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EFFECT OF PHYSICAL PRE-ENRICHMENT ON HUMIC SUBSTANCE RECOVERY FROM LEONARDITE

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Abstract: Leonardite mineraloid is known as a highly oxidized ore formed during carbonisation process of lignite containing humic substance. Humic substance is an organic material containing fulvic acid, humic acid, and humin, and that is mostly used as soil conditioner. Extraction of humic substances from leonardite ores that contain high amounts of humic acid (>50%) has become a prominent area of study in recent years. While humic substance extraction from leonardite is generally carried out by chemical dissolution technique (leaching) in alkali medium, physical enrichment methods were also used in limited number of studies. However, removing inorganics found in leonardites would decrease dissolving reactive consumption and would also prevent unnecessary capacity use. This study investigates the effect of physical pre-enrichment processes on humic substance leaching. This research was carried out in two stages. In the first stage, operational parameters such as amount of reactive, stirring time, temperature, and solid ratio for the leach process were studied, and the most suitable leach conditions were then determined. In the second stage, the effect of physical pre-enrichment experiments on leach process was investigated. While a product containing 48.2% humic substance was obtained with 87.63% humic substance extraction efficiency through chemical enrichment experiments, a product containing 62.74% humic substance (concentrate) was obtained with 92.4% humic substance extraction efficiency after pre-enrichment combined with leach processes.

Keywords: *physical enrichment, chemical enrichment, gravity separation, leonardite ore, humic substances*

Introduction

Leonardite ore is a completely natural and organic substance, which contains significant amount of humic substances such as humic acid, fulvic acid, and humins (Jackson, 2008; Kononova, 1966). Leonardite material is generally used in agriculture as soil conditioner. In addition, it is used to in pelletizing, briquetting, drilling, ion exchange resin, wastewater treatment, animal feed (Roybal and Barker, 1987; Mendez et al., 2005; Alak and Muftuoglu, 2014). Leonardites are classified as low, medium, and high quality materials. The classification is based on humic substance content,

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organic substance content, pH, C/N ratio, specific weight, and dissolution properties (Table 1).

Table 1. Leonardite ore quality classification (Engin, 2013)

Composition	Low quality	Medium quality	High quality
Humic substance content (%)	20-50	50-65	65-80
Organic substance content (%)	min. 35	min. 50	min. 65
pH	6.5 ± 1	5.5 ± 1	4 ± 1
C/N	21 ± 1	19 ± 1	17 ± 1
Density (g/cm^3)	1.4 ± 1	1.2 ± 1	0.8 ± 1
Solubility in alkaline solution	low	medium	high

The classic commercial method used in separating humic substances from leonardite ore is alkaline leaching. There have been numerous studies on humic substance extraction conducted by scientist. In extracting humic substances from leonardites, NaOH, KOH, NH_3, and $Na_4P_2O_7$ are generally used as alkaline solvents (Jezierski, et al., 2000; Silva, et al., 2013; Saito, et al., 2014). Saito (2014) studied optimal humic substance leaching conditions based on time (3-6-12-24 h), amount of feed, and KOH concentrations on leonardite samples obtained from four different locations. In their extraction study, Jezierski et al. (2000) used NaOH as alkali solvent based on International Humic Substances Society (IHSS) standard process. There are also studies in which leonardite was leached with combining alkali solvents. For example, Silva et al. (2013) conducted leonardite leaching procedure with pyrophosphate and KOH mixture of alkali solvent. In all chemical enrichment studies, it was observed that humic substances were extracted by solvation with a high efficiency and recovery rate. Although there are many studies on the use of NaOH as solvent in literature, studies in which KOH is used as solvent due to the fact that it is a source of potassium, and important element in plant development, are also found. On the other hand, in some chemical dissolution studies, solid/liquid separation was carried out with the help of a centrifugal procedure following dissolution. The extracted solution, rich in humic substance, can find direct uses, however, it can also be used in solid (powder) form as humate salts (sodium, potassium etc.) obtained after precipitation, filtration, vaporization, and crystallization stages (Chen et al., 2011; Karaman et al., 2012).

Although numerous studies can be found in literature on the use of alkali leach method for the extraction of humic acid and fulvic substance from leonardites, there are also studies that use a limited number of physical methods. However, sufficient number of studies on the enrichment of leonardites with inorganic substance content, that are classified as medium or low quality, is not available. Engin (2013) conducted studies on extraction of inorganic substances from leonardites through gravity separators such as jig, shaking table, and multi-gravity separator (MGS). Boylu et al.

(2012), on the other hand, carried out the humic substance extraction from leonardites through a dry method of air-based gravity separators rather than wet methods.

While inorganic substances contained in leonardite along with humic substances cause unnecessary capacity use in facilities, they affect chemical dissolution processes, and increase reactive consumption. This study investigates the applicability of physical enrichment methods as pre-treatment, which is rarely found in the literature and also their effect on chemical enrichment procedures.

Materials and methods

Materials

The leonardite sample was obtained from the Kahramanmaras province of Turkey. It was regarded, based on the quality classification, as medium quality material. Following size reduction to below 4 mm with the help of a jaw-crusher, the samples were stocked in order to use for chemical analysis and experimental studies. The characterization studies were performed for the purpose of definition of the samples. These studies comprised of chemical analysis for each size group, particle size analysis (Fig. 1), SEM (Fig. 2), and mineralogical analysis through XRD technique (Fig. 3), respectively.

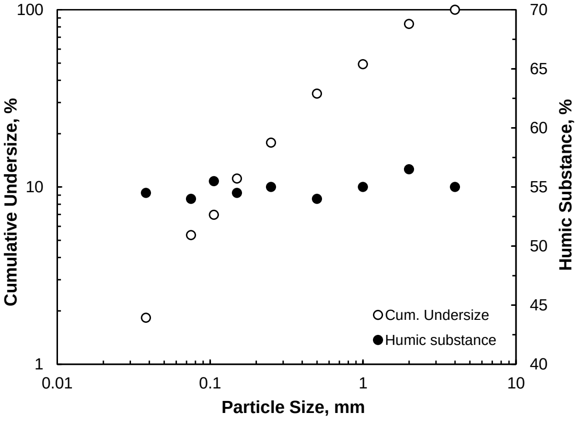

Fig. 1. Particle size analysis and chemical analysis along with the size distribution of leonardite sample

As can be seen in Fig. 1, the sample with 1.9 mm d_{80} was classified in different size groups. When the chemical analysis of the samples obtained in each size group was examined, it was found that humic substance amounts ranged between 54% and 56% in size groups (Fig. 1). The results revealed that there was no enrichment by the classification process.

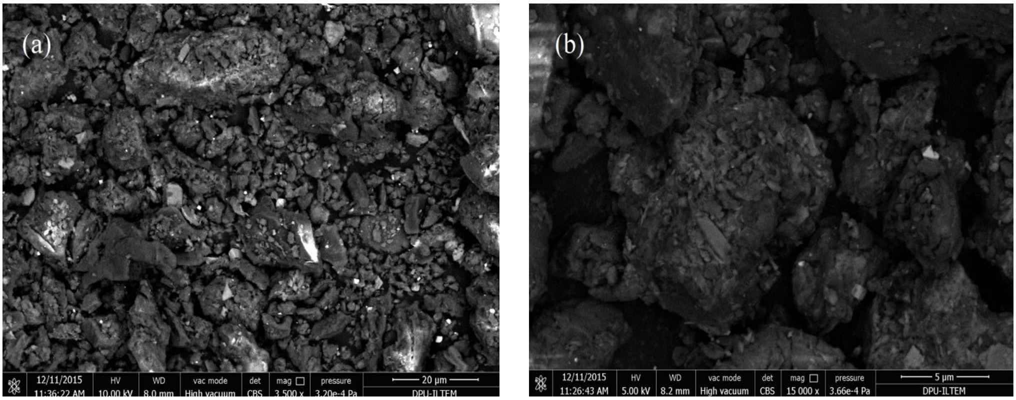

Fig. 2. SEM images of leonardite (a) 3500× (b) 15000×

Structural analysis of leonardite samples was conducted using a SEM device, and the SEM images of leonardite are given in Fig. 2 for two magnifications. It can be seen in Fig. 2 that leonardite surface was made up of lamellae, also noted by Ratanaprommanee and Shutsrirung (2014).

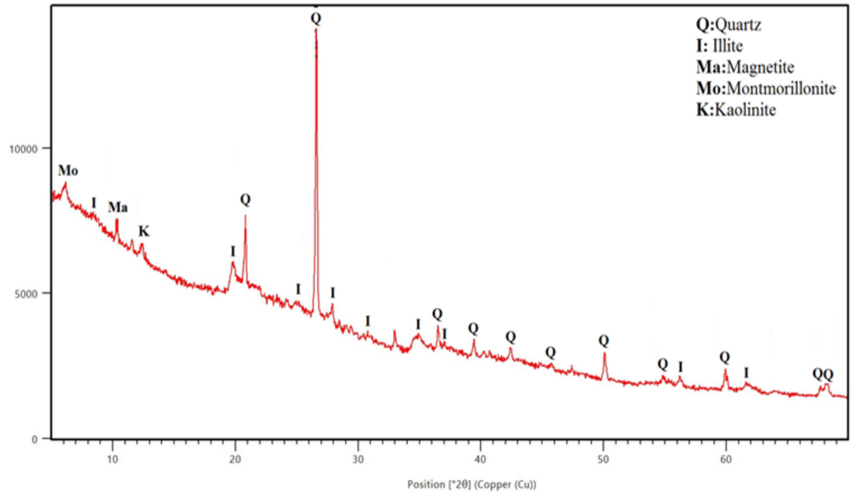

Fig. 3. Mineralogical compositions of leonardite by X-ray diffraction

According to the XRD results given in Fig. 3, the leonardite sample was formed to contain inorganic materials. While the highest amount of inorganic substance was quartz, clay minerals such as kaolinite, montmorillonite, and illite, and a lower amount of magnetite were also found.

Methods

In this study, the chemical enrichment (leaching) studies for the extraction humic substance from leonardites along with pre-physical enrichment studies were carried out systematically in two stages.

Chemical enrichment studies

The leaching studies were conducted under atmospheric pressure using a glass beaker and a magnetic stirrer for stirring and heating. In the chemical enrichment studies, KOH was preferred as alkali solvent due to the fact that agricultural soil needs potassium among macro elements. In the experiments, KOH amount (2, 4, 6, 8, 10 g/cm^3), temperature (25, 40, 60, 80 ^{o}C), stirring time (1, 3, 5, 10, 12, 24 h), and solid ratio (5, 10, 15, 20, 25%) were changed, while stirring speed (150 rpm), particle size (-75 μm) were taken as constant parameters. While selecting these parameters, the literature studies related with alkaline leaching and industrial experiences were used (Ozkan, 2007; Ozdemir, 2011; Saito, 2014). In the analysis on the concentrates obtained from these experiments, humic acid and fulvic acid were analyzed together, and were calculated as total humic substance. The flow sheet of the method adopted in chemical enrichment experiments is given in Fig. 4.

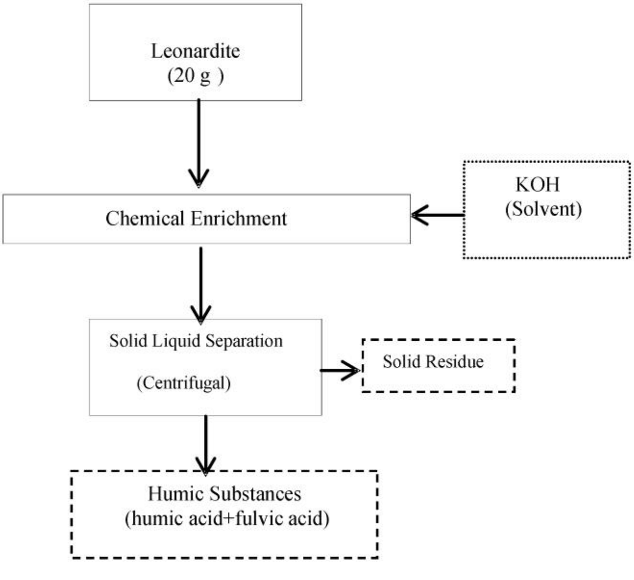

Fig. 4. Principle flow sheet of humic substances leaching

Humic substance content may account in different ways which are spectroscopic methods such as fluorescence spectroscopy, *ESR* spectroscopy, *FIA* (flow injection analysis) (Debora et al., 2002; Tarhan, 2011) and wet methods e.g. TSE 5869 ISO 5073. In this study, humic substance content was calculated according to "TSE 5869 ISO 5073 Brown Coals and Lignites Humic Substance Determination" method. With this method, the amount of total humic substance in brown coals and lignites was determined through calorimetric method. The essence of the method was the same as Walkley-Black method used for determining organic substance in soil (Ozkan, 2008). The method is based on oxidizing the organic part with chromate and the titration of the remaining chromate.

Physical pre-enrichment studies

The physical pre-enrichment studies that were performed for the purpose of the extraction of inorganic substances before the chemical enrichment were carried out with the help of vertical column with a length of 100 cm and a diameter of 10 cm. In a fluid medium formed by water fed from the bottom of the column as observed in Fig. 5, a selective separation carried out by using the density difference of minerals. While the light particles were obtained from the top of the column due to the effect of hydrodynamic forces, the heavy particles moving in the direction of gravity force (*Mg*) while beating hydrodynamic forces (*Fk*) were taken from the bottom of the column. In these tests, the water flow rate and particle size were investigated as variable parameters. In the experiments, concentrates were obtained from the upper flow depending on time and were coded as C_1, C_2, and C_3.

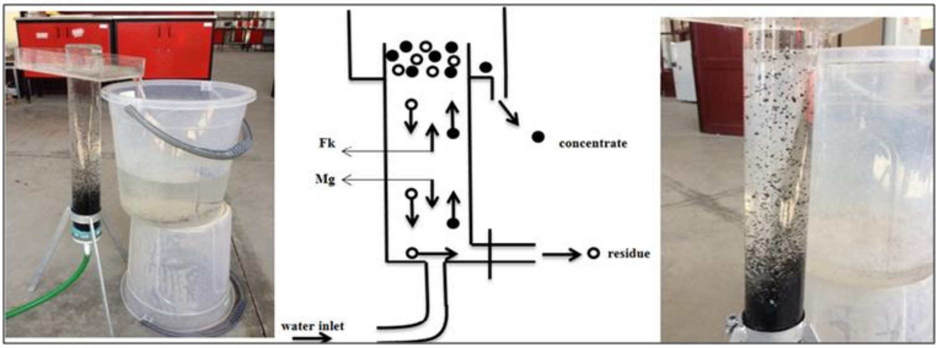

Fig. 5. Pre-enrichment tests used in vertical column (column height: 100 cm, column diameter: 10 cm, *Fk* denotes hydrodynamic force while *Mg* stands for gravity force).

Results and Discussion

As it is known, contact of solvent with the dissolving substance and dissolving time in chemical enrichment studies directly affect enrichment efficiency (Nan et al., 2005, Bas et al, 2015). For this reason, removal of impurities preventing dissolution in order to increase enrichment efficiency for certain ore formations becomes a necessity. As a result of the removal of impurities, contact of solvent and dissolved substance increases, while dissolving time decreases. Thus, valuable substance would be taken to solution economically and with higher efficiency using lower amount of dissolving reagent. In this study, the samples were subjected to enrichment process in two stages following crushing and grinding procedures in order to extract humic substance from leonardites ore. In the first stage, the chemical enrichment experiments were performed in alkali medium. In the second stage, the chemical enrichment tests were applied on to the concentrate obtained by the physical pre-enrichment.

Chemical enrichment studies

The studies of chemical enrichment by leaching conducted for the purpose of humic substance extraction from leonardites were carried out under alkali conditions by using KOH and a tank. While, KOH amount, stirring time, temperature, and solid concentration were investigated as variable parameters, stirring speed (150 rpm), and particle size (-75 µm) were taken as constant parameters in the leach experiments. The products obtained from the leach experiments were analyzed with at least three repetitions, and the results of analysis are given in Figs. 6(a-d) within 5% error limits.

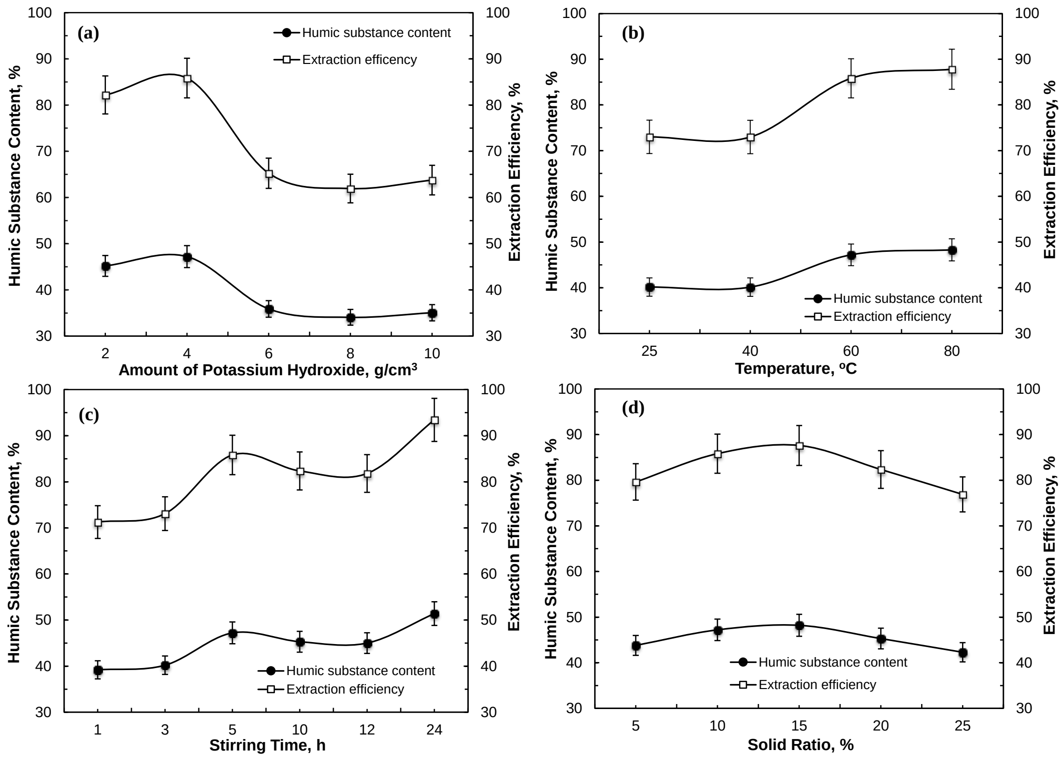

Fig. 6. The effect of some variable parameters on humic substance leaching. (a) amount of potassium hydroxide, (b) temperature, (c) stirring time, (d) solid ratio

The dissolution of humic substances in the leonardite sample increased up to 4 g/cm^3 along with increased KOH concentration, and when coming up to the indicated value, it was determined that humic substance content and extraction efficiency decreased (Fig. 6a). As a result of experimental studies that investigate KOH concentration, highest humic substance content and extraction efficiency were obtained as 47.21% and 85.83%, respectively, at 4 g/cm^3 KOH amount. Potassium (K^+) and (OH) ions that increase in the leaching medium after the indicated concentration cause complex structures formation (oxide, hydroxide, carbonate compounds) (Yildiz et al., 2006; Kibar et al., 2014). These complexes are believed to precipitate humic substances, and it is observed that the contact between solvent and humic substance decreases, which lowers dissolution (Fig. 6a). The XRD studies were performed on the products obtained by using 2, 4, and 8 g/cm^3 KOH for the determination of these compounds, and are given comparatively in Fig. 7. According to the XRD results, it was observed that the XRD patterns of samples changed with the amount of KOH, and that various complex compounds buetschlite ($K_2Ca(CO_3)_2$) and bobfergusonite ($Na_2Mn_5FeAl(PO_4)_6$) were formed (Fig. 7).

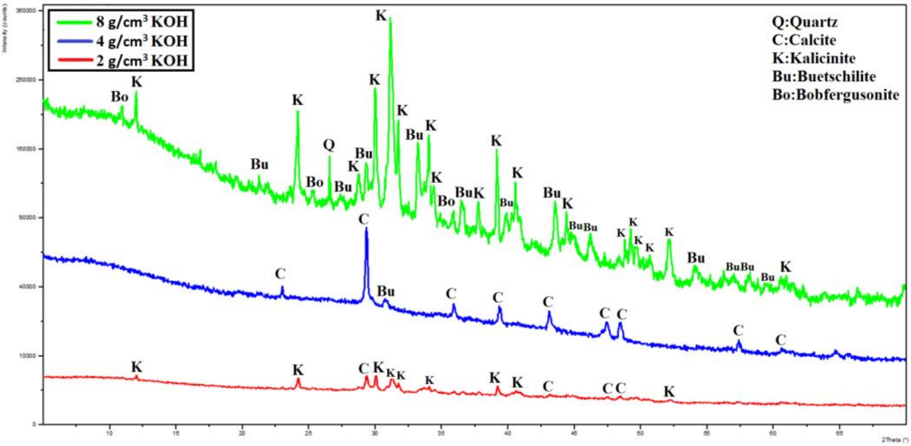

Fig. 7. Comparing by means of X-ray diffraction spectra humic substances obtained using different amounts of potassium hydroxide

It can be observed from Fig. 6b that humic substance content carried to the solution increased along with the increase in the stirring time in the optimal stirring time experiments. These results explained that the possibility of chemical reactions providing dissolution increased as the contact time increased (Abbruzzese et al., 1995; Nan et al., 2005, Olteanu et al., 2014, Bas et al., 2015). However, the 24-h stirring time that produced best results was considered as too long in terms of industrial application. For this reason, 5-h stirring time that produced 47.21% humic substances and 85.83% extraction efficiency was determined as the optimal stirring time.

The reaction temperature affected the dissolution rate of the sample, which dissolved easily at higher temperatures in shorter time (Altiner et al., 2015). Figure 6c shows humic substance content and efficiency increase due to rise in temperature. However, there is a risk of impairment in the structures of amino acids in humic acid molecule chain at higher temperatures (Yamamoto et al*.,* 1994). For this reason, higher temperatures were not preferred. The highest content and extraction efficiency was reached at 80°C in these tests. However, the temperature of 60 °C that produced 47.21% humic content and 85.83% efficiency was selected as the optimal value not to increase energy costs for industrial applications.

As can be observed in Fig. 6d, humic substance content and efficiency increased along with rise of solid ratio up to 15%. After this point, the content and efficiency began to decrease. Such a decrease in humic substance content and enrichment efficiency were also pointed out in studies conducted by Lin and Rao (1988) and Rath et al. (2003), and it occurs as a result of increased solid ratio and decreased solvent-particle contact. In addition to this, the high solid ratio also caused the difficulties in suspension mixing also noted by Kursun et al., 2015.

The optimum leaching parameters determined from leaching tests are as follows: KOH amount 4 g/cm^3, stirring time 5 h, temperature 60°C, solid ratio 15%, stirring speed 150 rpm, and particle size -75 µm. These parameters were also used in literature studies and exist in industrial applications.

Physical pre-enrichment + chemical enrichment studies

At this stage of the study, the physical pre-enrichment tests were applied with the help of vertical column on the sample that was determined to have inorganic substances through the XRD studies (Fig. 3). In the medium formed with water inside the column, density difference of particles and buoyancy of water were used for the removal of inorganics. In the studies, particle size and water flow rate were investigated as variable parameters. The particles fed into enrichment column by dividing the samples into size groups of –2+1 mm, –1+0.5 mm, and –0.5+0.25 mm. In the experiments, C_1, C_2, and C_3 samples were taken for each size group. According to the test results, it was determined that the C_1 coded concentrate had feasible amount of humic substances. The humic contents and the efficiencies of C_1 products obtained from each size groups were comparatively shown in Fig. 8.

When Fig. 8 was examined, humic substance contents of concentrates obtained for three different size groups were determined to range between about 65–70%. The obtained concentrates were observed as high-quality products according to the quality classification (Table 1). On the other hand, humic substance recovery was found to increase along with the increased water flow rate in each size group. Based on this, it was determined that humic substance was obtained with 59.11% recovery with 67.5% humic content at 15 dm^3/min for the –2+1 mm size group, with 22.55% recovery with 71% humic content at 5 dm^3/min for the –1+0.5 mm size group, and with 18.62% recovery with 65% humic content at 2.5 dm^3/min for the –0.5+0.25 mm size group.

The obtained result showed that particle weight was effective in separation in addition to particle liberation, and it also showed that smaller particles should be studied in lower flow rates and larger particles should be studied in higher flow rates. Consequently, it was observed that sample containing 55% humic substance before physical pre-enrichment could provide products with 70% humic substance, and that humic substance content could be increased by 15% (Fig. 8).

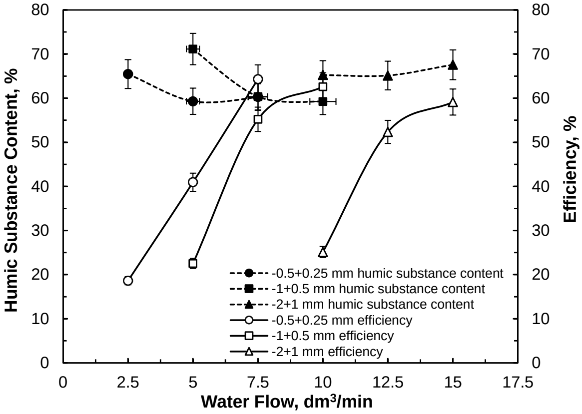

Fig. 8. Comparing the gain efficiency and content of the humic substances the enriched products in vertical columns and (–2+1 mm, –1+0.5 mm, –0.5+0.25 mm) particle

The chemical enrichment and the effect of physical pre-enrichment on chemical enrichment was investigated on the samples obtained under optimal study conditions of physical pre-enrichment (C_I). Previously determined optimal parameters (KOH amount: 4 g/cm^3, stirring time 5 h, temperature 60°C, solid ratio 15%, stirring speed 150 rpm, grain size -75 µm) were used for the chemical enrichment studies. As a result of the studies conducted, concentrate containing 62.74% humic substance was obtained with 92.4% extraction efficiency. However, the recovery of the chemical enrichment was found as 87.63% for the product that was not pre-enriched and containing 48.2% humic content. Meanwhile, the mass of discarded matter of the direct chemical enrichment and applied pre-enrichment were found to be as 10.4 g and 7.5 g out of 20 g, respectively. The residual amount of pre-enrichment test was less than that of the direct chemical test due to the removal of inorganic substances such as clay minerals from the samples by the physical process. Consequently, it was clear that the dissolution increased by 8±3%, and the humic substance can be gained with a higher recovery.

Conclusion

Leonardites, which are predominantly used in organic agriculture among other various sectors, contain significant amounts of humic substances (humic acid, fulvic acid). In this study, chemical enrichment and physical pre-enrichment together with chemical enrichment studies were carried out for humic substance production from leonardite. The results obtained from these studies are given below.

In chemical enrichment studies, the most important parameters affecting humic substance extraction were KOH amount and stirring time. The optimal working conditions were found as 4 g/cm^3 KOH, 5 h of stirring time, 60 ^{o}C of temperature, and 15% of solids.

Humic substance was obtained from the leonardite sample with 87.63% extraction efficiency before physical pre-enrichment. However, about 8±3% increase was produced (92.4% humic substance extraction/recovery ratio) following pre-enrichment method conducted by vertical column in which water was used as flowing fluid.

Consequently, it was determined that high quality (>65%) products could be produced from medium quality leonardite containing 55% humic substance according to the quality classification. As well known, there are abundant resources of low and medium quality leonardite on the earth, and evaluating these resources will contribute to the economy. In addition, new information and techniques developed for the use of these resources will also contribute significantly to the science and technology.

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