Research on Adsorption and Flotation Properties of Herbal Reagents in Processing of Refractory Ores

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Abstract

The results of experimental studies of the adsorption and flotation characteristics of herbal extracts which are produced from the leaves and stems of widely spread heracleum plant (HSE) and oak bark (OBE) are presented. Depending on flotation conditions – pH, plant extract concentration and the order of modifier and collector addition, the possibility of improvement of the quality of Cu and Au concentrates is discussed and the dominating factors of plant modifiers behavior in flotation process are defined. It was identified that tannin and plant extracts OBE may form stable insoluble complex compounds with Fe (III) on the surface of pyrrhotite and arsenopyrite which help to hydrophilize mineral surface and decrease its floatability under flotation conditions.

Experimental results of adsorption studies using UV-spectroscopy and scanning electron microscopy, added by lazer and atomic force microscopy reveales that components of herbal extracts may fix on the surface of sulfide minerals providing the selective hydrophilic coating on their surface.

The formation of the new phase of reactant on pyrite surface was identified, which changed greatly initial morphology of sulfide phase. Newly formed phase is characterized by discrete non-uniform distribution. Moreover, the extract forms rather stable coverage on the mineral surface which can't be clean off by distilled water.

The results of flotation tests justify that cheap plant extracts may be used as flotation modifying agents to separate hard-to-beneficiate pairs of sulfide minerals, replacing highly toxic chemical compounds by environmentally safe substances of plant origin.

Keywords: flotation, adsorption, herbal extracts, modifying agents, sulfide minerals

Introduction

In the context of rapid involvement of hard-to-beneficiate refractory ores with a low content and fine impregnation of valuable components into the processing of complex non-ferrous and precious metals ores, the efficiency of the flotation recovery of copper, gold and other valuable elements may be improved by creating new selective reagents and their combinations. In this way, the design of combinations of traditional collecting agents and new selective compounds with specific directional action, providing durable hydrophobic coating on the surface of gold-hosting minerals is a perspective trend in modern flotation studies.

Actual application of new plant extracts as modifiers in flotation of sulfide minerals is the possibility of replacing of highly toxic chemical compounds by environmentally safe substances of plant origin.

In world mineral processing practice, herbal agents (starch, dextrin, quebracho, etc.) are used for depression of oxidized gangue minerals in sulfide flotation. Tannin is applied as a depressant of calcite and dolomite in the flotation of scheelite and fluorite (Shubov et al., 1990). Organic polymers (guar gum and CMC) that incorporate phenolic ingredients with large number of OH groups are widely used in the flotation of Pt-containing ores for depression of talc gangue minerals (Robertson et al., 2003 Somasundaran et al., 2003). However the wide dissemination of these reagents is prevented because of insufficient knowledge of their composition and physico-chemical properties. The main disadvantage of usage of herbal reagents in sulfide flotation is considered to be their non-selectivity (Khan et al., 1986), but the studies that have been carried out in Russia by Trusov (1939) demonstrated the possibility to separate pairs of some sulfide minerals using organic colloids, for example, tannin to separate galena from chalcopyrite in soda flotation medium.

The article presents the experimental results of adsorption and flotation studies that have been carried out recently in IPKON RAS using cheap herbal extracts as flotation modifying agents to separate hard-to-beneficiate pairs of sulfide minerals. The oak bark extract (OBE) and Heracleum stems and leaves extract (HSE) were tested as the extracts of wildly spread and most available eco-friendly tannin-containing plants. Besides the hydrophilic properties these agents are able to form complex compounds with the metallic ions

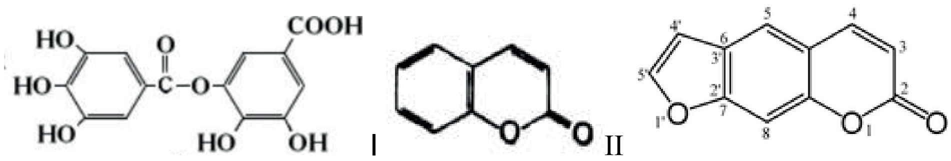

I II III

Fig. 1. Structures of tannin (I), coumarin (II) and psoralen (III)

Rys. 1. Struktura taniny (I), kumaryny (II) I psoralenu (III)

Tab. 1. The chemical composition of the mineral samples

Tab. 1. Skład chemiczny próbek minerałów

Minerals	Content, %						
	Fe	S	As	Cu	Oxides	Others	Au, ppm
Pyrite	39.3	43.7	2.5	0.8	12	1. 7	7
Arsenopyrite	29.7	19.3	40.5	0.04	10.4	<0.1	15
Chalcopyrite	28.1	28.3	-	26.4	15.4	1.8	1
Pyrrhotite	59	38.1	-	0.04	-	2.86	-

which may be used for modifying sulfide minerals in selective flotation.

Methods and materials

In this paper OBE extract was obtained by 3 step-by-step extraction of oak shavings into water under heating at the ratio S:L = 1:15 (Matveeva et al., 2012). The method helped to obtain an extract containing approximately 13% of extractives, including about 47% of tannins. The UV spectrum of the extract has a characteristic absorption maximum at 275 nm. HSE extract was produced by extraction of Heracleum leaves and stems into water-alcohol solution (3:1) at the ratio S:L = 1:50.

The concentration of tannin - the main component of OBE extract was determined by photometric method using Folin's reagent and sodium carbonate (Korenman, 1970) at 660 nm in a cuvette L-30 mm on UNICO 2100 spectrophotometer.

UV-spectrophotometer SHIMADZU-1700 was used to analyze the concentration of the components in OBE and HSE extracts.

The main component of OBE is tannin (Figure 1 – I). Tannins are known as a group of phenolic compounds of plant origin with a molecular weight of 500–3000, containing a large number of OH groups (Kretovich, 1986). Tannins can be extracted from bark into aqueous and alcoholic solutions containing from 10 to 40% of tannins by weight.

Condensed tannins are derivatives of flavanols, they are not hydrolyzed by acids and bases, and may form insoluble polymers. Being easily oxidized substances, tannins in the presence of alkali, absorb oxygen from air and act as reducing agents, for example, for salts of noble metals.

Heracleum leaves and stems extract (HSE) contains natural coumarins, including psoralen (Figure 1 – II, III).

Natural coumarins are known as biologically active phenolic compounds with antioxidant, antiviral, anticoagulant properties. In recent years, the biologically active compounds are widely used in various fields of biotechnology, medicine, food and cosmetic industries. Antioxidant properties of coumarins are considered to be determined by their ability to neutralize reactive oxygen species and to inhibit the free radical chain reaction. Moreover, coumarins are capable of forming complexes with transition metals.

HSE extract may contain also vegetable protein, tannins, amino acids, glutamine, essential oil, oily esters and acetic acid that have accumulated in the leaves and stems of Heracleum plant.

Scanning atomic force microscope NT-MDT and laser microscope KEYENCE VK- 9700 were used to identify the adsorption of the components of OBE and HSE extracts on the surface of polished section of pyrite and arsenopyrite.

The chemical composition of pyrite, arsenopyrite, chalcopyrite and pyrrhotite samples is demonstrated in Table 1.

The study of hydrophobicity (water wettability) of the surface of minerals in solution of the reagents was performed by measuring the force that is required to detach the air bubble from the mineral surface (DF).

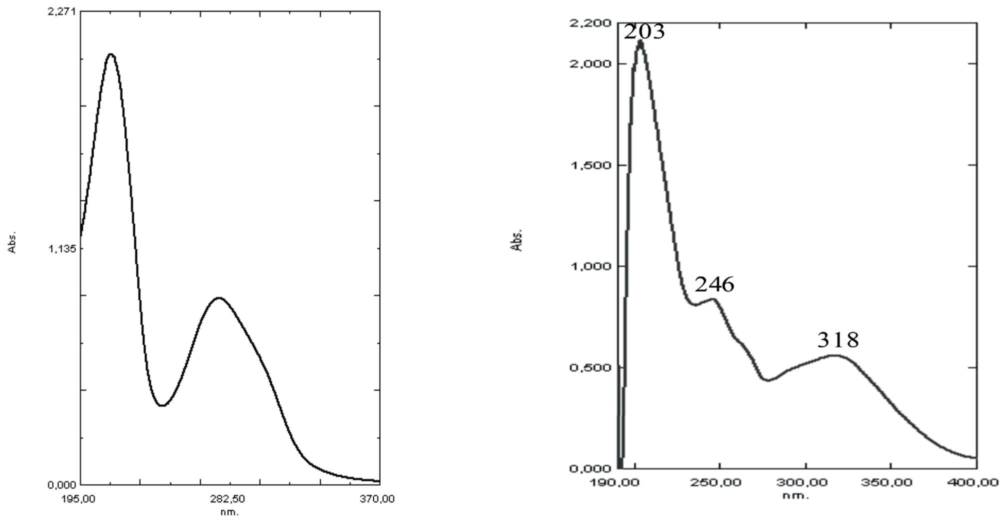


Fig. 2. UV spectra of OBE aqua extract (a) and aqua-alcoholic extract of HSE (b)

Rys. 2. Spektrum UV wyciągu wodnego heracleum plant (Barszcz- HSE) oraz kory dębu (OBE)

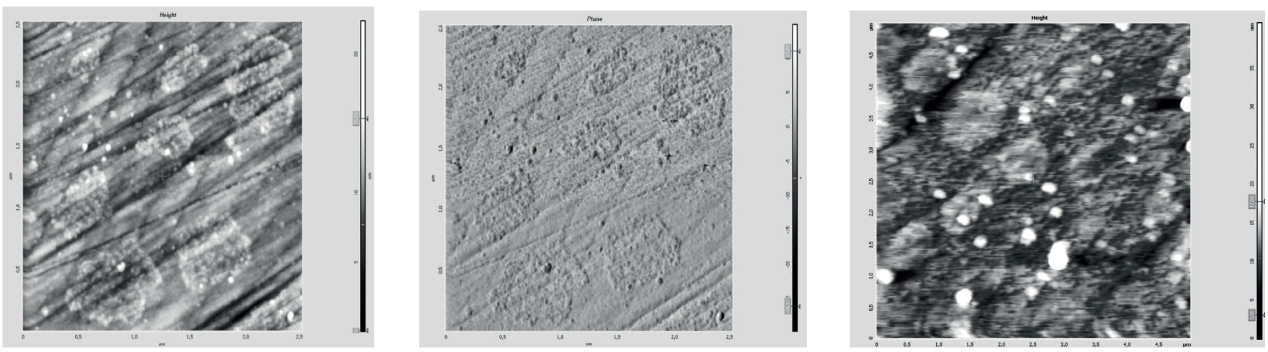


Fig. 3. The surface relief (a, c) and distribution of the phases (b) on the surface pyrite (5x5 micron portion) after contact with tannin solution (a, b) and HSE extract (c). Image of the section of pyrite (scanning atomic force microscope NT-MDT)

Rys. 3. Powierzchnia (a ,c) i rozkład faz (b) na powierzchni pirytu (wielkość 5 x 5 mikrometrów) po kontakcie z roztworem taniny (a, b) i HSE (c). Obraz uzyskany za pomocą mikroskopu NT-MDT

Results and discussion

Analyzing the UV spectrum of OBE extract the characteristic absorption maxima at 275 and 200 nm are determined (Figure 2a) which is very close to peaks in pure tannin UV spectrum at 275 and 212 nm. Similar peaks at 275 nm showed tannin incorporated into OBE extract and shift of the peaks at 200-212 nm may be explained as the result of the other herbal compounds extracted together with tanning substances.

In the UV spectra of HSE in water, ethanol and water-alcoholic solution absorption peaks were detected, and according to its magnitude it is possible to estimate the concentration of extractives in the mineral slurry and the adsorption of the reagent onto the mineral surface. Figure 2b shows characteristic absorption maxima at 318, 246 and 203 nm in aqua-alcoholic HSE extract.

The absorption peak at 203 nm in HSE extract is identical to tannin. The same peak presents in the spectrum of OBE. The absorption peak at 318 nm is closed to the absorption peak of coumarin (Kretovich, 1986). Shift of the peaks at 203 and 318 nm in the UV spectrum of the extract relative to the peaks of absorption of pure tannin solutions and coumarin, and a peak at 246 nm may be explained by extraction of the other components into HSE extract (amino acids, essential oils, etc.).

HSE extract was analyzed after its contact with pyrite and chalcopyrite samples (ground to -0.1+0.063 mm). It was determined that absorption peaks decreased and accounted 88–92% of initial absorption. It means that about 8–12% of the extract components may adsorb on the mineral surface.

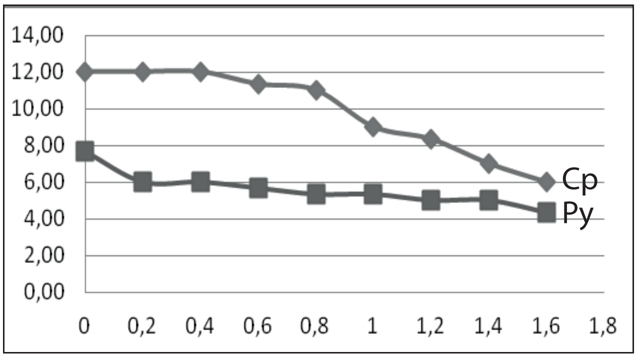
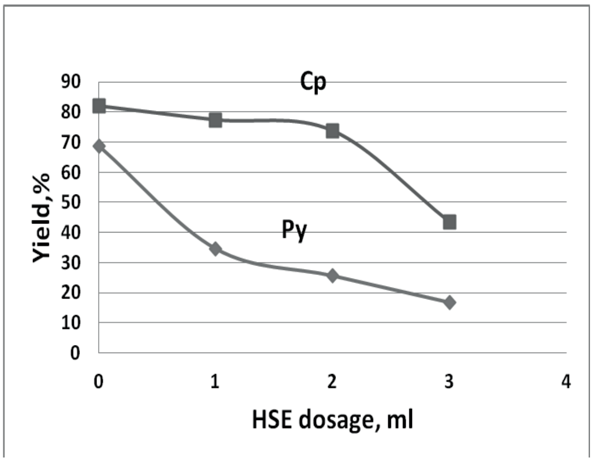


Fig. 4. Detach force (DF, 1.10–5 N) of the air bubble from the surface of the chalcopyrite and pyrite as a function of HSE extract dosage (Hostaflot X23 concentration 30 mg/l)

Rys. 4. Siła odrywania (DF, 1.10-5N) pęcherzyka powietrza od powierzchni chalkopirytu i irytu w funkcji ilości wyciągu HSE i dawki odczynnika flotacyjnego (Hostaflot X23, koncentracja 30 mg/l)



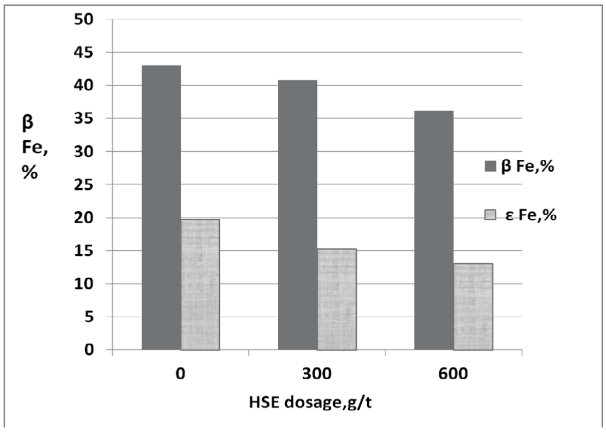


Fig. 5. Flotation of chalcopyrite and pyrite (a) and Fe content in by-product Cu concentrate (b) as a function of HSE extract dosage (Hostaflot X23 concentration – 30 mg/l)

Rys. 5. Flotacja chalkopirytu i pirytu (a) i zawartość Fe w półproduktach Cu (b) w funkcji ilości wyciągu HSE i dawki odczynnika flotacyjnego (Hostaflot X23, koncentracja 30 mg/l)

It was identified that tannin and plant extracts OBE may form stable insoluble complex compounds with Fe (III) on the surface of pyrrhotite and arsenopyrite which help to hydrophilize mineral surface and decrease its floatability under flotation conditions (Matveeva et al., 2012). The mechanism of modifying action of tannin-bearing reagents in flotation conditions was proved to be based on their adsorption on the surface of pyrrhotite and arsenopyrite forming strong complexes with Fe (III) at concentrations below the concentration of micelle formation, and the pre-adsorption of xanthate does not prevent the consolidation of OBE on the surface of the mineral (Matveeva et al., 2012).

In this paper scanning atomic force microscope NT-MDT was used to define tannin, OBE and HSE extracts adsorption on the surface of polished section of pyrite and arsenopyrite. Images obtained by NT-MDT microscope, help to study the topography (relief) of the surface with a resolution of tens of angstroms up to atomic dimension and may show the relief and phase changes on the mineral surface after its contact with reagent solutions.

Vision changes of surface relief and distribution of the phases on pyrite surface (5x5 micron portion) after its contact with tannin and HSE extract are demonstrated in Figure 3. As a result of contact of mineral with tannin solution the formation of the new phase of reactant on pyrite surface was identified, which changed greatly initial morphology of sulfide phase. Newly formed phase is characterized by discrete non-uniform distribution. Moreover, the extract forms rather stable coverage on the mineral surface which can't be clean off by distilled water.

The study of hydrophobicity (water wettability) of the surface of minerals in solution of the reagents was performed by measuring the force that is required to detach the air bubble from the mineral surface (DF). The curves in Figure 4 shows decrease of DF for chalcopyrite and pyrite with increasing concentration of the HSE extract.

Hydrophilic effect of the HSE is more evident for pyrite surfaces at 0.2–1.0 ml dosage of extract, and DF for chalcopyrite is rather stable at those extract concentrations. When HSE dosage exceeds 0.8 ml DF rapidly drops for chalcopyrite and at 1.4–1.6 ml is very close to Py. So, much difference in the wettability of the minerals is observed between 0.2 and 0.8 ml of extract dosage. Preferential hydrophilic effect of HSE may be applied in selective flotation of Cu-pyrite ores.

Flotation tests were performed on pyrite and chalcopyrite samples, Xostaflot X23 (300 g/t) was used as a collector, HSE extract as a modifier and MIBC as a foaming agent. HSE extract was 5 times diluted and added into mineral suspension after collector in dosages from 1 to 3 ml which is equal to 200–600 g/t if calculated on dry substance.

HSE extract dosage reduced the floatability of pyrite from 70 to 18%, being especially rapidly in the interval between 0.5–1ml. The flotation yield of pyrite did not exceed 34–27% at 1–2 ml HSE (200–400 g/t dosage) (Figure 5a). The greatest effect is achieved when using the X23. In the case of xanthate flotation of pyrite reduction is less than 25%.

Floatability of chalcopyrite in the similar HSE dosages (200–400 g/t) is maintained at a high level (75–80%), providing selective conditions to separate it from pyrite.

Laboratory flotation experiments on the sample of ore from Gaiskoye field in an open loop scheme incorporated the bulk Cu and control flotation, using a combination of Hostaflot X23 and ButX as collectors and HSE as a modifier agent in control flotation resulted in a 8% decrease of Fe content and 6.5% decrease of Fe recovery into control flotation concentrate (Figure 5b).

Conclusion

As a result of the study of adsorption and flotation properties of herbal extracts which are produced from the leaves and stems of widely spread heracleum plant (HSE) and oak bark (OBE), there was determined that the indicated reactants occurred the electoral effect on the studied minerals. UV-spectroscopy and scanning atomic force microscopy results revealed that components of herbal extracts may fix on the surface of sulfide minerals providing the selective hydrophilic coating on their surface.

Compared to chalcopyrite, preferential hydrophilic effect of HSE components on the surface of pyrite was identified by measuring the force that is required to detach the air bubble from the mineral surface (DF).

Tannin, coumarin and the other extractive components, incorporated into HSE and OBE extracts demonstrated modifying effect on pyrite and chalcopyrite floatability. HSE extract dosage helped to separate chalcopyrite from pyrite and improve the quality of Cu concentrate by decreasing Fe content in it.

The results of flotation tests justify that cheap herbal extracts may be used as flotation modifying agents to separate hard-to-beneficiate pairs of sulfide minerals, replacing highly toxic chemical compounds by environmentally safe substances of herbal origin in selective processing of complex Cu and Au-bearing ores.

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Badania nad właściwościami adsorpcyjnymi i flotacyjnymi odczynników roślinnych w przetwórstwie materiałów ogniotrwałych

Zaprezentowano wyniki badań eksperymentalnych nad właściwościami adsorpcyjnymi i flotacyjnymi ekstraktów roślinnych pochodzących z liści i łodyg powszechnie występującej rośliny heracleum plant (pol. barszcz; ang. skrót HSE) oraz kory dębu (ang. skrót OBE). W zależności od warunków flotacji – pH, stężenia ekstraktu roślinnego i kolejności dodawania modyfikatora i kolektora, omówiono możliwości podwyższenia jakości koncentratów Cu i Au, oraz określono dominujące cechy w zachowaniu modyfikatorów roślin w procesie flotacyjnym. Ustalono, że tanina i ekstrakty roślin OBE mogą uformować nierozpuszczalne złożone związki z Fe (III) na powierzchni pirotynu i arsenopirytu, co pomaga w hydrofilizacji mineralnej powierzchni i obniża jej flotowalność.

Wyniki badań eksperymentalnych nad adsorpcją przy użyciu spektroskopu UV i skaningowej mikroskopii elektronowej wykazały, że składniki ekstraktów ziołowych mogą adsorbować na powierzchni minerałów siarczkowych zapewniając selektywną powłokę hydrofilową. Odkryto powstanie nowej fazy odczynnika na powierzchni pirytu, co w znaczącym stopniu zmienia wstępną morfologię fazy siarczkowej. Nowopowstała faza charakteryzuje się skokowym, nierównomiernym rozkładem. Ponadto, ekstrakt formuje dość stabilną powłokę na powierzchni mineralnej, której nie można zmyć wodą destylowaną.

Wyniki testów flotacyjnych udowadniają, że tanie ekstrakty roślinne mogą być użyte jako czynniki modyfikujące flotację do oddzielania niskoopłacalnych minerałów siarczkowych, zamieniając wysokotoksyczne związki chemiczne na bezpieczne dla środowiska substancje pochodzenia roślinnego.

Słowa kluczowe: flotacja, adsorpcja, wyciągi roślinne, odczynniki modyfikowane, minerały siarczkowe