# Application of coagulation by sweep for removal of metals in natural water used in dairy cattle

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Aplicación de la coagulacion por barrido para la remocion de metales en aguas naturales empleadas en ganados lecheros

Aplicació de la coagulació per escombrat, per a l'eliminació de metalls en l'aigua natural que s'utilitza en el bestiar lleter

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#### **SUMMARY**

Use contaminated water to wash the teats of animals and tools, among others, is due to the presence of potential pathogens and pesticide residues, antibiotics and metals in raw milk. Washing with water of excellent quality, premilking is a key to reduce the contamination of milk and prevent these compounds are adsorbed on the skin of the udder and then migrate to milk gun. Aluminum sulfate, ferric chloride and chitosan for the removal of turbidity, color and TOC in natural waters used in the daily activities of a dairy herd, plus the removal of metals such as copper, cobalt and zinc was assessed found was used frequently in natural waters in some regions of Colombia, in this case using the sweep coagulation to improve the removal efficiency. Ferric chloride was the most effective coagulant for conventional removal of turbidity, color and TOC removal percentages greater than 70% and a coagulant dose of 60 mg/L, while for the optimum metal removal doses were 235 mg/L and 500 mg/L aluminum sulfate, and 300 mg/L and 510 mg/L of ferric chloride, achieving removal percentages above 80 % for most metals. Chitosan did not show large removal efficiencies compared to other coagulants.

**Keywords:** Coagulation; metals; chitosan; aluminum sulfate; ferric chloride

## **RESUMEN**

Utilizar agua contaminada para lavar las ubres de los animales y los utensilios, entre otros, es causa de la presencia de microorganismos patógenos y de posibles residuos de plaguicidas, antibióticos y metales en la leche cruda. El lavado con agua potable de excelente calidad, previo al ordeño, es un arma fundamental para reducir la contaminación de la leche y evitar que estos compuestos se adsorban en la piel de la ubre y luego migrar a la leche. Se empleó el sulfato de aluminio, cloruro férrico y chitosan, para la eliminación de la turbiedad, color y COT en aguas naturales empleadas en las actividades diarias de un ganado lechero, además se evaluó la eliminación de metales como el cobre, cobalto y zinc encontrados frecuentemente en aguas naturales de algunas regiones de Colombia,

empleando en este caso la coagulación por barrido para mejorar la eficiencia de eliminación. El cloruro férrico resultó ser el coagulante más efectivo para la eliminación convencional de turbiedad, color y COT con porcentajes de eliminación mayores al 70% y una dosis de coagulante de 60 mg/L, mientras que para la eliminación de metales las dosis óptimas fueron de 235 mg/L y 500 mg/L para sulfato de aluminio, y de 300 mg/L y 510 mg/L para cloruro férrico, logrando porcentajes de eliminación por encima del 80% para casi todos los metales. El chitosan no presentó grandes eficiencias de eliminación comparado con los otros coagulantes.

Palabras clave: Coagulación; metales; chitosan; sulfato de aluminio; cloruro férrico

## **RESUM**

Utilitzar aigua contaminada per rentar les mamelles dels animals i els estris, entre d'altres, és causa de la presència de microorganismes patògens i de possibles residus de plaguicides, antibiòtics i metalls en la llet crua. El rentat amb aigua potable d'excel·lent qualitat, previ al munyiment, és una arma fonamental per reduir la contaminació de la llet i evitar que aquests compostos s'absorbeixin a la pell de la mamella i després migrin a la llet. Sulfat d'alumini, clorur fèrric i chitosan es van fer servir per eliminar la terbolesa, el color i el COT en aigües naturals emprades en les activitats diàries d'un ramat lleter, i a més es va avaluar la eliminació de metalls com el coure, cobalt i zinc trobats frequentment en aigües naturals d'algunes regions de Colòmbia, emprant en aquest cas la coaqulació per escombrat per millorar l'eficiència de eliminació. El clorur fèrric va resultar ser el coagulant més efectiu per a la eliminació convencional de terbolesa, color i COT amb percentatges de eliminació majors al 70% i una dosi de coagulant de 60 mg/L, mentre que per a la eliminació de metalls les dosis òptimes van ser de 235 mg/L i 500 mg/L per sulfat d'alumini, i de 300 mg/L i 510 mg/L per clorur fèrric, aconseguint percentatges de eliminació per sobre del 80% per a gairebé tots els metalls. El chitosan no va

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presentar grans eficiències de eliminació comparat amb els altres coagulants.

Paraules clau: Coagulació; metalls; chitosan; sulfat d'alumini; clorur fèrri

## **INTRODUCTION**

The coagulation-flocculation processes are used in the purification of water, where the insoluble particles and / or organic matter coalesce to achieve precipitation; which facilitates its removal at a later stage of sedimentation, flotation and filtration. [1] These processes are affected by the characteristics of the water (alkalinity, temperature and pH), the type and dosage of coagulant used [1,2], and the rate and duration of the rapid mixing [2]. The coagulation-flocculation process not only removes suspended solids from the water, but it also helps to control the color and organic compounds [3,4].

Coagulants widely used to carry out these processes are the salts of iron and aluminum [1, 2, 3, 5] from which the clotting mechanism by scanning and charge neutralization [1] is given without But these salts increase metal concentrations in water and produce highly toxic sludge. Therefore, in recent years we have studied new products such as synthetic polymers [5], biopolymers and/or natural coagulants [1], which often tend to be less toxic to human health and to the environment, also biodegradable sludge produced (natural coagulants) in amounts less than 20 to 30%, compared to those produced by the aluminum salts [6].

Aluminum sulfate  $(Al_2(SO_4)_3)$  is the most widely used coagulant in water treatment process [7] due to their low cost, ease of use and availability in the market [1], in addition, the results have shown that different doses, aluminum sulfate removals achieved both high carbon and dissolved organic nitrogen [8] and removal of heavy metals such as lead [9]. However, its use has shown increased aluminum in the water above the permissible levels for human health [10], Alzheimer's causing problems [7].

Ferric chloride (FeCl<sub>2</sub>) is a coagulant that is primarily used in the removal of turbidity, which has been used to prevent health problems caused by aluminum sulfate [10], but the implementation of this coagulant causes the decrease pH in water [7], due to the high consumption of alkali present. Chitosan is a biodegradable polymer [11, 12], nontoxic [12, 13] and high molecular weight, [2] produced by the deacetylation of chitin, [1] which has been studied in the absorption of metal cations [14], in the coagulation processes in water purification [15], the removal of particles [16], the elimination of persistent pollutants [14], the color removal [17], the removal of heavy metals and coagulation proteins [18] and in the treatment of water oil production [19]. Coagulation mechanisms chitosan are charge neutralization, adsorption (related to protonated amine groups), precipitation, bridging (relative to the high molecular weight) and electrostatic [1] setting. The major disadvantage of chitosan with respect to aluminum sulfate and ferric chloride is its cost, which has restricted its use in the medium [20]. The difference between MT2 and MT3 chitosan is essentially the solubility, being more soluble MT2 and MT3 chitosan oligosaccharide, and further wherein the mesh size being 80 for MT2 and 200 for MT3 [1].

The poor quality of water used in dairy herds for cleaning the udder, milking utensils and cattle drink has led to

obtain milk with toxic waste (metals, pesticides and antibiotics) and pathogens [21], creating problems health and preventing the export of this product to countries with strict regulations on food products. Recently, there have been developed various processes for the removal of heavy metals in the water, the precipitation of hydroxides, the most widely used method because of its low cost and simplicity [22] has also been used coagulation-flocculation and sedimentation, but in some cases, the removal of heavy metals by the latter does not exceed 28 or 40% [23].

The present study evaluates the effect of aluminum sulfate, ferric chloride and MT2 and MT3 chitosan in the coagulation-flocculation process for the removal of heavy metals and improving the quality of the water supply of a dairy herd.

# **MATERIALS AND METHODS**

#### Sampling

Monthly samplings were conducted for 12 months in a dairy herd located in the town of San Pedro de los Milagros north of the department of Antioquia, Colombia, in order to meet water quality supply both dry season and wet season (Table 1), although daily temperatures are relatively stable between 13-19°C throughout the year, annual rainfall often varies between 1700-2000 mm during the months of April/May and October/November [21].

**Table 1.** Average physicochemical characterizations of the study site

acterizations of the study site					
Parameters	Average Values				
рН	6.82 ± 0.35				
O.D (mg/L)	$2.47 \pm 1.14$				
Temperature (°C)	$18.3 \pm 2.1$				
Saturation (%)	26.2 ± 11.4				
Turbidy (NTU)	$5.3 \pm 2.7$				
Apparent color (UPC)	51.8 ± 30.1				
Conductivity (µS/cm)	$30.3 \pm 19.7$				
Total Hardness (mg CaCO <sub>3</sub> /L)	$13.82 \pm 5.42$				
Total Iron (mg/L)	$1.729 \pm 1.520$				
Chlorides (mg Cl <sup>-</sup> /L)	$1.647 \pm 0.860$				
Nitrites (mg N-NO <sub>2</sub> -/L	$0.015 \pm 0.002$				
Nitrates (mg N-NO <sub>3</sub> -/L)	$0.18 \pm 0.05$				
Phosphate (mg PO <sub>4</sub> <sup>3-</sup> /L)	$0.197 \pm 0.085$				
Sulfates (mg SO <sub>4</sub> <sup>2-</sup> /L)	$1.427 \pm 1.330$				

Subsequently, tests for coagulation-flocculation, weekly samplings were performed for 4 months. The samples were transported to the laboratory at 4°C where they were used for test trials pitchers on the day of sampling. 2.2 Reagents

Aluminum sulfate ( $Al_2(SO_4)_3$ ) 1% w/v commercial grade (Protoquímica), Ferric Chloride (FeCl<sub>3</sub>) 3% w/v reagent grade (Mallinckrodt Chemicals) and Chitosan MT2 with 85.33% of deacetylated groups and mesh size of 80 and Chitosan MT3 with 85.17% deacetylated groups and a mesh size of 200, both distributed by Jinan Haidebei Marine Bioengineering Co., were used as coagulants. To increase the alkalinity of natural water from the dairy herd Sodium Bicarbonate NaHCO $_3$  was used with a purity of 99.5% (Merck). The zinc (II), cobalt (II) and copper metal (II) used to dope the natural water were prepared using

reagent grade zinc sulfate salts ( $ZnSO_4$ , $7H_2O$  Mallinckrodt), Cobalt Chloride (Baker Analyzed CoCl.6 $H_2O$ ) and copper sulfate ( $CuSO_4$ . $5H_2O$  Merck). 1000 ppm solution of each experiment were prepared.

## Coagulation-flocculation experiments

For assays of coagulation-flocculation of digital test jars (E&Q F6-300), with a stirring system of multiple blades and variable speed from 10 to 300 RPM was used. The test jar test was conducted in several steps of agitation following the methodology described in [9], to ensure the phases of coagulation, flocculation and sedimentation. Rapid mixing (bleeding) was performed at 300 RPM for 1 minute, the slow mixing (flocculation) at 40 RPM for 15 minutes at 0 RPM sedimentation for 15 minutes. To determine the optimum dose of aluminum sulphate dose of 20, 30, 40, 50, 60 and 70 mg/L were evaluated at 1% dose of ferric chloride of 15, 30, 45, 60, 90 and 120 mg/L 3% chitosan and doses of 2.5, 5, 10, 15, 20 and 30 mg/L of 1% for both the MT2 as MT3 were used, due to the low solubility of chitosan in high concentrations.

## Analytics methods

Colour, Turbidity and Alkalinity were done in the Diagnostics and pollution control group (GDCON) laboratory in accordance with protocols established in the Standard Methods [24]. The GDCON group laboratory is accredited by the Institute of Hydrology, Meteorology and Environmental Studies (IDEAM) del Ministerio de ambiente y desarrollo Sostenible de Colombia to perform such analyses. Parameters such as pH and Electrical Conductivity (EC) were evaluated using electrodes (Metter Toledo and Cond 720 WTW, respectively). Sulfate (SO42-) and Chloride (CI-) were determined by ion chromatography (using a Dionex ICS-1000 Ion Chromatography system, an IonPac AS23 column of 4 x 250 mm and ASRS-Ultra II 4 mm suppressor). Total Organic Carbon (TOC) was performed by TOC Analyzer Apollo 9000 Combustion with a non-dispersive infrared detector (NDIR). Aluminum (III), Iron (III), Zinc (II), Cobalt (II) and Copper (II) were carried out by Atomic Absorption (AA) GBC 932 plus with graphite oven GBC GF 3000.

#### Statistical Analysis

All experiments were performed in triplicate and in this way the average and standard deviation (STDEV) were determined. Experimental data were statistically analyzed using the Statgraphics Plus 5.1 program using an ANOVA analysis to find correlations between the different parameters analyzed.

## **RESULTS AND DISCUSSION**

## Effect on the physicochemical parameters

The results obtained for each coagulant at different doses are shown in Table 2. In the case of aluminum sulphate 1%, an increase in electrical conductivity as coagulant doses were increased, a situation that was correlated with an increase of sulfate ion in the water, observed from 2.613  $\pm$  3.280 mg SO $_4^2$ -/L for natural water at 32.180  $\pm$  0.300 mg SO $_4^2$ -/L for a dose of 70 mg/L of aluminum sulfate 1%.

The greatest removal color, turbidity and TOC were about 71.4%, 65.7% and 48.3% respectively, with a dose of 40 mg/L aluminum sulfate, at doses greater tendency of the particles was observed to stabilize, which consistent with the results obtained by [15]. However, there was a decline in turbidity as the coagulant dosage was increased, similar

to what happened to [15]. The residual aluminum to the optimum dose was 1.069 mg/L. No significant amount of floc was observed, due to this low amount of suspended solids in the initial sample.

In the case of ferric chloride to 3%, 15 mg/L, 90 mg/L and 120 mg/L, caused increase in color and initial haze of the sample due to floc rate obtained with apparent characteristics dispersed and low sedimentation. The optimal dose was 60 mg/L, with a percentage of 74.0 % removal, 78.1 % and 43.0 % for color, turbidity and TOC, respectively. As with the aluminum sulfate, the conductivity was also influenced by the increase of the dose of coagulant, observed increased concentrations of chloride ion, from an initial concentration of 0.502  $\pm$  0.143 mg Cl·/L Water natural, at a concentration of 1.078  $\pm$  0.097 mg Cl·/L for optimal dose of 60 mg/L. Both aluminum sulfate and ferric chloride for consumption occurred alkalinity and pH decrease as the dose is increased coagulant.

For the Chitosan MT2 1%, the optimal dose was 5 mg/L, reaching removal percentages of 66.12%, 66.44% and 32.23% for color, turbidity and TOC, respectively. Chitosan MT2 dose above the optimum, increased color, turbidity and TOC and generated low sediment floc shaped fibers perceptible to the eye. In [15] evaluated the chitosan as a coagulant in the purification and had low removal of turbidity, and were not observed flocs, due to the low initial turbidity (7.81 NTU) affecting the formation of the floc, and the turbidity initial (5.3 NTU) water study also observed flocs. The results warn initial turbidity affect coagulation efficiency of chitosan. In the case of the alkalinity and pH, no significant changes were observed, whereas the increased conductivity due to protonation of the chitosan is solubilized because.

For the Chitosan MT3 1% the optimal dose was 10 mg/L, with removals of 52.66%, 36.11% and 25.36% for color, turbidity and TOC, respectively. As Chitosan MT2, no considerable variations in alkalinity and pH are presented, while in the conductivity, the MT3 showed protonation at lower proportion to MT2. Comparing the results in an optimal dose for the removal of color, turbidity and TOC between Chitosan MT2 and MT3, we observed that the Chitosan MT2 is much more efficient than the MT3, with higher percentages of removal using a lower dose of coagulant.

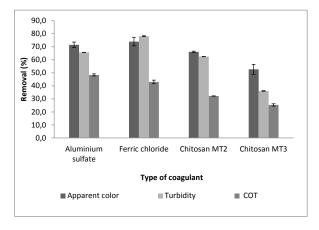


Figure 1. Percentage of removal of the optimal dosage of each coagulant; Aluminum sulfate (40 mg/L), ferric chloride (60 mg/L), Chitosan MT2 (5 mg/L) and MT3 Chitosan (10 mg/L). Table 2. Results of the analyzes performed for each coagulant at different doses

In Figure 1, the optimum doses of coagulants used for removal of color, turbidity and TOC are observed. Most color and turbidity removal was obtained with a dose of 60 mg/L of ferric chloride with removal percentages of 74.0% and 78.1%, respectively, this agrees with the results of [25], who obtained higher removals of suspended solids Total compared to aluminum and Ferric Chloride biopolymer. Most TOC removal was 48.4% obtained with 40 mg/L of aluminum sulfate.

The optimal dose for the removal of colloidal particles with aluminum sulfate was 40 mg / L and ferric chloride was 60 mg/L with removal percentages Turbidity, Color and similar TOC. Considering coagulants used were reagent grade, more expensive to make water treatment with ferric chloride. In addition to these coagulants adding alkalinity is required, if the water does not contain the required amount naturally. Such an addition leads to extra costs and expenses during treatment. In the case of chitosan, the addition of alkalinity is required since it is a coagulant that acts without the presence of the natural alkalinity not consume water, but others lower efficiencies coagulants evaluated are obtained and the obtained floc is negligible [15].

# Effect on metals

In Table 3, obtained by removing copper, cobalt and zinc to different doses of the coagulant is observed. In the case of aluminum sulfate coagulation predominated sweep where the bulk cobalt removal was obtained with a dose of coagulant of 235 mg/L to obtain a removal rate of 30.7%. With Copper and Zinc, the greater removal was obtained with a higher dose (500 mg/L) where removal of 86.7% and 99.6% respectively were achieved.

Very high doses showed that an excess of coagulant usually causes low efficiency due to restabilizing the particle charge. The optimal dose of coagulation with aluminum sulfate (40 mg/L) removal of colloidal particles and organic matter (TOC) is achieved, but not removal of metals, it is necessary to increase the dose above 200 mg/L and en-

sure sweep coagulation. In [9] obtained higher efficiencies at 99.0% Lead with Aluminum Sulfate concentrations of 1200, 2000 and 4000 mg/L, are leading to higher costs in the coagulant added e increases in alkalinity.

In the case of ferric chloride predominates, like aluminum sulfate, the coagulation by sweeping. In the case of Cobalt and Copper, the optimum coagulant dosage was 510 mg / L with a removal percentage of 73.0% and 96.5%, respectively. In Zinc, the optimal coagulant dosage was 300 mg/L with a percentage of 94.5% removal. A very low or high dose of coagulant significant reductions of metals were obtained. For higher doses, the amount of sludge obtained was so high that matched the level of sampling water, this amount of sludge could cause problems in a treatment process or compel perform major maintenance to the structures of sedimentation and filtration.

For the chitosan, clotting mechanisms are different from those of Aluminum Sulfate and Ferric Chloride. Therefore, we choose to work with optimal doses of removal of organic matter due to its low solubility [15]. If the MT2 Chitosan for removal of copper and cobalt, the optimal dose was 10 mg/L with a removal percentage of 15.1% and 50.9%, respectively. These percentages when compared with the removals obtained by Aluminum Sulfate and Ferric Chloride, is not very high, since in these higher removal was obtained. In the case of zinc, the best dose of coagulant for removal was 30 mg/L with a percentage of 25.8% removal. For the Chitosan MT3, the optimal dose of coagulant for the removal of cobalt was 20 mg/L, with a percentage of 25.6% removal for the removal of copper optimal dose was 10 mg/L with a removal percentage 24.6% and for the removal of Zinc optimal dose was 30 mg/L with a percentage of 39.4% removal.

When comparing the results of MT2 and MT3 chitosan was observed that showed a higher removal Zinc and Cobalt with MT3. During rehearsals with chitosan, the amount of sludge generated is, at first glance, much less than the trials Aluminum Sulfate and Ferric Chloride.

Table 2. Results of the analyzes performed for each coagulant at different doses

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Type of coagulant	Dosage (mg/L)	Apparent color (UPC)	Turbidity (NTU)	TOC (mg/L)	Conductivity (us/cm)	рН	
	0	52.269 ± 10.280	1.57 ± 0.19	4.84 ± 1.72	81.15 ± 0.64	7.229 ± 0.136	
Aluminium Sulfate	20	35.308 ± 1.632	1.27 ± 0.18	2.678 ± 0.63	90.60 ± 9.48	7.049 ± 0.152	
	30	28.384 ± 0.544	0.98 ± 0.01	2.448 ± 0.23	93.35 ± 10.39	6.857 ± 0.115	
	40	14.923 ± 2.176	0.54 ± 0.07	2.502 ± 0.81	96.60 ± 10.61	6.630 ± 0.137	
1 70	50	20.692 ± 0.544	0.57 ± 0.08	2.026 ± 0.49	99.10 ± 10.61	6.531 ± 0.019	
	60	19.538 ± 4.351	0.75 ± 0.26	2.340 ± 0.39	101.50 ± 9.90	6.392 ± 0.049	
	70	27.231 ± 9.791	1.09 ± 0.42	2.342 ± 0.44	104.10 ± 9.62	6.121 ± 0.047	
	0	51.538 ± 9.247	2.10 ± 0.55	4.708 ± 1.52	51.45 ± 41.37	6.692 ± 0.624	
	15	115.769 ± 25.021	2.40 ± 0.79	4.564 ± 1.25	97.30 ± 15.13	6.845 ± 0.057	
Ferric Chloride	30	15.606 ± 1.944	0.47 ± 0.13	3.494 ± 2.09	103.25 ± 15.91	6.658 ± 0.088	
3%	45	15.423 ± 7.234	0.54 ± 0.34	3.251 ± 1.61	110.10 ± 15.41	6.463 ± 0.112	
370	60	13.423 ± 3.318	0.46 ± 0.31	2.684 ± 1.41	115.00 ± 15.56	6.044 ± 0.317	
	90	306.884 ± 15.829	3.66 ± 2.47	3.862 ± 0.67	154.60 ± 24.75	4.684 ± 1.109	
	120	373.423 ± 8.757	3.19 ± 0.40	5.792 ± 0.00	261.50 ± 47.38	3.544 ± 0.254	
	0	61.076 ± 2.176	1.93 ± 0.69	5.540 ± 0.73	79.30 ± 3.25	7.307 ± 0.025	
	2.5	33.000 ± 5.984	0.92 ± 0.08	4.629 ± 1.99	79.95 ± 3.75	7.402 ± 0.088	
Chitosano MT2 1%	5	20.692 ± 0.544	0.72 ± 0.11	3.755 ± 0.07	81.00 ± 4.10	7.400 ± 0.255	
	10	38.000 ± 7.616	1.64 ± 0.08	4.279 ± 0.75	81.90 ± 4.81	7.400 ± 0.085	
	15	48.384 ± 5.983	1.82 ± 0.17	6.179 ± 0.35	83.10 ± 4.95	7.270 ± 0.212	
	20	53.619 ± 7.283	2.13 ± 0.33	$6.930 \pm 0.23$	83.45 ± 3.75	7.414 ± 0.050	
	30	53.769 ± 0.544	$2.00 \pm 0.33$	11.187 ± 3.66	86.80 ± 1.27	7.311 ± 0.040	
	0	66.461 ± 9.791	1.44 ± 0.00	7.049 ± 1.40	83.80 ± 3.11	7.234 ± 0.129	
Chitosano MT3 1%	2.5	62.615 ± 22.844	2.31 ± 0.74	5.908 ± 1.15	84.05 ± 2.76	7.403 ± 0.117	
	5	49.773 ± 15.986	1.53 ± 0.05	5.657 ± 2.07	84.90 ± 2.97	$7.390 \pm 0.086$	
	10	31.461 ± 3.808	0.92 ± 0.24	5.262 ± 0.90	86.10 ± 4.10	7.471 ± 0.201	
	15	24.923 ± 4.352	0.92 ± 0.17	6.896 ± 0.73	86.65 ± 4.74	7.296 ± 0.583	
	20	31.077 ± 6.527	1.14 ± 0.22	7.181 ± 0.11	85.95 ± 7.14	7.294 ± 0.240	
	30	40.692 ± 5.983	1.45 ± 0.14	8.715 ± 0.44	87.15 ± 9.69	7.339 ± 0.182	

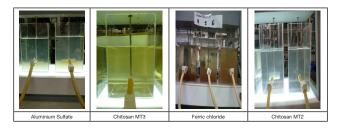
In [25] used in the removal of Lead, Chromium, Copper, Zinc and Nickel ferric chloride plus polymer as assistant coagulation metals, obtaining removals of 95% Lead, 92% chromium, 79% copper, 57% of zinc and 17% Nickel. Such removals warn that coagulation could be improved using biopolymers as helpers.

**Table 3.** Results of the removal of Copper, Cobalt and Zinc for each coagulant at different doses

Type of	Coagulant dosage	Removal (%)			
coagulant	(mg/L)	Copper	Cobalt	Zinc	
	20	9.59	4.15	18.50	
	30	26.58	6.12	17.40	
	40	19.72	6.65	21.90	
	50	25.75	7.18	22.35	
	60	23.33	8.04	20.90	
Aluminium	70	49.97	11.93	35.25	
sulfate 1%	100	70.81	10.97	65.90	
	200	77.50	8.33	88.25	
	500	86.68	30.66	99.63	
	700	86.32	7.32	98.25	
	1000	62.58	7.32	85.65	
	2000	13.08	7.00	42.60	
	30	10.79	0.10	21.47	
	60	70.51	8.50	35.63	
	120	88.90	1.35	34.46	
Ferric chloride 3%	210	86.76	63.00	91.65	
	300	95.00	68.25	94.47	
	510	96.46	73.00	77.73	
	705	94.48	68.40	50.16	
	1200	0.89	54.00	8.20	
	2010	0.42	7.40	17.96	
	5	7.66	4.55	18.50	
Chitosano MT2 1%	10	50.86	15.05	23.90	
	15	20.79	9.55	11.75	
	20	9.17	0.00	18.75	
	30	8.03	1.35	25.85	
Chitosano MT3 1%	2.5	8.65	0.61	17.72	
	5	18.34	2.48	27.33	
	10	24.65	3.29	34.60	
	15	10.63	0.91	33.52	
	20	12.45	25.65	37.65	
	30	12.71	1.98	39.38	

Aluminum Sulfate and Ferric Chloride coagulants are efficient, since removals achieved above 80% of Zinc and Copper. However, in the case of cobalt these coagulants usually not equally effective.

During the removal of Zinc, Cobalt and Copper metals Aluminum Sulfate and Ferric Chloride, optimal doses were 235 mg/L and 500 mg/L with Aluminum Sulfate and 300 mg/L and 510 mg/L with ferric chloride, achieving removal percentages above 80% for most metals. Therefore, for the removal of heavy metals with these types of coagulants high doses are required, predominating sweep coagulation. For the Chitosan, removal is not as high but with this residual metals such as aluminum and iron, which in high concentrations become harmful to health and are legislated in the 2115 Decree 2007 for drinking water is avoided in Colombia.



**Figure 2.** Experiments with optimal doses of each coagulant used

## CONCLUSION

For removal of colloidal material in the water sample dairy herd, the optimal dosage of aluminum sulfate, ferric chloride, MT2 and MT3 and chitosan are 40 mg/L, 60 mg/L, 5 mg/L and 10 mg/L, respectively. For the removal of metals, aluminum sulfate and ferric chloride high doses are required, ensuring sweep coagulation, being this process optimal for the removal of metals in the water, with the disadvantage of requiring high doses of coagulants. These results warn that the optimal dosage of colloidal material removal differ dose for removal of metals and require different procedures.

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#### **REFERENCES**

- Matilainen, A., Vepsäläinen, M., Sillanpää, M. (2010). Natural organic matter removal by coagulation during drinking water treatment: A review. Advances in Colloid and Interface Science, 159: 189-197.
- Li, M., Wu, G., Guan, Y., Zhang, X. (2011). Treatment of river water by a hybrid coagulation and ceramic membrane process. *Desalination*, 280 (1-3): 114-119
- Hua, C., Lo, S., Chang, C., Chen, F., Wu, Y., Ma, J. (2013). Treatment of highly turbid water using chitosan and aluminum salts. Separation and Purification Technology, 103: 322–326
- Pablo, L., Chávez, M., Abatal, M. (2011). Adsorption of heavy metals in acid to alkaline environments by montmorillonite and Ca-montmorillonite. *Chemical Engineering Journal*, 171 (3): 1276–1286.
- Ng, M., Liana, A., Liu, S., Lim, M., Chow, C., Wang, D., Drikas, M., Amal, R. (2012). Preparation and characterisation of new-polyaluminum chloride-chitosan composite coagulant. *Water Research*, 46 (15): 4614–4620.
- Run Fang, R., Cheng, X., Xu, X. (2010). Synthesis of lignin-base cationic flocculant and its application in removing anionic azo-dyes from simulated wastewater. *Bioresource Technology*, 101: 7323–7329.
- Moi Pang, F., Kumar, P., Teng, T., Mohd, A., Wasewar, K. (2011). Removal of lead, zinc and iron by coagulation–flocculation. *Journal of the Taiwan Institute of Chemical Engineers*, 42, 809–815.
- Gougha, R., Hollimanb, P., Willisc, N., Freemana, C. (2014). Dissolved organic carbon and trihalomethane precursor removal at a UK upland water treatment works. Science of The Total Environment, 468–469: 228–239.
- Ellouze, E., Tahri, N., Amar, R. (2012). Enhancement of textile wastewater treatment process using Nanofiltration. *Desalination*, 286: 16–23
- Martín, M., González, I., Berrios, M., Siles, J., Martín, A. (2011). Optimization of coagulation–flocculation process for wastewater derived from sauce manu-

- facturing using factorial design of experiments. Chemical Engineering Journal, 172 (2–3): 771–782.
- Matilainen, A., Gjessing, E., Lahtinen, T., Hed, L., Bhatnagar, A., Sillanpääa, M. (2011). An overview of the methods used in the characterisation of natural organic matter (NOM) in relation to drinking water treatment. *Chemosphere*, 83: 1431–1442.
- Yang, Z., Gao, B., Wang, Y., Zhang, X., Yue, Q. (2013). Relationship between residual AI species, floc operational parameters and coagulation performance during reservoir water treatment by PAC-PDMDAAC. Separation and Purification Technology. 102: 147–156.
- Wontae, L., Westerhoff, P. (2006). Dissolved organic nitrogen removal during water treatment by aluminum sulfate and cationic polymer coagulation. Water Research, 40: 3767 – 3774.
- Englehardt, J., Ashbolt, N., Loewenstine, C., Gadzinski, E., Ayenu-Prah, A. (2012). Methods for assessing long-term mean pathogen count in drinking water and risk management implications. *Journal of Water and Health*. 10 (2): 197-208.
- 15. Šciban, M., Klašnja, M., Antov, M., Škrbic, B. (2009). Removal of water turbidity by natural coagulants obtained from chestnutand acorn. *Bioresource Technology*, 100: 6639–6643.
- Samrani, A.G., Lartiges, B.S., Villiéras, F. (2008).
  Chemical coagulation of combined sewer overflow: Heavy metal removal and treatment optimization. Water Research, 42 (4-5): 951-960.
- Rizzo, L., Gennaro, A., Gallo, M., Belgiorno, M. (2008). Coagulation/chlorination of surface water: A comparison between chitosan and metal salts. Separation and Purification Technology, 62 (1): 79–85.
- Guocheng, Z., Huaili, Z., Zhi, Z., Tiroyaone, T., Peng, Z., Xinyi, X. (2011). Characterization and coagulation–flocculation behavior of polymeric aluminum ferric sulfate (PAFS). Chemical Engineering Journal, 178: 50-59.
- Renault, F., Sancey, B., Badot, P., Crini, G. (2009). Chitosan for coagulation/flocculation processes – An eco-friendly approach. European Polymer Journal, 45: 1337–1348.
- Wanga, J., Chena, Y., Wang, Y., Yuana, S., Yua, H. (2011). Optimization of the coagulation-flocculation process for pulp mill wastewater treatment using a combination of uniform design and response surface methodology. Water Research. 45 (17): 5633– 5640
- Roussy, J., Vooren, M., Dempseyc, A., Guibala, E. (2005). Influence of chitosan characteristics on the coagulation and the flocculation of bentonite suspensions. Water Research, 39: 3247–3258.
- Henneberry, Y., Kraus, T., Fleck, J., Krabbenhoft, D., Bachand, P., Horwath, W. (2011) Removal of inorganic mercury and methylmercury from surface waters following coagulation of dissolved organic matter with metal-based salts. Science of the Total Environment, 409: 631–637.
- Pang, F. M., Teng, S. P., Teng, T. T., Mohd, A. K. (2009). Heavy Metals Removal by Hydroxide Precipitation and Coagulation–Flocculation Methods from Aqueous Solutions, Water Qual. Res. J. Can., 44: 174-182.

- American Public Health Association (APHA), American Water Works Association (AWWA), Pollution Control Federation (WPCF), 2012. Standard methods for examination of water and wastewater 22th ed. Washington.
- Rodríguez, D.C., Pino, N., Peñuela, G. (2012). Microbiological quality indicators in waters of dairy farms: Detection of pathogens by PCR in real time, Science of the Total Environment, 427-428: 314-318.
- Soto, E., Lonzano, T., Barbarin, J., Alcalá, M., (2004). Eliminación de metales pesados en aguas residuales mediante agentes químicos. *Ingenierias*, VII, 23, 46-51.
- Zemmouri, H., Drouiche, M., Sayeh, A., Lounici, H., Mameri, N. (2012). Coagulation Flocculation Test of Keddara's Water Dam Using Chitosan and Sulfate Aluminium. *Procedia Engineering*, 33: 254-260.
- Werathirachot. R., Danwanichakul, P., Kongkaew, C., Loykulnant, S. (2008). Water Soluble Chitosan as an Environment-Friendly Coagulant in Removal of Rubber Particles from Skim Rubber Latex. *Journal* of Metals, Materials and Minerals, 18: 93-97.
- Roussy, J., Chastellan, P., Vooren, M., Guibal, E. (2005). Treatment of ink-containing wastewater by coagulation/flocculation using biopolymers. *Water SA*. 31: 369-376.
- Gamage, A., Shahidi, F. (2005). Use of chitosan for the removal of metal ion contaminants and proteins from water. Food Chemistry. 104 (3): 989–996.
- 31. Borovicková1, M., Dolejš, P. (2005). Chitosan a new type of polymer coagulant. Sborník soutěže Studentské tvůrčí činnosti Student, 97-100.
- Johnson, P., Girinathannair, P., Girinathannair, K., Ritchie, S., Teuber, L., Kirby, J. (2008). Enhanced Removal of Heavy Metals in Primary Treatment Using Coagulation and Flocculation. Water Environment Research, 80: 472-479.
- Caldera, Y., Clavel, N., Briceño, D., Nava, A., Gutiérrez, E., Mármol, Z. (2009). Quitosano como Coagulante Durante el Tratamiento de Aguas de Producción de Petróleo. Boletín del Centro de Investigaciones Biológicas, 43: 541-555.