

## Combined use of natural polymers (chitosan and humic acid) for treatment of Ni tailings containing fine particulate material

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Dewatering unit operations are essential steps in mineral processing routes to obtain materials with high levels of solid content (60-70 wt.%). Polymers have been used for coagulation and flocculation in wastewater treatment for many years, and its application is mostly based on the adsorption mechanisms. In the case of fine nickel ore tailings, wastewaters typically contain large amounts of particles within microscale ( $d_{50} = 9.5 \mu\text{m}$ ). The use of flocculant polymers, mostly polyacrylamides, acts to remove colloids from these effluents. Environmentally friendly natural polymers, such as chitosan and humic acid, when used combined can be a highly effective reagent for the treatment of these tailings. Therefore, the purpose of this study is to evaluate the use of these natural polymers in the treatment of wastewater containing colloidal material to adequate the fine particles content to less than 50 NTU, satisfying environmental standards. Particle removal efficiency was calculated based on turbidity on wastewater as well as on thickener overflow. For fine nickel tailings containing 2.15% (wt./vl.), a mixture of chitosan/humic acid of 24.9/6.3 g/t at pH=6.7 achieved a sedimentation of 95 wt.%. The turbidity was reduced to 40 NTU, motivating the use of this technique to adequate wastewater to water reuse.

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### 1. Introduction

Nickel (Ni) is one of most relevant mined metals, that combined with iron (Fe), aluminum (Al), manganese (Mn), copper (Cu), zinc (Zn) and lead (Pb); forms a group of metallic elements responsible for more than 98 wt.% of all mining production worldwide [1]. Moreover, the present context of technological transition to low-carbon society has produced an increased interest on sustainable mining to provide the foundations for high technology devices manufacturing without compromising the environment [2-4]. In the case of Ni, the importance of this metal is boosting recently in relation to the expansion of affordable electrochemical cells to power updated electric mechanisms, transports and other equipment, in which this element is an important component for the lithium-ion battery (LIB) industry [5-6].

On what touches Ni mining, there are two typical occurrences that are explored to attend global demand, the sulfide ores and nickeliferous laterite in which the former is responsible for more than 60 wt.% of current world production [7]. However, the consumption and effective allocation of nickel resources is not balanced at the present time, presenting a substantial challenge to attend global demand [8]. This context also motivates the development of alternative extraction methods for Ni recovery from silicate laterites [9] and electronic waste materials [10].

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In 2020, Brazilian mine production of nickel was estimated at 73 thousand metric tons, produced from nickeliferous laterite occurrences as well as sulfide ores [11]. The mineral processing of the latter typically covers froth flotation operations for Ni concentration with the concomitant formation of tailings, also bearing the metal of interest, which report to ponds. The monitoring of such deposits, in operation or decommissioned, is imperative as Ni could be leached from sediment to water column diminishing the environmental quality of the area [12]. Therefore, it is very interesting that such tailing could be submitted to environmentally friendly treatments to remove Ni and other contaminants [13-20].

Within that context, in this manuscript we propose a treatment method for tailings containing fine particles, which are typical of flotation of operations, producing a slurry of high concentration of solids, focusing on the ease and safety of Ni ore processing effluent disposal. The motivation is on the waste dewatering, enabling some sort of water reuse in this type of mineral-metallurgical operation. It is well known that colloids have electrical properties that create a repulsive force that reduces agglomeration and sedimentation of particles. The dispersion state of these particles is directly related to the surface electrostatic potential [21]. In most industrial effluents, the particles of a colloid are negatively charged, requiring destabilization of charges and aggregation to produce pulps or slurries, using specific reagents for fine particles coagulation and flocculation to promote efficient separation between the solid and liquid phases. Most reagents used for particle aggregation in mineral processing are polyacrylamide (PAM) based flocculants, with average molecular weights around 10 MDa or more [22]. However, other substances have been recently efficiently applied, while also attending some sustainable mining requirements, such as humic-acid (HA) and chitosan [23-27], which is a cationic polysaccharide widely used in water treatment. However, when this polymer is applied as a flocculant, two potential drawbacks must be considered: its poor water solubility and low molecular weight compared to commercial polymers.

On what touches its physical-chemistry, chitosan it is described as a very promising biodegradable biopolymer [28], with good film forming while also having antimicrobial activity. It is also reported that chitosan's molecular structure contains several aminogroups ( $-NH_2$ ) and hydroxyl groups ( $-OH$ ) on the molecular chain, which contain single-pair electrons that can interact with metal ions, forming stable metal chelate complexes ( $-N-M-O-$ ) [29]. Therefore, chitosan can be used for removal of many undesirable metal ions from wastewater. The active amino groups presented in the chitosan molecule can be protonated with  $H^+$  in water into a cationic polyelectrolyte, producing a molecule able to promote static attraction and adsorption [30]. Consequently, chitosan can also flocculate particles into agglomerates called flocs improving dewatering operations. On the other hand, HA are substances with similar properties as weak acidic polyelectrolytes, whose surface charges are strongly influenced by pH and presence of neutral salts. It is suggested that the presence of HA enhanced the Cd(II) uptake at low pH, and additionally attributed this the existence of more negatively charged surfaces, enabling its use to coat biochar [31]. HA can also effectively bind to metals and is a promising adsorbent for remediation of pollution by  $Cu^{2+}$ , a common aqueous contaminant [32]. Finally, regarding the combination of HA and chitosan, it has been reported that the former can be adsorbed on the latter's molecular surface, promoting a reduction in the overall zeta potential [33].

Therefore, the present work hypothesis is that these two polymers can act in co-flocculation processes to capture very fine particles for wastewater treatment, such as those related with tailings from Ni sulfide ores mineral processing. To investigate this premise, we assessed the potential using of chitosan and HA as flocculants for removal of fine particulate material in nickel tailings and their efficiency as a function of ratio between these components and solids concentration.

## **2. Materials and methods**

### **2.1. Involved materials**

A sample from nickel processing tailings produced at a mineral processing plant in the state of Minas Gerais (Brazil), containing fine particulate material, was used as raw material in the present study. Synthetic analytical grade chitosan and HA, both from Sigma-Aldrich, were used as

flocculation agents. Both chemicals were purchased as dry granules and prepared as solutions, following the procedure detailed in sequence.

## 2.2. Preparation of chitosan and humic acid solutions

The chitosan solution was prepared by dissolving 1.0 g of chemical in 1 L of a 0.025M HCl solution and stirring it for 24 hours according to the procedure described by Bratskaya, Chervonetsky and Schwarz [34]. On the other hand, the humic acid solution was set up by dissolution of 1.0 g of chemical in 1 L of a 0.1 M KOH solution, stirring for 48 hours and then filtrated through quantitative filter paper (Whatman no. 1), according to the method proposed by Zouboulis, Jun and Katsoyiannis [35].

## 2.3. Materials characterization and analytical procedures

The sample was dried at 60 °C for 3 hours in laboratory oven and subsequently disaggregated until all sample was below 297 µm. The particle size distribution was determined with Mastersizer 2000 laser diffractometer (Malvern Instruments), using sonication for 3 min. The determination of the molar masses of HA and chitosan was an important measurement as this property has a strong influence on particles adsorption. It is expected that polymers with high molar mass achieve direct contact with surfaces of the pulp particles, having adsorption kinetics higher than those of the polymers with lower molar mass, because of better penetration within inter-particle spaces [36]. Therefore, molar mass was estimated with a Zetasizer Nano equipment (Malvern Instruments), using static light scattering (SLC).

On what touches surface charges measurements, the sample was also ground to particle sizes smaller than 20 µm, following the instructions contained in the Zeta Potential Analyzer (Brookhaven Instruments Corp.) user's guide. A total of 0.5 g of fine nickel ore was added to 0.5 L of Milli-Q water, at two indifferent electrolyte concentrations (0.001 M and 0.01 M KNO<sub>3</sub>). Subsamples of the pulp were taken for pH adjustment with 0.1 M HCl and 0.1 M KOH solution, maintaining the mixture under continuous stirring and controlled temperature at 25 °C. The solution was then left to rest for 5 min before analysis.

For chitosan, the surface charge measurements were made directly in the stock solution, after pH adjustments in the range of 3 to 12. For HA, one aliquot of the stock solution was collected to prepare a 100 ppm solution. Small aliquots of this solution were submitted to pH adjustment, also within the 3 to 12 range, with 0.1 M HCl and 0.1M KOH solutions.

Turbidity was measured to detect the presence of solids in the clarified solution. It was determined by the attenuation of intensity of a light beam passing through the solution. Turbidity measurements were performed with a 2100P turbidimeter (Hach) to quantify the solids removal efficiency. The turbidity target stipulated for the flocculation/sedimentation tests was 40 NTU, based on Resolution 357 from the Brazilian National Environmental Council [37]. After sedimentation, small aliquots of the supernatant liquid were taken to determine the turbidity. With this result, it was possible to calculate the solids removal efficiency.

In the project, the materials were also characterized by means of Scanning Electron Microscopy (SEM; Bruker Corporation), for morphology analysis, and X-ray Diffraction (XRD; Bruker Corporation), for mineral speciation analysis. The chemical analysis was performed through humid method by means of acid leaching in an Atomic Absorption Spectrometer (Varian).

## 2.4. Flocculation procedure

The flocculation tests were carried out in a jar test equipment (Nova Etica). The amount of samples used in each test followed an experimental design based on the following variables: solids concentration, dosage of flocculating reagents, stirring speed and time. The pulp was initially stirred rapidly at 106 rpm for 3 min for homogenization. For the Ni tailings, no pH adjustment was needed due to the characteristics it presented in the surface charge analysis. The proportions in the mixture of flocculants (chitosan and HA) varied on the conditions of the experimental design. The solution was then submitted to slow stirring for 80 rpm for 1 min to promote flocs growth, and then it was allowed to rest for 1 hour until sedimentation was achieved.

### 3. Results and discussion

#### 3.1. Chitosan and humic acid molar mass

Figure 1 presents the Debye plots of Chitosan (a) and HA (b) which are equivalent to the projection of the intersection of the abscissa axis of the inverse of linear coefficient of the generated line ( $KC/RoP = 1/Mw$ ). The respective calculated molar mass of chitosan was 232 kDa while for HA it was 25.1 kDa. These measurements indicate that chitosan has a much greater influence on adsorption, since it has a molar mass almost nine times that of HA.

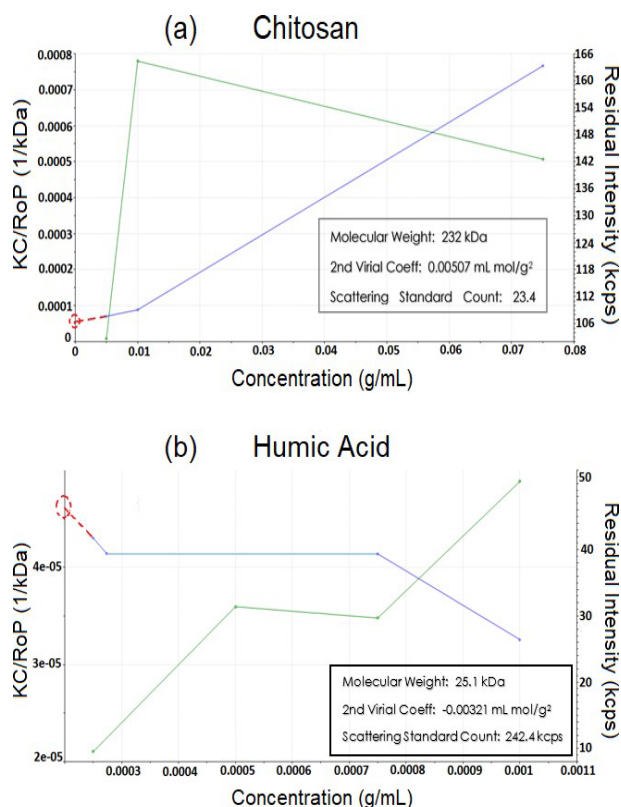


Fig. 1. Debye plots for molar mass calculation: (a) for chitosan; (b) for HA.

#### 3.2. Ni processing tailings characterization

Figure 2 presents the particulate material size analysis. The material features a granulometric behavior showing an average fine throughputs of  $d(0.1) = 2.1 \mu\text{m}$ ,  $d(0.5) = 9.5 \mu\text{m}$  and  $d(0.9) = 55 \mu\text{m}$ , which reflects the presence of colloids in the Ni pulp, in an approximate proportion of 10% (by volume).

Figure 3, on the other hand, shows an image obtained through SEM of the tailings material (below 20  $\mu\text{m}$ ). The image reveals the main features of smooth lamellar morphology and formation of blocks. Flocculation tests as a function of pH were used to assess the aggregation force of the particles.

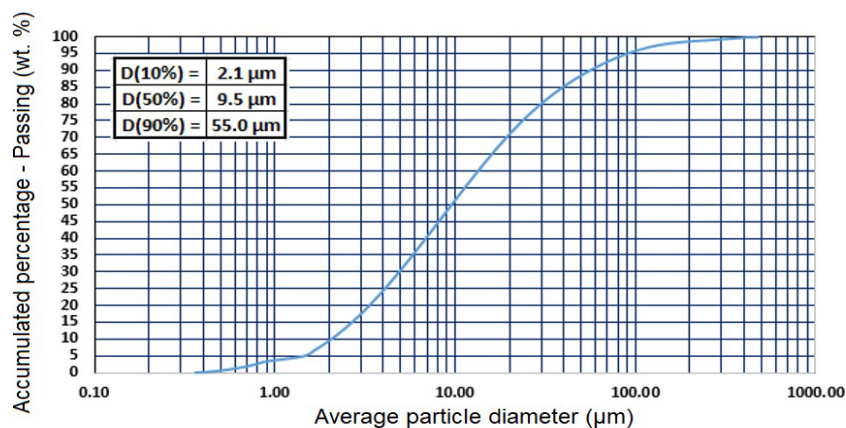


Fig. 2. Particle size distribution of the Ni processing tailings sample.

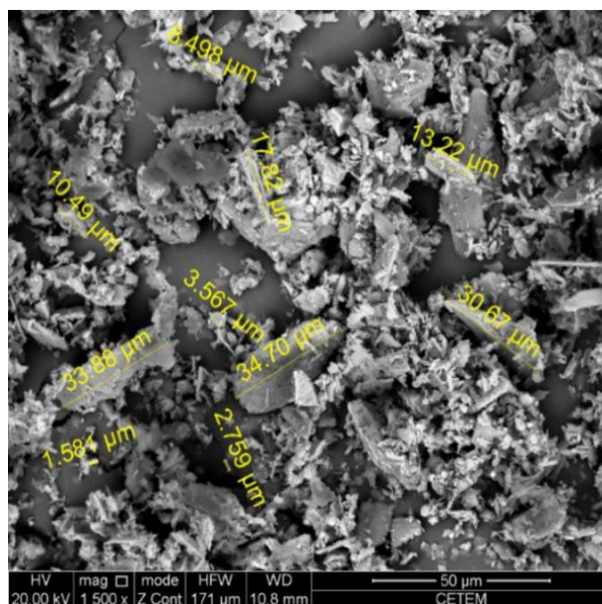


Fig. 3. SEM of the Ni processing tailings sample (below 20 µm).

Figure 4 provided, by means of XRD, an overall understanding of the mineralogical distribution within the Ni processing tailings while Table 1 presents the chemical analysis of the same sample. It was identified peaks of dolomite, quartz and sepiolite. The latter in low concentration based in its minor presence in the natural occurrence. On what touches Fe, pyrite and magnetite were identified as the major carriers of this metal. It is interesting to mention that some minerals bearing magnesium (Mg) were also detected in the XRD analysis.

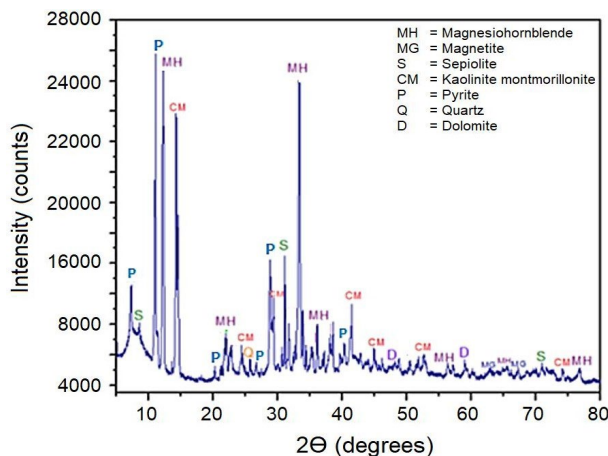


Fig. 4. XRD analysis of the Ni processing tailings sample.

It is interesting to mention that silicon (Si) was observed, as expected as the major metal in the sample, mostly associate of the silicate gangue of the ore, while Fe and Mg were identified as other metals of significative presence in the sample (~ 10 wt.%).

Table 1. Chemical analysis of the Ni processing tailings sample.

Element	Concentration (wt. %)
Al	2.4
Si	43.3
Ca	3.7
Mg	9.0
Fe	13.9
Na	6.8
Ni	0.29
Cu	<u>0.03</u>

### 3.3. Electrostatic interaction

The zeta potential analysis of chitosan, HA and waste from Ni are shown in Figure 5. HA has negative potential in the pH range from 3 to 12. The lower repulsion at pH of 3 to 5 can be attributed to the protonation of the carboxylic (-COOH) groups, so its pKa is 3.65 [34]. There is no other protonation behavior above pH of 5, indicating the presence of the carboxylic compounds in macromolecules [33]. In contrast, chitosan granules have positive zeta potential in acidic solutions and negative potential solutions in basic solutions, with an isoelectric point at pH matches the value of 6, showing its solubility in water in the acidic medium by protonation of the amino group (-NH<sub>2</sub> to -NH<sub>3</sub><sup>+</sup>) at pH lower than 6, as reported previously by other authors [33,38] as well as= close to its pKa at 6.3 and 6.7 [39]. For pH values from 7 upwards, its neutralization occurs due to the deprotonation of -NH<sub>2</sub> to -NH- groups [38-40]. In the case of Ni tailings, the original measured pH of the pulp was in the range between 6.5 and 7. For the zeta potential tests, we prepared two electrolyte concentrations solution (0.001M and 0.01M KNO<sub>3</sub>). It had two isoelectric points, at pH equals to 3 and at pH equals to 10.5, and the electrolyte was indifferent, with a stable colloidal zone in the fixed range of between 6.8 and 9. Above pH of 10.5, Ni tailing particles showed a reversal of net surface charge to positive, and in the acidic range (up to pH equals to 3), the particles had negative net surface charge, but were found in the unstable colloidal zone.

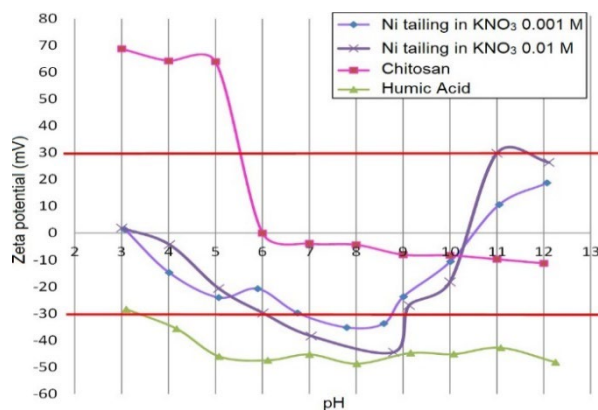


Fig. 5. Zeta potentials of Ni tailings with average particle size smaller than  $20 \mu\text{m}$  and with  $0.001\text{M}$  and  $0.01\text{M}$   $\text{KNO}_3$  electrolyte, and chitosan (pure solution at  $1000 \text{ ppm}$ ) and HA ( $100 \text{ ppm}$  pure solution) in Milli-Q water.

The same situation happened from pH of 9 to 12, where the particles had negative net surface charge but formed an unstable suspension.

### 3.4. Determination of size of aggregates (flakes) as a function of pH

Monitoring the size of aggregates is a way to assess the degree of aggregation of a system, since it is expected that in the region of the isoelectric point, the material will be more agglomerated due to the absence of repulsive charges on the surface. The measurement was performed using the light scattering technique, without activating the ultrasound so as not to mischaracterize the actual size of the aggregates. Figure 6 shows the results of mean particle size as a function of pH for Ni tailings. In the pH region close to the isoelectric point (pH of 3), the material had larger particle sizes. The graph also shows that the region with larger aggregates was at pH of 2; the same was observed at pH equals to 12, and a slight aggregation of particles was observed near the second isoelectric point of the Ni tailings at pH near 10.5 (Figure 5). This approximation between the particles is mainly due to the reduction in the electric double layer, allowing greater cohesion between them [41].

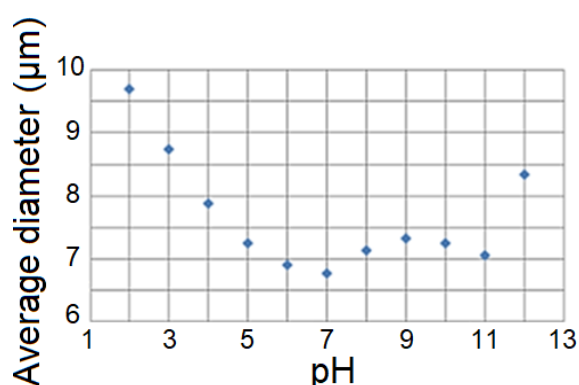


Fig. 6. Aggregation of Ni tailing particles ( $0.1\%$ ) as a function of pH, determined with a Malvern Mastersizer 2000P in Milli-Q water.

### 3.5. Flocculation tests

Based on characterization analyses, electrostatic interaction and particle aggregate size, flocculation tests were performed to adjust the parameters of the experimental design. Figure 7 presents the overall behavior of the effluent in the jar test. It is important to mention that the received tailing suspension had a turbidity of  $271 \text{ NTU}$ .



Fig. 7. Ni tailings flocculation jar test.

### 3.5.1. Effect of HA/Chitosan (HA/Ch) ratio

In the interaction of HA with chitosan (HA/Ch), different pH values were observed in the resulting solution (each reagent has a natural pH). As can be seen in Figure 8, it had two points that reflect efficient flocculation of particles, at pH equals to 6.75, with turbidity response of 32 NTU, 40% HA and 60% chitosan, and at a pH equals to 8.08, with a turbidity response of 25 NTU, 75% HA and 25% chitosan, reflecting the effect of the pKa of HA on the adsorption of particles, as described by other authors [34].

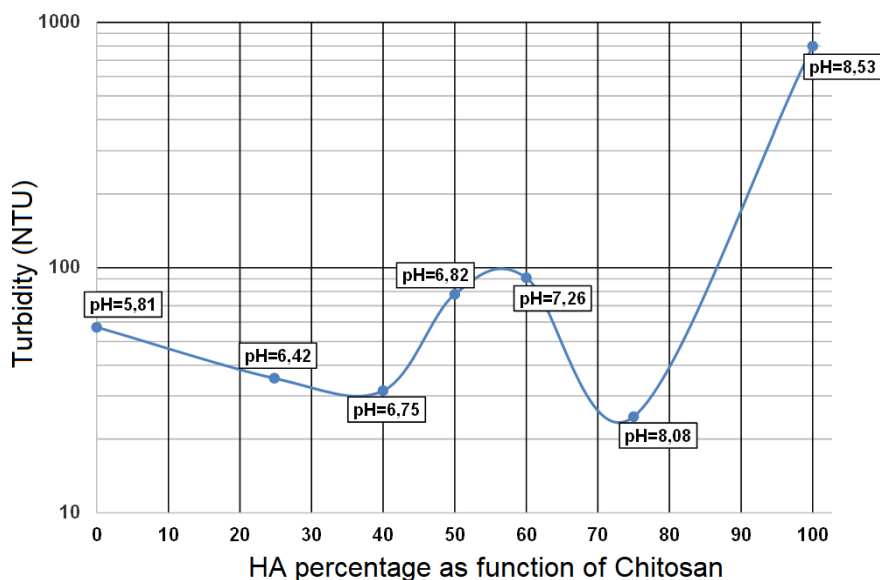


Fig. 8. Flocculation at different percentages of HA/Ch in Ni tailings (0.5%), with stirring at 225 rpm in the jar test.

### 3.5.2. Effect of solids concentration

To adjust the amount of solids according to the adsorption capacity of chitosan and humic acid, different percentages of solids were used (Figure 9). The adsorption capacity in the presence of 680 g/t of chitosan and 80 g/t of humic acid was limited to 1% solids, in compliance with the limit set by on Resolution 357 from the Brazilian National Environmental Council [37], which requires having a limit of 40 NTU of turbidity.



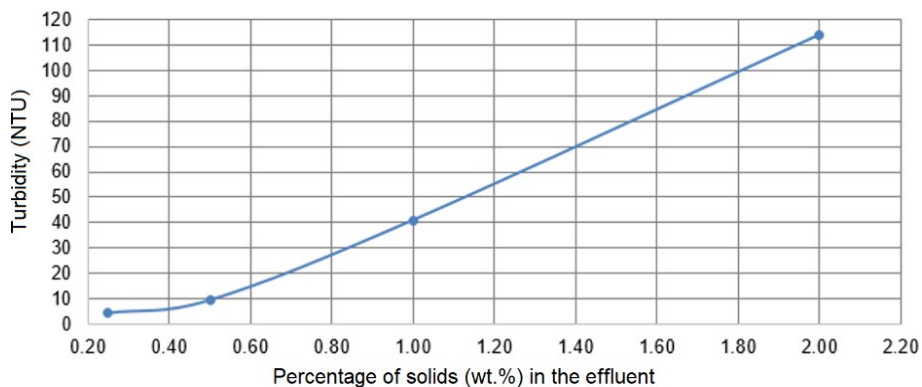


Fig. 9. Flocculation test for adsorption of chitosan (680 g/t) and HA (80 g/t) on the particles of Ni tailings, at pH 7 and 225 stirring at rpm in the jar test.

### 3.5.3. Materials characterization

In Figure 10, a SEM picture of pulp flocculation at pH equals to 5 is shown, where it is possible to visualize larger particles, possibly from aggregates formed by the flocculation process itself, which is not reflected in Figure 11, with flocculation test performed at pH 10, showing a greater dispersion of particles, with no evident aggregation.

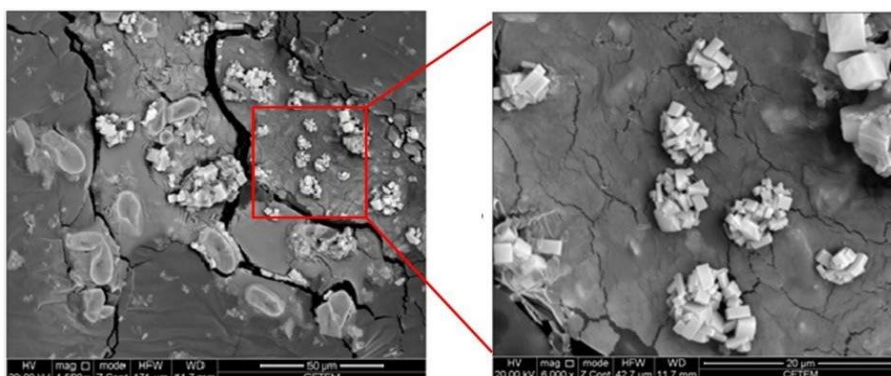


Fig. 10. SEM of the Ni processing tailings sample (below 20  $\mu\text{m}$ ), pulp flocculation at pH of 5.

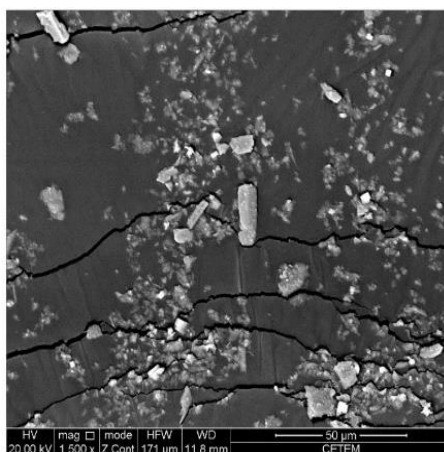


Fig. 11. SEM of the Ni processing tailings sample (below 20  $\mu\text{m}$ ), pulp flocculation at pH of 10.

#### 4. Conclusion

The results presented here showed the zeta potential of the isoelectric points, at pH 3 and pH 10.5, above which the Ni particles underwent inversion of the positive net surface charge. In the range of pH 3 to around 7, the particles had negative net charge, and were in an unstable colloidal zone, as shown in Figure 9. However, the particle aggregation was effective at pH 7, with the polymers (chitosan and HA). Removing solids contained in mineral pulps is of environmental interest, since they are biodegradable polymers. The adsorption of chitosan with HA by the particles was efficient in acidic to neutral range, but the adsorption of chitosan was more efficient than of HA. This was possibly due to the differences in their molar masses (232 kDa of chitosan and 25.1 kDa of HA).

The zwitterion character of HA (buffering action) allowed small amounts of added H<sup>+</sup> to be adsorbed by the negative groups of carboxylates and phenolics, while small amounts of OH<sup>-</sup> ions were adsorbed by the positive charge of NH<sub>3</sub><sup>+</sup> ions present in HA. The adsorption of chitosan together with HA from Ni tailing particles was more efficient in the acidic range.

#### Author Contributions

All authors have read and agreed to the published version of the manuscript. Conceptualization, S.F. and E.B.; methodology, P.V. and S.F.; formal analysis, P.V. and R.S.; investigation, S.F.; resources, S.F. and E.B.; data curation, P.V.; writing—original draft preparation, P.V. and R.S.; writing—review and editing, R.S.; visualization, R.S.; supervision, S.F. and E.B.; project administration, S.F.; funding acquisition, S.F., E.B. and R.S.

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