

CHENG LIU*[#], QIMING FENG**[#], GUOFAN ZHANG**[#]**EFFECT OF AMMONIUM SULFATE ON THE SULFIDATION FLOTATION OF MALACHITE****WPLYW OBECNOŚCI SIARCZANU AMONU NA PRZEBIEG PROCESU SULFIDACJI (SIARCZKOWANIA) W TRAKCIE FLOTACJI MALACHITU**

The effect of ammonium sulfate on the sulfidation flotation of malachite was investigated by micro-flotation tests, scanning electron microscope (SEM) and energy dispersive spectrometer (EDS) measurements. Micro-flotation results show that the sodium sulfide concentration and stirring time are difficult to control on the sulfidation flotation of malachite. However, when ammonium sulfate was used, the detrimental effect of mixing time and high dosage of sodium sulfide on the sulfidation flotation of malachite can be efficiently eliminated. SEM results showed that sulfidized film on malachite in the presence of ammonium sulfate, and EDS analysis results showed that more S element absorbed and distributed equally on the malachite surface, which was agreed well with the macro-flotation results.

Keyword: malachite, ammonium sulfate, sulfidation-flotation, surface morphology

Badano wpływ siarczanu amonu na przebieg procesu siarczowania w trakcie flotacji malachitu przy wykorzystaniu badania mikroskopowego, mikroskopii elektronowej skaningowej (SEM) oraz pomiarów spektrometrycznych rozpraszania energii EDS. Testy mikroskopowe wykazały, że stężenie siarczku sodu i długość czasu mieszania są parametrami, które niezwykle trudno kontrolować w trakcie procesu siarczowania towarzyszącego flotacji malachitu. Z kolei przy zastosowaniu siarczanu amonu, udaje się skutecznie wyeliminować niekorzystne efekty związane z czasem mieszania oraz wysokimi stężeniami siarczku sodu w trakcie flotacji malachitu poprzez siarczowanie. Wyniki mikroskopii skaningowej wskazują, że przy zastosowaniu siarczanu amonu powstaje cienki film siarczkowy na malachicie zaś pomiary spektrometryczne wykazały większe ilości zaabsorbowanej i bardziej równomiernie rozłożonej siarki pierwiastkowej S na powierzchni malachitu, co pozostaje w pełnej zgodności z wynikami uzyskanymi z badania procesu flotacji w skali makro.

Słowa kluczowe: malachit, siarczek amonu, flotacja poprzez sulfidację (siarczowanie), budowa powierzchniowa

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1. Introduction

Copper is the second base metal in importance, following only iron, aluminum, which is used in the galvanizing, electronic, as well as other industries (Sarquís et al., 2014). Copper is conventionally produced from sulphide ores, but these ores are depleted. Hence beneficiation of oxidized copper ore is becoming increasingly attractive in recent years due to the depletion of copper sulfide ores and the restrictions on sulfur emission. This situation increases the need to process these ores to produce a marketable product (Corin et al., 2017).

Oxidized copper ores are found in silicate or carbonate forms (Hope et al., 2012), malachite being a typical oxide mineral of zinc. Flotation is the commonly used method for beneficiation of malachite and other oxidized copper minerals (Li et al., 2015). However, malachite possesses a hydrophilic surface which does not respond well to traditional sulphide copper collectors such as xanthanes (Li et al., 2015; Lee et al., 2009; Sergio et al., 1974). The classical method involves controlled potential sulphidisation (CPS) to sulphidise the surface of the oxide minerals by the addition of a sulphidisation agent, such as sodium hydrogen sulphide (NaHS). When NaHS is used for CPS the pulp redox potential (Eh) is reduced to a target value between -450 and -550 mV (Soto & Laskowski, 1973; Jones & Woodcock, 1978). The key of this method is to control potential sulfidization and the main disadvantage of CPS is that the optimum concentration of the sulphidisation agents is highly dependent on the time of conditioning, procedures of mixing and other variables, leading usually to poor reproducibility in a plant situation (Castro et al., 1974a,b). Insufficient addition of the sulphidisation reagents will cause poor recoveries and an excess will cause the depression of oxide copper minerals (Lee et al., 1998).

Ammonium sulfate has been researched in flotation of pyrite can restore the floatability of pyrite without the need to use copper sulfate or sulfuric acid. The recovery of pyrite increases from less than 10% to more than 85% (Xu & Kelebek., 2000). Wu et al (2017) found that ammonium ions could enhance sulfidation flotation of smithsonite. However, very little research has been conducted concerning the sulfidation flotation of malachite under ammonium sulfate, the flotation mechanism of sulfidation behavior of malachite under ammonium sulfate is unclear. The objective of this study is to explore the flotation sulfidation behavior of malachite in the presence of ammonium sulfate. This was accomplished through the use of various techniques, including micro-flotation tests, scanning electron microscope (SEM) and energy dispersive spectrometer (EDS) analysis.

2. Materials and methods

2.1. Samples and reagents

Malachite samples used for the experiments were obtained from Yuanjiang Yunnan Province, China. The samples were crushed and ground using in agate mortar. The products were then dry sieved to obtain a particle size of -74 μm . The XRD analysis and chemical constitution of sample were shown in Fig. 1 and Table 1, respectively. The X-ray diffraction (XRD) analyses indicated that the purity of malachite samples were very high (Fig. 1).

Kalium butyl xanthate (KBX) with 85% purity was used as the collector, which was obtained from Jiangxi Copper Corporation. Analytical-grade $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ and methyl isobutyl carbinol (MIBC) was used as the sulfurizing agent and frother, respectively. ammonium sulfate is also

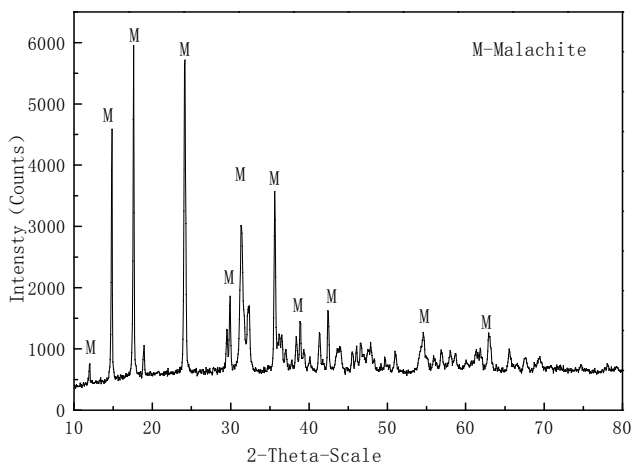


Fig. 1. X-ray diffraction of malachite sample

analytical-grade in this work. Analytical-grade NaOH and HCl were utilized as the pH modifiers in the experiments, and distilled water with a resistivity of 18.2 Ω cm was used for all the tests.

TABLE 1

Chemical composition of malachite

CuO	SiO ₂	Fe	S	Others
70.69	1.09	0.86	0.08	37.27

2.2. Micro-flotation tests

Micro-flotation experiments were performed in a 40 mL hitch groove flotation cell. The purified mineral particles (2.0 g) were placed in a Plexiglas cell, which was filled with 35 mL of distilled water. The pH of the suspension was adjusted by HCl or NaOH for 3 min. 1 min with the sodium sulphide (when required, the stirring time was changed), When needed, sodium sulphide was added prior to the conditioning of ammonium sulfate. After the addition of KBX collector and methyl isobutyl carbinol (MIBC), the pulp was continuously stirred for 2 min and 1 min, respectively. Then flotation was conducted for 3 min. Both froth and tailings products were collected, dried and weighed. The mineral recoveries were calculated based on the dry weights of the obtained products.

2.3. SEM and EDS tests

SEM-EDX was used to observe the morphology and the adsorption of S on the malachite surface. After adsorption, the ore samples were thoroughly washed with deionized water of the same pH to remove loosely attached composition. Before observation, the floated fractions were dried in an oven at 50 °C and gold coated under vacuum using an ion coater. Images were acquired using a XL30W/TMP type scanning electron microscope.

3. Result and discussion

3.1. Micro-flotation

Fig. 2 shows the flotation recovery of malachite as a function of pH in the absence and presence of sodium sulfide when 50 mg/L KBX. It can clearly show from Fig. 2 that the floatability of malachite using the KBX collector is weak. A maximum recovery of approximately 60% of the malachite mineral was obtained around pH 9, this phenomenon may be attributed to the hydrophilic surface of malachite, resulting in weak floatability. However, with the addition of sodium sulfide, the results (Fig. 2) show that the flotation recovery of the malachite increases with increasing pH until pH 9.0 and then decreases rapidly. A maximum recovery of approximately 80% of the malachite was obtained at approximately pH 9.0.

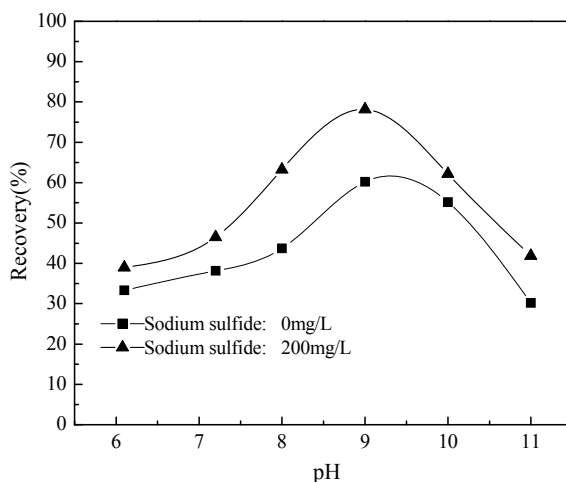


Fig. 2. Recovery of the malachite flotation with and without sodium sulfide (50 mg/L KBX and 10 mg/L MIBC, pH = 9)

The species distribution diagrams for sulfur ions as a function of pH are shown in Fig. 3. It can be seen from Fig. 3 that H_2S species dominates at $\text{pH} < 7.0$, and HS^- species dominates at $\text{pH} 7.0\text{--}13.9$, whereas sulfur ions were predominantly in the form of S^{2-} when $\text{pH} > 8.5$, respectively (Somasundaran & Wang, 2006). the optimum pH of malachite flotation is located in the range where HS^- is the predominant species, indicating that HS^- species interact with cupric ions on the malachite surface and forms a sulfidized surface film, thus activating the flotation of the malachite (Ejtemaei et al., 2014).

The objective of this study was to investigate the effects of ammonium sulfate on the sulfidation flotation of malachite in the presence of KBX. Fig. 4 shows sodium sulfide concentrations on the flotation of malachite in the absence and presence of ammonium sulfate. It can be seen from Fig. 4 that the flotation recovery of the malachite increases with increasing sodium sulfide concentration until 200 mg/L sodium sulfide and then decreases rapidly, indicating that the recovery of malachite depressed over a fixed sodium sulfide concentration, similar to the inves-

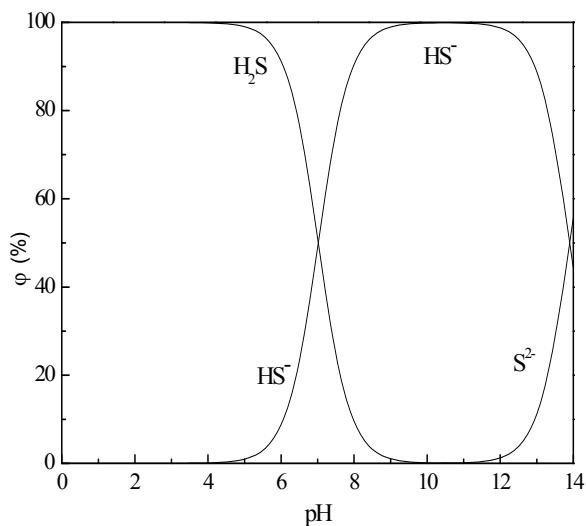


Fig. 3. Species distribution diagrams of sulfur ions as a function of pH

tigation of Park et al (2016). With the addition of ammonium sulfate, the recovery of malachite is not affected when the concentration of sodium sulfide is more than 200 mg/L, indicating that ammonium sulfate can eliminate an excess of sodium sulfide concentration which carry negative effect on the flotation of malachite.

The stirring time also should be considered on the sulfidization flotation of malachite. Fig. 5 presents the stirring time on the flotation recovery of malachite in the absence and presence of ammonium sulfate. It can be seen from Fig. 5 that the flotation recovery of the malachite increases

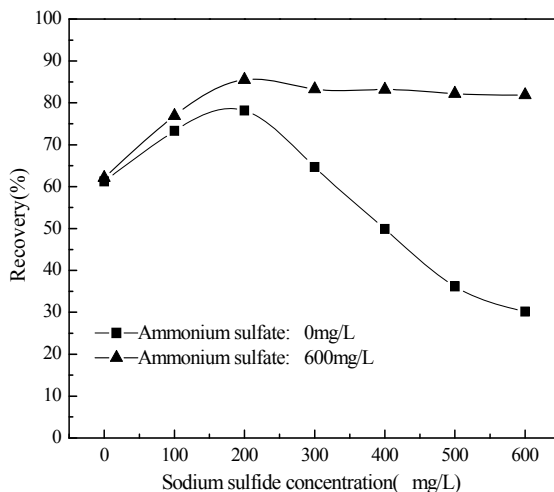


Fig. 4. Recovery of the malachite sulfidization flotation with and without ammonium sulfate (50 mg/L KBX and 10 mg/L MIBC, pH = 9)

with increasing mixing time until mixing time is 1 min and then decreases rapidly, indicating that the recovery of malachite depressed when mixing time is more and/or less than the fixed time. However, when ammonium sulfate is used on the sulfidization flotation of malachite, a different tendency is observed, malachite flotation recovery changed little with increases of stirring time (over 1 min), the detrimental effect of mixing time on the sulfidization flotation of malachite can be efficiently eliminated by the utilization of ammonium sulfate.

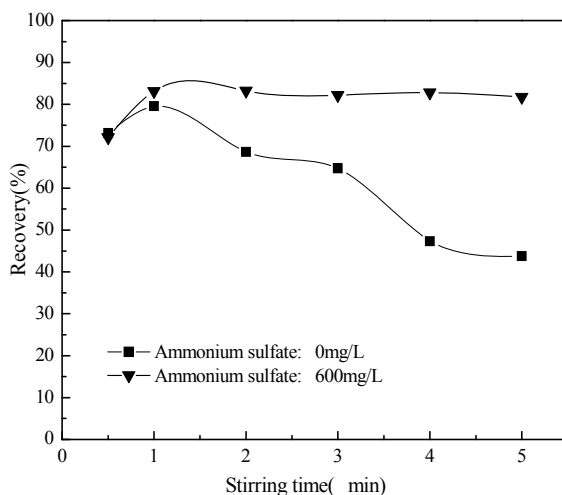


Fig. 5. Effect of stirring time on malachite sulfidization flotation with and without ammonium sulfate (200 mg/L Na_2S , 50 mg/L KBX and 10 mg/L MIBC, pH = 9)

3.2. SEM-EDS analysis

Fig. 6 presents the morphology of malachite surface under different conditions. Fig. 6(a) shows the surface of bare malachite are clean. Fig. 6(b) shows that sulfidized film formed on the malachite surface with 200 mg/L sodium sulfide concentration (stir for one minute). Fig. 6(c) shows that the sulfidized film fell off easily from malachite surface with 200 mg/L sodium sulfide when the mixing time (3 min) is more than 1 min, indicating that the sulfidized film is unstable on the surface of malachite. Fig. 6(d) shows that the sulfide film is loosen on malachite surface in the presence of excess sodium sulfide. Fig. 6(e) illustrates that strong adsorption layer of sulfide film formed on the surface of malachite using excess sodium sulfide dosage when ammonium sulfate is added, and Fig. 6(f) shows that there is no obvious shedding of sulfidized film from malachite surface when the mixing time is 3 min with 600 mg/L ammonium sulfate and 200 mg/L sodium sulfide, indicating that the sulfidized film is stabilized on the surface of malachite which is matched well with the micro-flotation results.

SEM test is commonly used in combination with EDS analysis, EDS analysis is employed to explore the distribution of element of malachite surface. Fig. 7 and Fig. 8 show the distribution of element of sulfidized malachite surface in the absence and in the presence of ammonium sulfate. Malachite treated with individual sodium sulfide and stirred for 3 min, four micro regions were selected and EDS results show that the regional average S element atomic concentration is

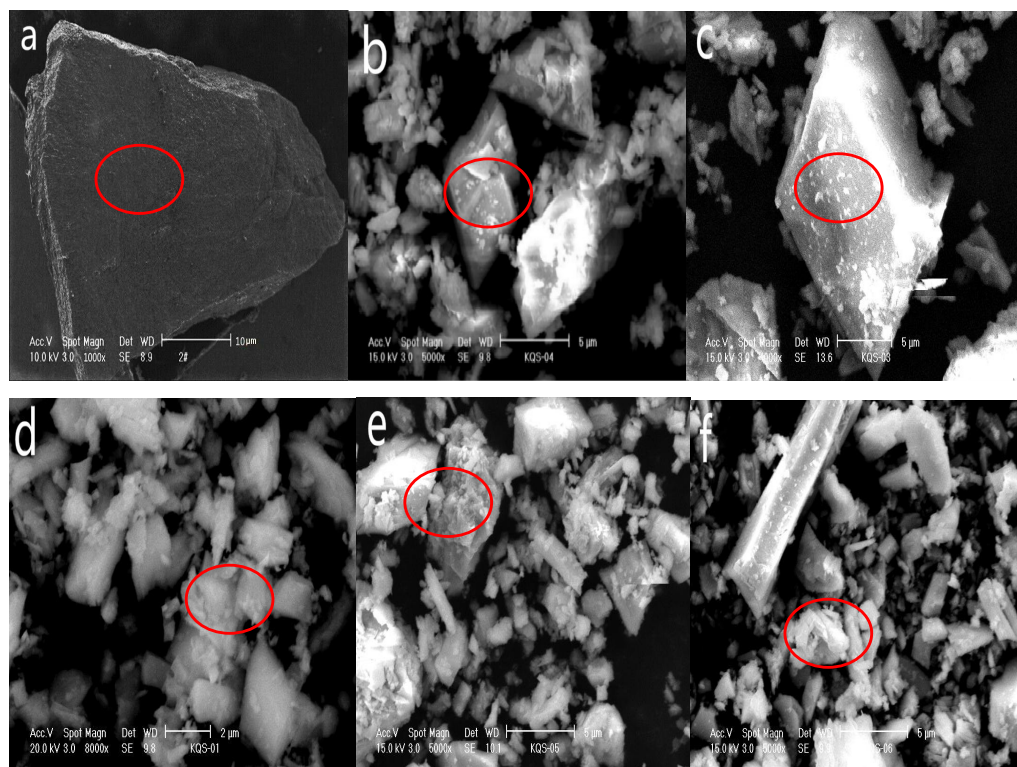


Fig. 6. SEM of malachite samples. (a) untreated (b) Na_2S :200 mg/L, stir for 1 min (c). Na_2S :200 mg/L, stir for 3 min (d). Na_2S :400 mg/L, stir for 1min (e). $(\text{NH}_4)_2\text{SO}_4$:600 mg/L; Na_2S :200 mg/L, stir for 1min (f). $(\text{NH}_4)_2\text{SO}_4$:600 mg/L; Na_2S :200 mg/L, stir for 3 min

2.94% on malachite surface, and the standard deviation is 1.71%. When the sulfidized malachite was treated with ammonium sulfate, the S element atomic concentration increased to 5.29%, and the standard deviation is 0.70%. The EDS results in Fig. 7 and Fig. 8 also show that the absorption of S element enhanced on malachite surface in the presence of ammonium sulfate, and the calculation results of standard deviation indicate that the distribution of S element more evenly on malachite with ammonium sulfate than without ammonium sulfate, which also agreed with the micro-flotation results.

4. Conclusions

The micro-flotation tests demonstrate high concentration of sodium sulfide and long time stirring strongly depress the flotation recovery of the malachite in the presence of SBX, the detrimental effect of sodium sulfide concentration and mixing time on the sulfidation flotation of malachite can be efficiently eliminated by the utilization of ammonium sulfate. The SEM results show that the sulfidized film is more stabilized on the surface of malachite when ammonium sulfate is used in the pulp. EDS results the absorption of S element enhanced on malachite sur-

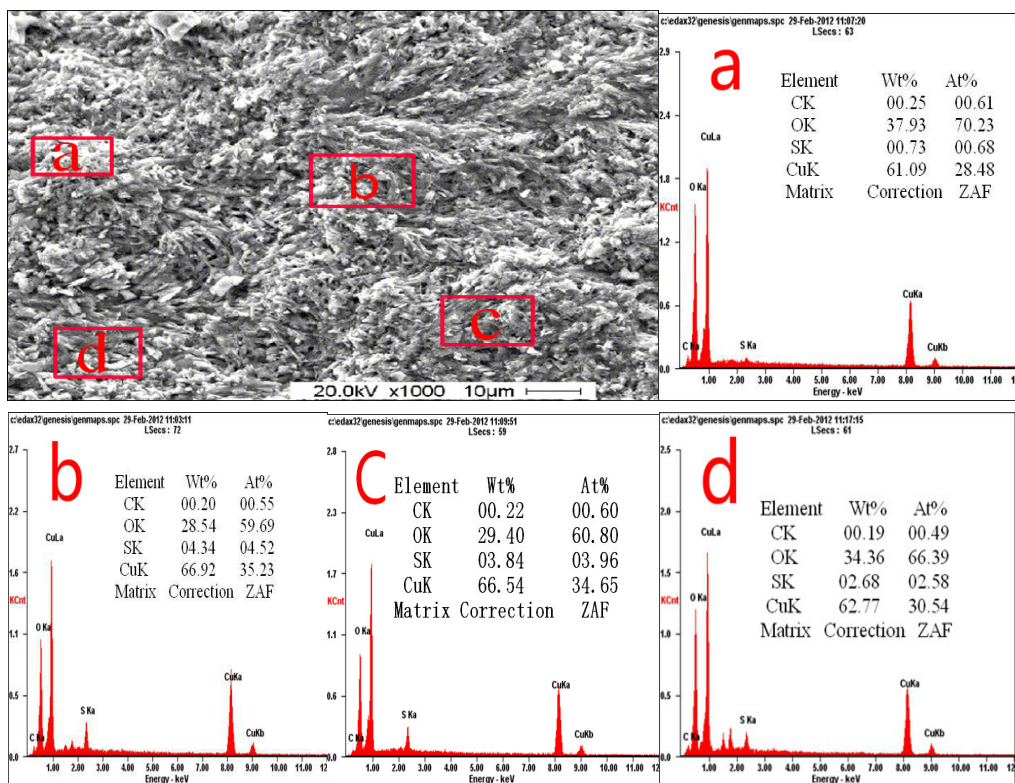


Fig. 7. EDS result of elements content on malachite surface (Na₂S 200 mg/L, stir for 3 min)

face, and the calculation results of standard deviation indicate that the distribution of S element more evenly on malachite with ammonium sulfate than without ammonium sulfate. Thus, ammonium sulfate might be as a potential reagent to limit the detrimental effect of sodium sulfide concentration and mixing time on the sulfidation flotation of malachite.

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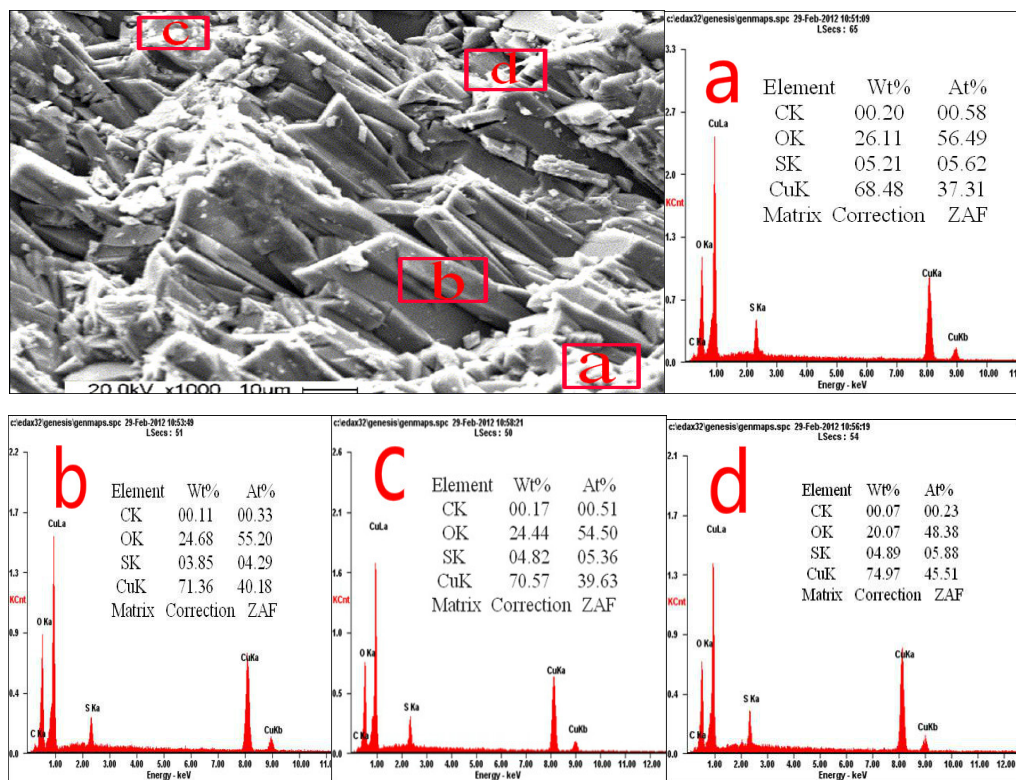


Fig. 8. EDS result of elements content on malachite surface
 ((NH₄)₂SO₄:600 mg/L, Na₂S:200 mg/L, stir for 3 min)

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