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Vegetable coagulants as alternative for treatment of wastewater in Mexico

Coagulantes vegetales como alternativa para el tratamiento de aguas residuales en México

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Abstract

This review addresses the various properties of natural coagulants, water, the chemical substance essential for life and the ideal solvent for a large number of compounds, it is commonly used with domestic, commercial and industrial purposes. After its use, it presents sewage to be retired before use it once again. To remove pollutant, water is subject to different physical, chemical and biological processes. Here, the clarification process uses aluminum and iron materials to remove the solids present; these materials are reported as health hazardous and toxic. In Mexico, regulatory frame work stablish that treated wastewater should do not exceed 0.2 mg/L of aluminum even though has been reported an increased risk of Alzheimer's in populations when water exceeds 0.1 mg/L. Natural coagulants have showed coagulation properties when are used in the clarification process, proven its advantages over traditional ones; such as low cost, good coagulant properties and safe health and non-toxic properties. Here, we enlist some vegetable species as alternatives to the traditional based on aluminum and iron. Additionally, these species are known to have origins on Mexico or being present extensively in the territory, making possible to think about them as alternative coagulants in the clarification process of the wastewater treatment process.

Keywords

Vegetable coagulants; wastewater treatment; clarification process

Resumen

Esta revisión aborda las diversas propiedades de los coagulantes naturales, el agua, la sustancia química esencial para la vida y el disolvente ideal para un gran número de compuestos, que se utiliza comúnmente con fines domésticos, comerciales e industriales. Después de su uso, las aguas residuales deben ser tratadas antes de ser usadas una vez más. Para eliminar el contaminante, el agua está sujeta a diferentes procesos físicos, químicos y biológicos. Aquí, el proceso de clarificación utiliza materiales de aluminio y hierro para eliminar los sólidos presentes; estos materiales son reportados como peligrosos para la salud y tóxicos. En México, el marco

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normativo establece que las aguas residuales tratadas no deben exceder 0.2 mg / L de aluminio, aunque se ha reportado un mayor riesgo de Alzheimer en poblaciones cuando el agua excede de 0.1 mg / L. Los coagulantes naturales han mostrado propiedades de coagulación cuando se usan en el proceso de clarificación, demostrando sus ventajas sobre los tradicionales; tales como bajo costo, buenas propiedades coagulantes y propiedades saludables y no tóxicas. Aquí, se enlistan algunas especies vegetales como alternativa a la tradicional basada en aluminio y hierro. Además, se sabe que estas especies tienen orígenes en México o están presentes extensamente en el territorio, haciendo posible pensar en ellas como coagulantes alternativos en el proceso de clarificación del tratamiento de aguas residuales.

Palabras Clave

Coagulantes vegetales; tratamiento de aguas residuales; proceso de clarificación

Introduction

Water is one of the most important resources in planet due to their properties as good and non – toxic solvent, being colorless, odorless and tasteless to human senses. It could be found on earth either in solid, liquid or vapor. It is present superficially in the 70% of earth, then it is one the most abundant molecules on earth too. Its dipolarity make it the ideal solvent for a large number of compounds and solids. And most important, it is essential for life⁽¹⁾.

Due to their abundance, properties and importance to life, it is used extensively with domestic, commercial and industrial purposes. In 2014, data indicated that in Mexico $81.65 \times 10^9 \text{ m}^3$ of water was used; which 75.52 percent was in agriculture, 14.65 in public supply, 5.55 in electric plants (carbon-power plants, combined-cycle plants, etc) and 4.09 in industries⁽²⁾. Generally, water after its use is collected and treated according its utilization. The half of the wastes from the public and domestic sewage is treated in public wastewater treatment plants. Industries treat an 80 percent of their wastes in their own facilities⁽²⁾. The importance of eliminate the pollutant on water is because even if water is present in a great quantity on earth, only the 0.02 percent could be utilized for human purposes. Then, its purification makes possible its use once again in diverse human activities. If not, data points a lack of this resource in next years⁽³⁾.

To remove the contaminants, water is subject to different physical, chemical and biological processes. Each of these individual steps or methods are known as unit operations or processes. In unit operations the pollutant is removed by physical forces; in unit processes, by chemical or biological reactions. Similarly, they can be named by its place occupied in the wastewater treatment processes (primary, secondary and tertiary). Firstly, the primary or physical treatment removes the large solids. The second treatment comprised by biological and / or chemical processes removes the organic matter. Finally, the tertiary treatment eliminates the residual small suspended solids and bacteria coming from the previous step. Water then is discharged into the watercourse⁽⁴⁾.

In the full process the presence of small suspended solids and bacteria to be removed is inherent. In these cases, the clarification process (coagulation, flocculation and sedimentation process) is implemented in order to agglomerate fine particles and colloids in large clusters that are retired as sludge in the bottom of the process tank⁽⁵⁾. First, in the coagulation step, the coagulant agent is introduced via violent agitation into the wastewater to destabilize the suspended particles. Here, pollutant is destabilized through the neutralization of their negative charges, where the reduction of its zeta potential allows to the particles to agglomerate^(6,7). Next, in the flocculation step, the gentle agitation of the medium permits the easy recollection of the agglomerated particles (flocks)^(7,8). At the end, the sedimentation process forces to the heavy particles formed in the previous steps (coagulation and flocculation) go to the bottom of the process tank; where a sludge composed of sands, silts and colloids is formed⁽⁹⁾. In consequence, due to the effectiveness of clarification process, it could be used extensively in all process as pre-treatment, post-treatment, or even as the main treatment. As example, in the primary treatment exists the advanced primary step where the small suspended solids and organic matter

is eliminated by coagulation and a further filtration. Similarly, sometimes is used in the tertiary treatment to obtain final clarified water⁽⁴⁾.

Usually, wastewater plants uses in the clarification process the traditional coagulants based in aluminum (alum, aluminum, chloride, sodium aluminate, polyaluminum chloride, polyaluminum sulfate and polyaluminum chloro-sulfate) or iron (ferric chloride, ferric sulfate, ferrous sulfate and ferric chloride sulfate) metals^(10,11) because they are economical, easily accessible, and highly effective to remove the color, turbidity and pathogenic microorganisms such as bacteria and viruses from water⁽¹²⁾.

Wastewater treatment normativity in Mexico

Mexican normativity related with water treatment dates since the end of eighties and early nineties when it was promulgated the Law of the Environmental Equilibrium and Environmental Protection; and Law of National Waters (Ley General de Equilibrio Ecológico y la Protección al Ambiente; and Ley de Aguas Nacionales, respectively). Both laws established the necessity to control the water contamination and the hydric resources. In this context, it was established that each Mexican president at the beginning of its limited six-year term should present a plan conceived to protect, preserve and utilize the water resources of the country⁽¹³⁾.

In 1996, 1997, 1998 a more specific normativity was promulgated related to the sewage present in water discharged into the watercourse, the sewage system, and water to be reutilized in the public services. Specifically, between its all requirements, normativity demands a turbidity of a maximum of 5 nephelometric turbidity units (NTU) and 20 true color units on the platinum-cobalt scale (or Hazen scale) in water in treated wastewater^(10,11,14). To comply this requirement, Mexican wastewater treatment plants uses in its clarification process aluminum and iron coagulants due its advantages previously described. It is interesting to note that these kind of coagulants are still used even though they are reported as health hazardous due to its toxic nature^(10,11); and even more because the Mexican regulatory framework establish that treated wastewater should do not exceed 0.2 mg/L of aluminum⁽¹⁵⁻¹⁷⁾ besides this, existing reports show an increased risk of Alzheimer's in populations where the average residual aluminum concentration in water exceeds 0.1 mg/L⁽¹⁸⁻²³⁾. Additionally, extra normativity appeared⁽¹⁸⁻²³⁾ in order to use the treated wastewater as recharge for the aquifers that currently are overexploited^(24,25), being a risk of possible contamination of natural non-polluted waters.

Vegetable coagulants

Natural extracts derived from seeds, leaves, tree barks and roots have being found to form clots or flocs when are used in the clarification process of wastewater treatment. Moreover, they have proven advantages over traditional ones; such as being of low cost, to have an antimicrobial power and the ability to work at low concentrations (Table 1 and 2); but also and more important, they are safe health and non-toxic⁽²⁶⁻²⁸⁾. Some of these vegetable coagulants are widely distributed in Mexico, for example:

| Table 1. Advantages and disadvantages of the vegetable coagulants. | |
|--|--|
| Advantages | Disadvantages |
| ➤ Low cost | ➤ Not as effective as Ammonium Sulfate |
| ➤ Antimicrobial power | ➤ Not all have the same performance |
| ➤ Low concentrations | ➤ <i>Zea mays</i> and <i>Phaseolus vulgaris</i> are widely used in agriculture in México |
| ➤ Safe health | |
| ➤ Non-toxic | |
| ➤ Residuals do not generate pollution | |

Table 2. Removal percent of some vegetable coagulants.

| Origin | Removal percentage | Reference |
|---------------------------------|--|---|
| <i>Guazuma ulmifolia</i> | 50-70 percent of inicial color | Feria-Díaz, 2016 |
| <i>Phaseolus vulgaris</i> | 40-45 percent of coagulant | Antov, 2007 |
| <i>Zea mays</i> | 89 percent of removal dye. | Patel, 2011 |
| <i>Opuntia ficus</i> | 48 to 91 percent of turbidity | Almendárez, 2004 |
| | 54 percent of color removal and 72 percent of turbidity | Villabona, 2013 Olivero 2013 |
| <i>Manihot esculenta</i> | 94 percent of color removal | Solis-Silvan, 2012 |
| <i>Tamarindus indica</i> | 76 percent of removal NTU of turbidity | Pritchard, 2009 |
| <i>Pithecellobium saman</i> | 99 percent of removal NTU of turbidity | Ospina & Ramírez, 2011(a); Ospina & Ramírez 2011(b) |
| <i>Malvaviscus areus</i> | 5-30 percent coagulant but is dependent on the amount used | Ramírez-Estrada,2011 |
| <i>Hylocereus undatus</i> | | |
| <i>Heliocarpus popayanensis</i> | | |

Guazuma ulmifolia

The *Guazuma ulmifolia* (commonly known as West Indian or bay cedar) was used on raw water obtained from the Sinu river in Colombia to determinate its effectiveness as water clarifier. Here, samples with turbidity of 56, 104, 200 and 301 NTU were tested in presence of 5 to 60 mg/L of the *Guazuma ulmifolia* as coagulant. Alkalinity, pH and watercolor was measured before and after the treatment to verify the efficacy of the process. Results showed a removal around 50 – 70 percent of initial color. An author claims then that its invention could be considered as an alternative for water treatment⁽²⁹⁾.

Phaseolus vulgaris

Usually named as string bean, flageolet bean, haricot bean or only as “bean”, its extract was used at first as coagulant in jar tests at different dosages of eluates. The results showed different coagulation activities depending the dose of coagulant utilized in each protein fraction, indicating different coagulation mechanisms in each case⁽³⁰⁾. Later, studies to determine the coagulant and protein activity of this bean extract showed that in a crude extract are close to 40 percent; different conditions could generate values as high as a 45 percent. Hence, authors suggest the application of this kind of natural coagulant for water purification⁽³¹⁾.

Zea mays

Studies using *Zea mays* (Maize) seeds as an alternative to the removal of the Congo Red dye on textile wastewater indicated that it is possible to eliminate it as a maximum of 89.4 percent. Parameters such as pH, coagulant dose (Maize), flocculation time and temperature should be maintained around 4.0, 25 mg/L, 60 min and 340 K respectively to obtain the maximal removal⁽³²⁾.

Opuntia ficus

Polymer “Cochifloc” obtained from the *Opuntia ficus* fruit (Tuna) was studied as coagulant to treat water from the lake “Xolotlan” in Nicaragua. Results showed that turbidity was eliminated from 48 to 91 percent depending on the pH basically⁽³³⁾; in consequence, it indicates a good coagulant behavior. In base to those results, similar experiments were performed in raw water with turbidity of 171 NTU. After treatment when 90 mg/L of coagulant was used, color removal was about 54 percent; for turbidity 72 percent⁽³⁴⁾. At same time, experiments performed by Olivero *et al*; corroborate its effectiveness as coagulant when water from the Magdalena River in Colombia was treated. Samples with 35 and 40 mg/L of *Opuntia ficus* showed a removal of turbidity of 93.23 percent. Althought these parameters not satisfied the Colombian

normativity for potable water, it accomplished the requirements needed for an advanced primary step in the water treatment process⁽³⁵⁾.

Manihot esculenta

Commonly known as yucca or cassava, this tubercle is used in the southeast of Mexico as principal ingredient for stewed foods in regional dishes; in consequence, its importance lies in its demand as aliment⁽³⁶⁾. Initially, it was found that mixed with starch and aluminum sulphate reduce the demand of the aluminum compound in the clarification process; additionally it increases the efficiency about a 94 percent in the color removal when a treatment of 2 mg/L of cassava and 28 mg/L of aluminum sulphate is used as coagulant⁽⁵⁾. Recently, Renuka *et al*, testing different plants to use in the clarification process, found that only using *Manihot esculenta* as coagulant it is effective to purify drinking water and waste water⁽³⁷⁾.

Tamarindus indica

This leguminous tree and its pod-like fruita (Tamarind) has been reported to work as coagulant when its extracts are implemented in the clarification process. These studies performed in a pilot-plant and full-scale test show that it could work in raw water with 50 - 700 NTU of turbidity. Optimal results (76 percent of removal) were obtained with a content of 50 mg/L of coagulant at 30 °C. Finally, authors propose the use of the *Tamarindus indica* preferably in water with values highers than 300 NTU of turbidity^(26, 38).

Pithecellobium saman

Frequently found as Monkey-pod (Saman), or rain tree, was studied by Ospina *et al*, as a natural coagulant to treat raw turbid water from the Combeima River in Colombia. The importance of this study lies in the fact that this water source supplies the urban aqueduct of the city of Ibagué in Colombia. Samples collected before treatment presented 1500 NTU of turbidity; at the end of the clarification process using 36 - 105mg/L of the natural coagulant a significant diminution was obtained, resulting in values around 3 – 5 NTU, similar to those reclaimed by the Colombian normativity. Therefore it was demonstrated its use as an efficient coagulant⁽³⁹⁾.

Malvaviscus arboreus*, *Hylocereus undatus* and *Heliocarpus popayanensis

Malvaviscus arboreus (Turkap or ladies teardrop), *Hylocereus undatus* (Pitahaya or dragon fruit) and *Heliocarpus popayanensis* (White balsum) are known by natives to act as natural coagulant when are used to prepare candies or sweeteners for its regional gastronomy. Stems, leaves and flowers were used as clarifier agents on waters obtained from La Salada River at Colombia in order to determinate if its properties are affected by their specie or coagulant concentration. Results indicate that only *Hylocereus undatus* and *Heliocarpus popayanensis* have a remarkable coagulant effect regarding to the *Malvaviscus arboreus*. Authors recommend that water treated could be used with purposes other than for human use⁽⁴⁰⁾.

Final considerations

This review presents some vegetable species with coagulant properties as alternatives to those based on aluminum and iron. Basically, because literature enlists already some works where marine organisms (chitosan), trees (*Acacia*, *Castanea*), tree seeds (*Moringa oleifera*), plants (*Cassia obtusifolia*, *Acacia*, *Castanea*), humus (Humic acid), starches (Rice, Corn and Potato), and even snail shells, all coming from natural sources show same or better results than

traditional metal coagulants; with the advantage of not being health hazardous and toxic. Moreover, the vegetable species listed here are known to have origins on México (*Guazuma ulmifolia*, *Phaseolus vulgaris*, *Zea mays*, *Malvaviscus arboreus*, *Opuntia ficus*) or being present extensively in the territory (*Manihot esculenta*, *Tamarindus indica*, *Pithecellobium saman*, *Hylocereus undatus*, *Heliocarpus popayanensis*), making possible to think that in some moment they could be used for a “local” and affordable clarification process in the wastewater treatment process at low cost of operation, minimizing the use of chemical agents without endanger the population health. Although many more studies are required to validate this alternative in the wastewater treatment process.

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