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Research Article

Investigation of dewatering of chromite tailings with lignin

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ABSTRACT

Every year, a large amount of chrome ore is produced in our country. Dewatering of tailings generated during the beneficiation of these ores is one of the problems faced by the mineral processing industry. In this study, flocculation performance was investigated by using lignin in the dewatering of tailings obtained from chrome ore beneficiation. The sample used in the study was obtained from Burdur Yesilova chrome ore beneficiation plant tailings dam. The effects of flocculant dosage, stirring speed, pulp density and suspension pH value on turbidity were investigated. Experimental results using lignin showed that the optimum turbidity value was 24.4 NTU. Flocculation experiments showed that the optimal flocculation conditions were as follows: flocculant dosage of 50 g/t, stirring speed of 250 rpm, pulp density of 15% and pH 9.2. This study is important in terms of being carried out using tailings from actively operating chrome ore beneficiation plant and determining the flocculation properties of the tailings. By carrying out this study, it has been shown that dewatering these tailings can be done in an effective and environmentally friendly way in order to combat water scarcity and supply clean water for reuse in the plant.

Introduction

Chrome is one of the most widely used metals in various industries. Chromite mineral, the main source of chrome, is an essential raw material for the production of stainless steel, ferrochrome alloys, refractories and chemicals [1]. In chrome mining, which is a significant industry for Turkey, 1.5 million tons of chrome ore were produced in 2023 [2]. The production of high-grade concentrates (Cr_2O_3>45wt%) from low-grade ores is carried out in chrome ore beneficiation plants.

In these plants, large quantities of tailings are produced by processing low-grade ores and before these tailings are sent to tailings pools, solid-liquid separation methods must be applied. The suspension consisting of fine-sized particles and water should be subjected to dewatering. Because there is a significant need for clean water in ore enrichment plants and therefore, water recovery is crucial for the sustainable plants.

It is impossible for the particles in the suspension to settle spontaneously in a short time. Therefore, the flocculation process is necessary [3]. Flocculation is a widely used technique in many industrial applications to facilitate the solid-liquid separation process [4]. It allows suspended particles to come together and reach a size where they can settle with the help of gravity. High settling rates and low turbidity are desired outcomes of flocculation. Flocculation is a complex process and flocculant type and dosage, suspension pH, particle size, molecular weight and stirring conditions are the main factors affecting floc properties, settling rate and turbidity value [3, 5].

There are a wide variety of polymeric flocculants used in dewatering processes. Synthetic flocculants have attracted considerable interest due to their low required dosages, easy handling process, ability to form strong and large solid aggregates, and to easily remove flocs from wastewater. Nevertheless, synthetic flocculants are typically not environmentally friendly as they are not biodegradable and their by-products may release monomers that may have carcinogenic effects [4, 6]. Organic biopolymer-based flocculants, and especially lignin-based flocculants, are increasingly gaining attention as raw materials with low cost and biodegradable potential. Natural polymers such as starch, chitosan, guar gum, sodium alginate, cellulose and microbial flocculants have also been widely used as for this purpose [7–13].

Lignin, which can be recycled from bioethanol and paper production waste, is among the largest renewable resources. However, studies and practical applications for the sustainable utilization of lignin are extremely limited, with most of them focusing on its combustion for energy generation [14]. The physicochemical advantages of lignin include (a) being rich in functional groups, (b) high adsorption capacity, and (c) strong potential for the production of value-added products [15]. Its renewable, non-toxic, and biodegradable nature allows lignin to be effectively used in producing environmentally friendly materials [16]. Three types of lignin can be extracted from pulping black liquor: lignosulfonate, kraft lignin, and organic solvent lignin. Among these, kraft lignin is the most commonly used [14].

In a study on the flocculation characteristics of tailings from the beneficiation of chrome ore, it was observed that there was no change in the sedimentation rate of nonionic type flocculant with increasing dosage, but the sedimentation rate of anionic and cationic flocculants was directly proportional to the dosage and ionicity had a significant effect on the flocculation rate. It was also determined that low molecular weight anionic flocculants improved flocculation properties, while cationic flocculants performed better at higher molecular weight and nonionic flocculant did not show any flocculation effect [17].

The tailings formed in chrome ore beneficiation plants generally contain clays and also have some difficulties in dewatering due to their colloidal size and amorphous structure. On the other hand, while there are few studies in the world on the dewatering of these tailings [17, 18], no studies have been found in our country. The aim of this study is to determine the optimal conditions according to the sedimentation behavior of chrome ore beneficiation plant tailings using lignin as natural flocculant.

Material and Methods

Material

In this study, a sample taken from the tailings pool of Burdur Yeşilova chrome ore beneficiation plant was used. After the crushing process in the plant, the ore under 0.6 mm is fed to the hydrosizer and the different fractions formed are enriched on different shaking tables. All tailings obtained from the tables are sent to the tailings dam. The clean water obtained is reused in the plant. Mineralogical and chemical analyses were carried out to determine the characteristic properties of the sample. Particle size distribution was examined by wet sieving, mineral compositions by X-ray diffraction (XRD) and chemical content by X-ray fluorescence (XRF). According to the particle size distribution, it was determined that 80% of the sample was finer than 280 μm. XRD analysis results revealed that gangue minerals such as quartzite, lizardite and pyrrhotite were present together with chromite. The chemical analysis results are presented in Table 1. The sample contains 1.57% chromite, and as expected, the tailings are primarily composed of SiO_2 and MgO.

Kraft lignin, used as a flocculant in this study, is an anionic type flocculant. Kraft lignin is typically a heterogeneous polymer with a wide molecular weight distribution and chemical structure is given in Fig. 1 obtained from Sigma Aldrich. As seen in Fig. 1, it contains phenolic, carbonyl, carboxylic, aliphatic hydroxyl groups and methoxy groups. Prior to the experiments, lignin was prepared at a concentration of 0.1%, in a volume of 50 mL and stirred for 1 hour using a magnetic stirrer. While pure water was used for the preparation of the reagent, tap water was used in the experiments. Analytical grade NaOH and HCl were used for pH adjustment. All experiments were carried out at room temperature. The sample density was determined to be 2.49 g/cm^3 using a pycnometer.

Table 1. Chemical analysis results of the sample

Components	Amount, %
Cr_2O_3	1.57
SiO_2	38.30
Al_2O_3	0.36
CaO	0.36
Fe_2O_3	6.72
MgO	34.60
SO_3	0.05
NiO	0.30
ZrO_2	0.29
LOI*	16.95

*LOI: Loss-on-ignition

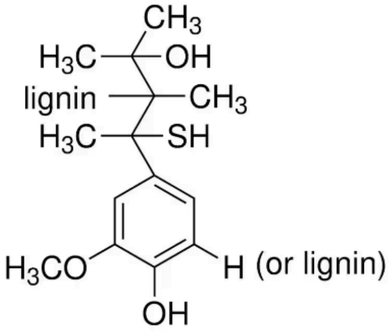

Figure 1. Kraft lignin chemical structure

Method

Flocculation experiments were carried out in a glass beaker with a volume of 400 mL using various pulp densities. First, suspension was stirred for 5 min and at 1750 rpm using a mechanical stirrer to ensure homogeneity. Subsequently, the stirring speed was reduced, and flocculant was added to the suspension. After the addition, the shear effect was slowly reduced and kept at a slow speed. The suspension was allowed to settle for 3.5 min. Turbidity was determined by taking 10 mL of supernatant from a certain distance below the air-water interface. The general flow chart of flocculation experiments was given in Fig. 2.

The effects of flocculant dosage, stirring speed, pulp density and pH parameters were investigated by considering the turbidity values of the suspension. Experimental parameters and their levels are given in Table 2. In order to see the repeatability of the flocculation test, each experiment was repeated twice and the average results were recorded.

Table 2. Experimental conditions

Variables	Levels
Flocculant dosage (g/t)	50, 100, 200, 300, 400, 500
Stirring speed (rpm)	100, 250, 500, 750
Pulp density (%)	2.5, 5, 10, 15, 20
pH	5, 7, 9.2, 11

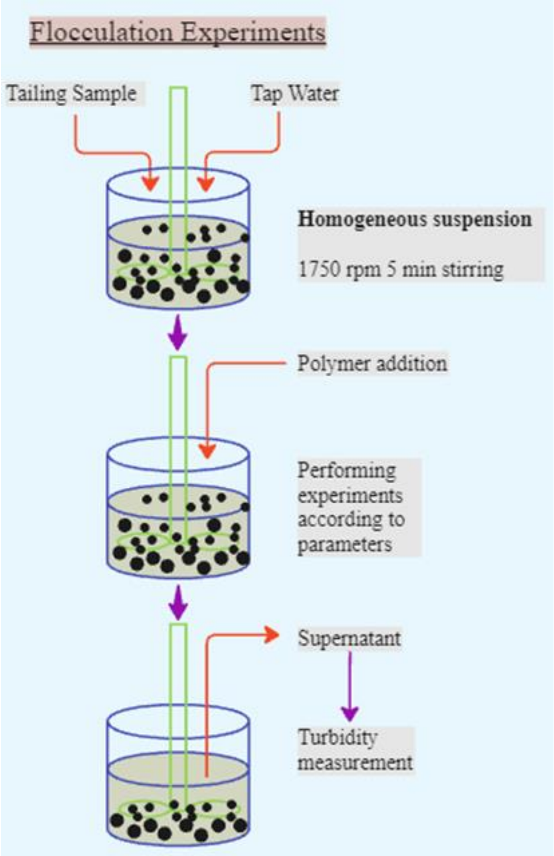

Figure 2. Flow chart of flocculation experiments

Results and Discussions

Natural settling behaviour of sample

In order to determine the free settling behavior, the sample was stirred at a pulp density of 5% in a 500 mL beaker and a stirring speed of 1750 rpm for 15 min. The pulp was transferred into a graduated cylinder and inverted twice to ensure uniform dispersion. Free settling was monitored by observing the solid-liquid interface and measuring the interface height at 15 sec intervals. The time-dependent interface height is presented in Fig. 3. When the settling behavior of the sample was examined, the settling rate was high in the 4 min, but after this period the settling rate slowed down considerably. A rapid settling time can make the dewatering process more efficient.

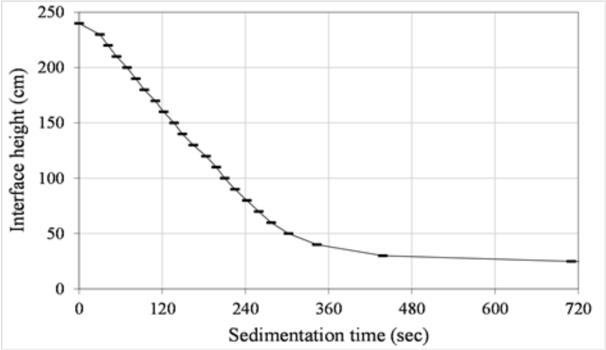

Figure 3. Time-dependent interface height change

Flocculation experiments with lignin

Flocculation experiments were performed to investigate the effects of flocculant dosage, stirring speed, pulp density, and pH on the turbidity of the supernatant. The results are summarized in Fig. 4. When Fig. 4a was examined depending on the lignin dosage at natural pH, the optimal turbidity value was obtained as 71.4 NTU at a dosage of 50 g/t. While similar turbidity values were obtained at 100-300 g/t dosages, a notable increase in turbidity was observed at 500 g/t. At lower dosages, sufficient bridging between particles occurred; however, at high dosage (500 g/t), bridging was prevented and turbidity increased due to the lack of a suitable place for adhesion. As a result, overdosage reduced the stability of the suspension. Organic polymeric flocculants can replace inorganic salt form coagulants by showing high performance at lower dosages [18]. However, compared to synthetic organic polymers, bio-based polymers are effective at high dosage [19].

The stirring speed is crucial in the flocculation process, influencing floc formation, size, strength, and settling rate. Fig. 4b shows the turbidity change of the suspension depending on the stirring speed. While the optimal stirring speed was determined as 250 rpm, lower speeds prevented sufficient particle-flocculant interaction. In addition, it causes difficulties in applying the bridging effect of the flocculant, resulting in high turbidity values. At low stirring intensity, the contact among the particle surfaces and polymer is insufficient, which can lead to excessive polymer consumption and result in poor flocculation performance [3]. The stirring speed is important in shearing or breaking the formed flocs [6, 20].

There is an optimum pulp density in which the maximum flocculation rate is achieved. Fig. 4c shows the results of suspension at pulp densities of 2.5-20wt%. Turbidity decreased by 69 NTU as the pulp density increased from 2.5% to 15%. When the pulp density increased to 20%, it became difficult to distribute the reagent evenly in the suspension and therefore the turbidity value increased. High pulp density resulted in higher collision efficiency between particles [21] and hence increased flocculation rate by up to 15%. Excessively high-density pulp causes high viscosity, making stirring inefficient and increasing shear stress, which causes flocs to break down.

The pH value of the suspension has a great influence on the flocculation efficiency, especially for ionic flocculants. To investigate the effect of pH, experiments were carried out at different pH values and the results are given in Fig. 4d. The lowest turbidity value of 24.4 NTU was obtained at the natural pH (9.2). Higher turbidity values were observed at a suspension pH of 5. It has been stated that the reason for this is that lignin loses its stability easily in acidic media [14]. Additionally, the strength of flocs has been reported to decrease with decreasing pH value [22]. The natural pH of the sample is 9.2, which means that there are more OH^- ions in the suspension. Therefore, the solid surface has a positive charge. Since kraft lignin is an anionic type flocculant, flocculation occurs due to the presence of electrostatic attraction forces.

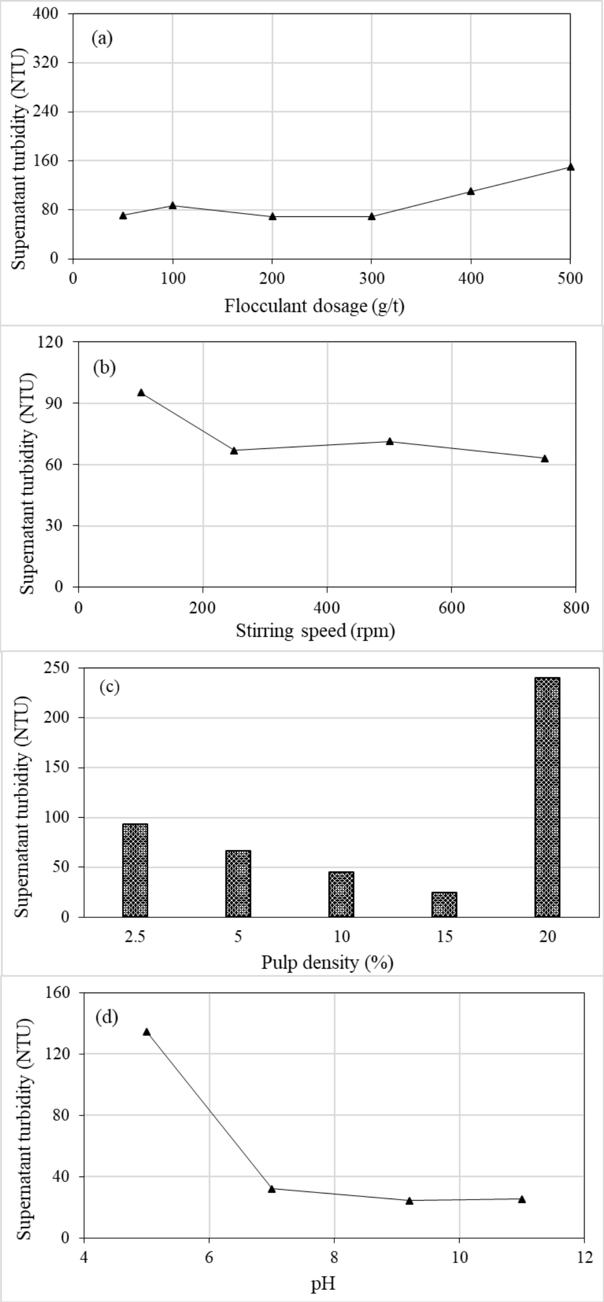

Figure 4. Effects of flocculant dosage (a), stirring speed (b), pulp density (c) and pH (d) on turbidity with lignin

To determine the natural settling behavior of the tailing in the presence of lignin, the pulp was stirred in a 500 mL beaker, at 5% pulp density and 1750 rpm stirring speed for 15 min. The stirring speed was reduced to 250 rpm and 50 g/t flocculant dosage was added. After conditioning for 1 min, the pulp was transferred from the beaker to the graduated cylinder and inverted twice to ensure good dispersion. Fig. 5 shows the time-dependent interface height variation under optimum flocculant conditions. Under this condition, a distinct interface was formed between the flocculated tailing and the supernatant. The settling rate increased in the case of using optimum condition with lignin in comparison with the natural settling rate of the tailing given in Fig. 3. During natural settling, the sedimentation rate was slower. With the use of lignin, the interface height was further reduced from 20 mm to 13 mm. Clarification of the tailing was also achieved in 3 min with lignin compared to the natural settling time of approximately 6 min.

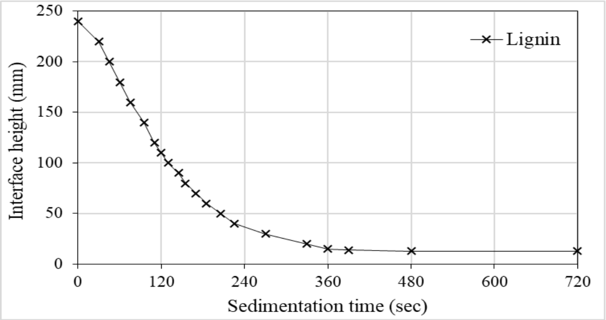

Figure 5. Time-dependent interface height change

In general, lignin-based flocculants are regarded as safe, non-toxic, completely biodegradable and environmentally friendly. However, compared to currently used synthetic polymer flocculants, the charge density of lignin-based flocculants is generally small, resulting in lower flocculation efficiency [14, 23]. To improve flocculation performance, modification of lignin is necessary to obtain new functional groups and increase both its charge density and molecular weight. Biodegradable flocculants are beneficial for environmental protection and meet the needs of today's green sustainable development.

Conclusions

In this study, the feasibility and effectiveness of using lignin as a flocculant for dewatering tailings from a chrome ore beneficiation plant was investigated. Mineralogical composition of the tailings was determined to contain chromite, quartz, lizardite and pyrrhotite. Lignin used at low dosage was found to be an effective flocculant in obtaining low turbidity. It was found that both pulp density and suspension pH have a direct effect on flocculation performance. Flocculation was more effective under basic conditions, while acidic environments resulted in higher turbidity.

Optimal flocculation was achieved with a turbidity of 24.4 NTU using 50 g/t lignin, 250 rpm stirring, 15% pulp density, and pH 9.2. Lower turbidity values mean that the supernatant is clearer and contains fewer fine particles after flocculation. Lignin considerably decreased the supernatant turbidity of the suspension through the bridging mechanism. In chrome ore beneficiation plants, a large amount of water is generally used. Efficient dewatering is essential for water recycling and sustainable plant operations. In addition, the use of organic lignin as a flocculant in dewatering would be a good approach for resource conservation, low carbon footprint and green mining.

Conflict of Interest Statement

"There is no conflict of interest with any person / institution in the article prepared."

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