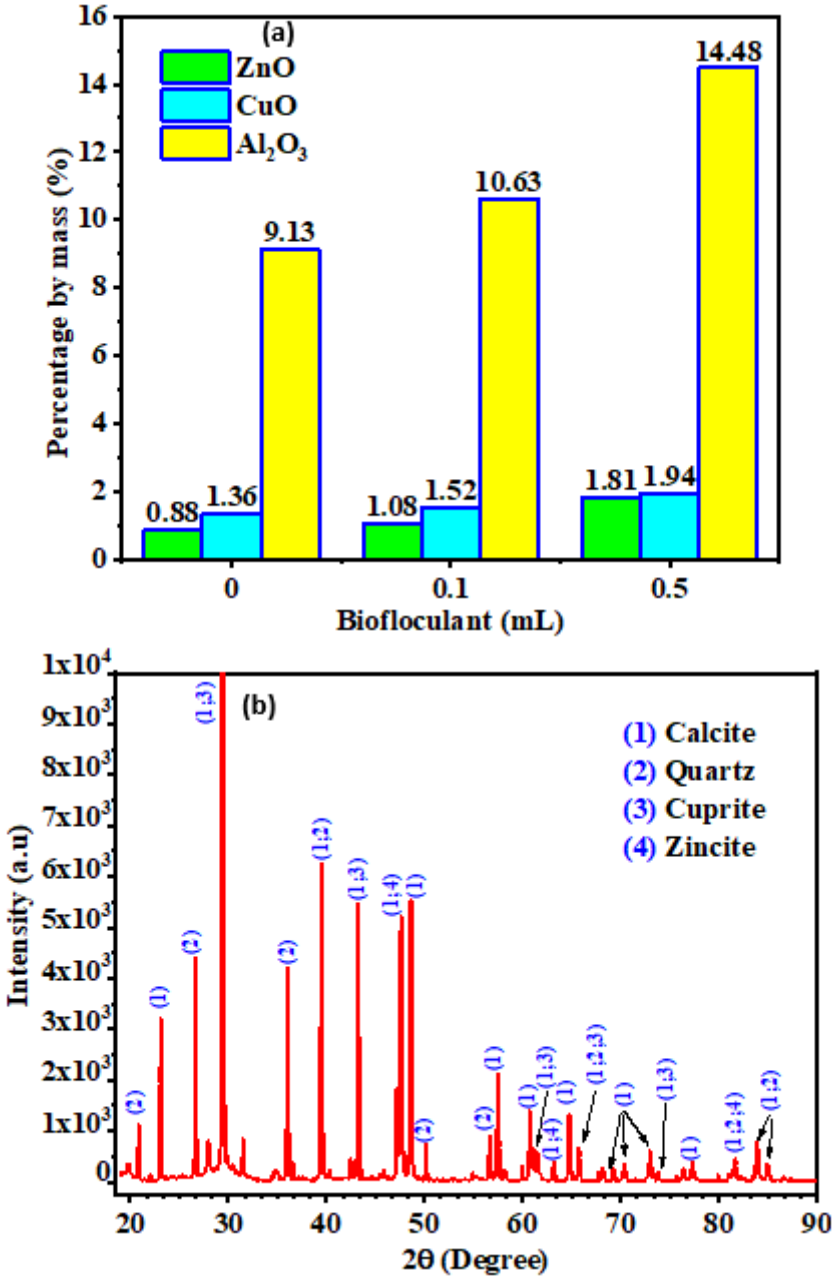



**Figure 6**

**(a)** Mass percentage of Cu, Zn and Al elements in the oxide state trapped in the flocs from the treatment with and without (BF). And **(b)** Spectrum from the (XRD) analysis (with AS= 20 mg/L and BF = 0.1 mL)

# Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- Highligh.docx
- GraphicalabstractAsmae.docx