Regeneration of Degraded Extractant by Sodium Hydroxide Activated Clay and Evaluation of Its Performances in Copper Solvent Extraction

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Abstract - In copper solvent extraction, phenolic hydroxy oximes-based extractant has been observed to deteriorate progressively during extraction. Hydrolysis, rather than oxidation or Beckmann rearrangement, produce majority of the degradation products. Degradation products impact the solvent extraction method by lowering extraction efficiency, reaction kinetics, and Cu/Fe selectivity, slowing the phase disengagement time and polluting the electrolyte. Activated clay using sodium hydroxide (NaOH) was used to regenerate deteriorated extractant. After the regeneration step, the organic phase's performance improved: extraction efficiency increased from 67 to 97.3 % maximum, Cu/Fe selectivity increased from 169 to 283 and phase disengagement time decreased from 113 to 88 seconds.

Keywords: Hydroxyoxime, extractant, LIX 984N, degradation, regeneration, clay, activation, copper solvent extraction.

1. Introduction

Solvent extraction (SX) is a critical procedure in the hydrometallurgical processing of different base and precious metals, made possible by the immiscible characteristics of organic and aqueous phases. The organic phase generally consists of a hydrogenated and desulfonated kerosene-based solvent (often referred to as a 'diluent') and an active 'extractant' susceptible of reversibly solvating specified metal ions [1]. In the extraction of different metals, including copper, numerous extractants are utilized commercially in SX processes. For copper procedures, phenolic hydroxyoxime-based SX extractants are preferred, e.g LIX984N, which comprises of 2-hydroxy-5-nonylbenzaldehyde oxime and 2-hydroxy-5-nonylacetophenone oxime. Hydroxyoxime compounds are well-known as effective selective extractants which are used in industrial applications[2].

Organic SX solutions must be continuously recycled for economic and other reasons, enabling organic degradation products and contaminants into the circuit to accumulate to an equilibrium level in the organic phase. For many years, phenolic oxime reagents were used commercially to extract copper from acidic sulfate solutions, and because of their cost, much research on phenolic oxime degradation has focused on improving performance efficiency and reducing cost. The effects of identified phenolic oxime degradation pathways on SX operation are well summarized [3]. Beckmann rearrangement, hydrolysis, and sulphofication are all reactions that degrade LIX 984N. The most frequent degradation reaction of hydroxyoxime is hydrolysis, which exists in acidic environment and result on the production of related aldehyde or ketone particles [4]. Phenolic oxime oxidation is hardly the most prevalent yet essential degradation process. Low circuit efficiency is already connected to oxidation, such as high oxidation stage manganese compounds under acidic environments. SX is severely affected by extractant degradation, which results in complicated phase disengagement, polluted electrolyte, reaction kinetics and extractant capacity reduction, as well as a decrease in interfacial tension and Cu/Fe selectivity [1]. As a result, plants have to renew their reagents, which increase the cost of production. Since the degradation of hydroxyoxime products allows copper solvent extraction to fail, it is important to minimize the production of degradation products or regenerate the degraded hydroxyoxime extractants in copper solvent extraction.

According to researchers, extractant that has been regenerated can be used in place of the new extractant [5, 6]. The most of previous researchers looked at the components of degradation in copper solvent extraction circuits, as well as the impact of hydroxyoxime degradation products on metal extraction. [5] studied the impact of the degradation product of hydroxyoxime on copper extraction and investigated the regeneration of degraded hydroxyoxime with hydroxylamine. After the oxidation

of cobalt (II) to cobalt (III) in the Queensland process for the separation of cobalt and nickel, nickel is selectively removed from cobalt (III) by hydroxyoxime LIX 84I (2-hydroxy-5-nonylacetophenone oxime) [7] . The extractant was oxidatively degraded due to cobalt (III). To preserve the extractant capacity, an additional regeneration process for re-oximation was performed [8].

This paper investigated the regeneration of degraded LIX 984N with sodium hydroxide activated clay. The influence of activated clay on the regeneration of degraded extractant based on the comparison of the performances of extractant before and after regeneration was studied. Experiments of solvent extraction from acidic solution were carried out on metal extraction kinetics, metal selectivity, phase disengagement time, and Cu/Fe selectivity in order to analyse the efficiency of regeneration. The effects of concentration of sodium hydroxide; temperature and contact time on activation of clay were investigated on the influence of the regeneration of organic phase.

2. Material and methods
2.1. Organic and aqueous reagents
LIX 984N and Kerosene supplied by Merck, South Africa were used as supplied. Aqueous solutions were prepared using AR grade copper sulphate.

2.2. Analysis
The chemical composition of the clay was determined through X-ray fluorescence (XRF) Rigaku ZSX Primus II equipped with the EZ scan software for quantification. The scan analysis took place under vacuum while the X-Ray source was set at the voltage of 30kV and the intensity of 40mA. The mineralogical composition of the clay was determined using an X-ray diffractometer (XRD) Rigaku Ultima IV. Phases were identified using PDXL software loaded with an ICDD PDF card of pure compound. The Scanning Electron Microscope (SEM) was used surface morphology analysis, while the EDS was used for the chemical composition of targeted spots. The German model TESCAN instrument equipped with the Vega 3X was used to collect the image by means of a secondary electron detector while operating in the nanospace under a voltage of 20kV. The Fourier Transform Infrared Spectroscopy (FTIR) was used to investigate the structural changes of the clay mineral and the solvent at different stages. The ATR_FTIR (Perkin-Elmer Spectrum 100 spectrometer) was used at a spectral range of 4000-400 cm-1 with a resolution of 4 cm-1. The concentrations of copper and iron ions in different solutions were analysed using atomic absorption spectroscopy analyses (AAS Type Solar Series M-II-K manufactured by Thermo Electron Corporation). During the analysis, the sample was atomized to a temperature of about 2000 °C to allow the excitation of the targeted elements to the required energy.

2.3. Experimental procedures
2.3.1. Purification and activation of clay
A well-blended bentonite powder sample was mixed with Hydrochloric acid (HCl) solution in the ratio of 1:10. Therefore, about 20g of the clay sample was washed using a 2M HCl solution. During the washing process, the mixture was heated to about 60°C for 45 minutes while being continuously stirred. After reaching the required time, the clay sample was separated from the acidic solution and washed with the deionized water until a pH between 5 and 6 was reached. The washed clay sample was oven-dried at 100°C for 24 hours and characterized using different analytical techniques to assess the changes. The washed clay was mixed with the alkaline solution in the ratio clay/alkaline of 0.1. Therefore, 10 g of clay was added to 100 ml of sodium hydroxide solution already prepared at different concentrations, reaction times and temperatures according to runs generated by the design of experiments (DoE) using Taguchi method [9]. The current study consists of three factors at three levels leading to L9A = 9, the number of experiments to be performed. Table 1 displays the number of parameters (3) and the number of levels (3). The activated clay was filtered after reaching the assigned time according to the experimental setup design shown in Table 1. The collected activated clay was washed using deionized water to remove the extra alkaline solution. After this step, the activated clay was oven-dried at 100°C for 24 hours. The emanating activated clay products were characterized using similar analytical equipment.

Table 1: Orthogonal array (L9) proposed by Taguchi method for Bentonite clay activation.

Runs	Concentrations (M)	Temperature (^{O}C)	Time (min)
1	7	60	30
2	7	80	60
3	7	90	90
4	8	60	60
5	8	80	90
6	8	90	30
7	9	60	90
8	9	80	30
9	9	90	60

2.3.2 Degradation of organic phase

The degradation of the organic phase was achieved by exposing it to several series of loading, extraction and stripping processes. The organic phase sample was exposed to 5 cycles in this study to evaluate its degradation level. Since the organic phase needs to be used several times, it needs to be recycled. About 100ml of the organic phase was used to recover copper from a synthetic solution prepared from copper sulphate salt estimated at 13%w/w. The organic phase was a mixture of LIX984N as extractant solvent and kerosene as a diluent in the ratio of 22 % v/v. It should be noted that for 100 ml of the organic phase, 22ml of LIX984N and 78ml of kerosene were used. The loading was done by mixing 100ml of copper sulphate solution with the organic phase under perfect agitation. The magnetic stirrer was used for a perfect mixture to promote Cu ions diffusion from the aqueous phase to the organic phase for 5 minutes.

After loading, the organic phase carrying Cu ions was subjected to striping in the presence of 13% of H_2SO_4 to recover Cu to the aqueous phase. After the stripping process, the spent organic phase was regenerated, while the solution after stripping was analysed using the AAS.

The removal efficiency was determined using the equation 1,

$$\%E = \frac{[Cu]_0 - [Cu]_e}{[Cu]_0} * 100 \qquad (1)$$

Where [Cu]o and [Cu]e (g/l) are the initial and equilibrated concentrations of copper in the aqueous phase.

2.3.3. Regeneration of organic solvent

2g of activated clay was added to 100ml of the spent organic phase. The mixture was magnetically stirred. After 1 hour, the mixture was filtered to remove the clay. The organic phase was analysed to characterize and assess the regeneration's efficacy. After regeneration, performances of organic phase was evaluated and compared with the fresh and degraded organic phases.

2.3.4. Extraction efficiency and Cu/Fe selectivity

100 mL of organic phase was put in a magnetic stirred beaker for each experiment, and 100 ml of the aqueous solution was promptly added. These two phases were separated after 5 minutes of mixing. All aqueous samples were analyzed for Cu and Fe. The efficiency of extraction was evaluated by calculating percentage extraction (%E) using equation 1 while the Cu/Fe selectivity was calculated using equation 2.

Cu/Fe = ([Cu] loaded organic – [Cu] stripped organic) / ([Fe] loaded organic – [Fe] stripped organic)   (2)

2.3.5 Extraction kinetics

For every experiment, 100 ml of the organic phase was put in a beaker, and 100 mL of the aqueous solution was promptly added. The mixture was stirred using a magnetic stirrer. Samples (about 10 mL) were obtained from the mixed emulsion after 30, 60, 120, and 300 seconds, and mixing was stopped. The aqueous and organic phases of each tested emulsion were separated. The Cu and Fe content of all aqueous samples were determined using AAS.

2.3.6 Phase disengagement time

All organic phases were subjected to phase disengagement time (PDT) testing. Organic (100ml) and aqueous (100ml) solutions were mixed for 5 minutes. The emulsion was quickly transferred to a 250 mL separator funnel, and the separation of the two phases was observed by noting the time necessary for 90 % disengagement of the clear organic and aqueous phase.

3. Results and discussions
3.1. Characterization of raw clay material

The raw clay mineral's chemistry, mineralogy, morphology, and functional groups were performed using XRF, XRD, SEM-EDS, and FTIR. The XRF results presented in Table 2 revealed that the Bentonite clay contains a considerable amount of SiO_2 (53.6%) and Al_2O_3 (17.81%) mineral phases. Major impurity was Fe_2O_3 that required to be removed. It was also noticed that negligible amounts of CaO, MgO, K_2O, Na_2O, and MnO were present.

Table 2: Chemical composition of raw clay

Elements	SiO_2	Al_2O_3	Fe_2O_3	Na_2O	CaO	MgO	K_2O	MnO
Mass %	53.6	17.81	13.7	2.32	4.5	4.48	1.6	0.16

The examination of the XRD pattern given in Fig.1 revealed that the clay employed in this study is dominated by the presence of smectite in the form of bentonite. The minerals found in the clay indicated that the raw clay mineral contains a significant amount of quartz. As a result, it is classified as a quartz-dominated clay. More analysis discovered that the impurity element Fe exists in two forms: magnetite and wustite. Anorthite was discovered as a Ca-bearing clay mineral in an aluminosilicate material, in addition to the primary clay mineral. It's worth noting that the bentonite clay fraction, often known as the montmorillonite, exists in the sample.
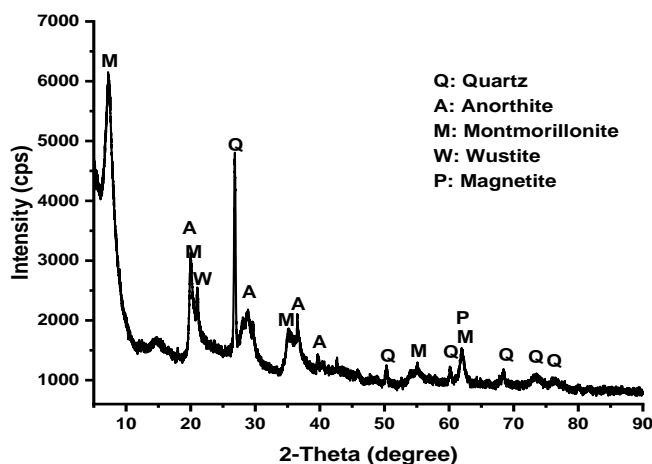

Fig 1: X-ray diffraction pattern of the raw clay

3.2. Clay chemistry changes after pre-treatment

After drying, the chemical composition of the washed and activated samples was determined, and the results were compared to the as-received sample. After washing, the effects of acid washing and activation were examined, and the findings are shown in Table 3.

Table 3. Comparison of the chemistry change of the washed and the activated clay

		SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	Na$_2$O	CaO	MgO	K$_2$O	MnO
Elements Mass %	raw	53.6	17.81	13.7	2.32	4.5	4.48	1.6	0.16
	washed	64.3	18.48	11.15	0.18	0.8	1.23	1.4	0.07
	activated	53.1	19.32	14.36	4.74	1.28	3.1	2.18	0.09

The comparison of the washed sample to the as-received sample indicated a change in chemical composition. Fe$_2$O$_3$, Na$_2$O, CaO, MgO, K$_2$O, and MnO weight percentages reduced from 13.7, 2.32, 4.5, 4.48, 1.6, and 0.16 to 11.15, 0.18, 0.8, 1.23, 1.4, and 0.07, respectively. The reduction might be ascribed to the elimination of contaminants that were not stable on the clay. Simultaneously, a significant rise in the quantity of SiO$_2$ was found, along with a small amount of Al$_2$O$_3$. These are elements that constitute the clay mineral structure.

The composition of the bentonite altered dramatically after the alkaline treatment. In comparison to the washed clay, the Al$_2$O$_3$, Fe2O3, Na$_2$O, and CaO content falls while the Al$_2$O$_3$, Fe$_2$O$_3$, Na$_2$O, and CaO content increases. The lower silica concentration in the treated sample may be ascribed to the hydrolysis of the Si^{4+} ions from the octahedral layer under alkaline conditions, which caused the Si^{4+} ions to leach from the octahedral layer. The concentration of the reagent employed during the process causes the salt content to rise.

3.3. Clay mineralogical phase changes

The strength of the typical peaks for montmorillonite and quartz decreased in the purified clay, as shown in Fig. 2. These changes imply that once the clay was purified, the crystallinity of accessory components like CaO and Na$_2$O in the as-received sample were lowered. The elimination of muscovite, wustite, and magnetite in the washed and activated samples suggested that iron oxide had been reduced.
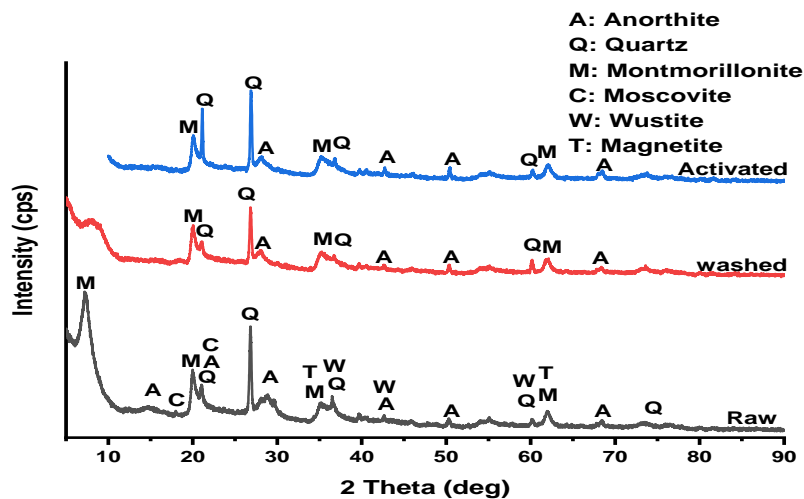

Fig. 2: X-Ray Diffraction comparison of raw, purified and activated clay

There is an increase in the peak intensity of quartz after alkaline treatment. The rise in peak intensity might be linked to a reduction in mean lattice strain and an increase in crystallite size.

3.4. Clay morphological changes

Because both the washed clay and the as-received sample are generating agglomerations, their morphology was and the results are shown in Fig. 3. The washed clay, on the other hand, was more clustered than the as-received, with a number of white particles in the form of precipitated, which might be owing to hydration after water washing, resulting formation of hydroxide compound.
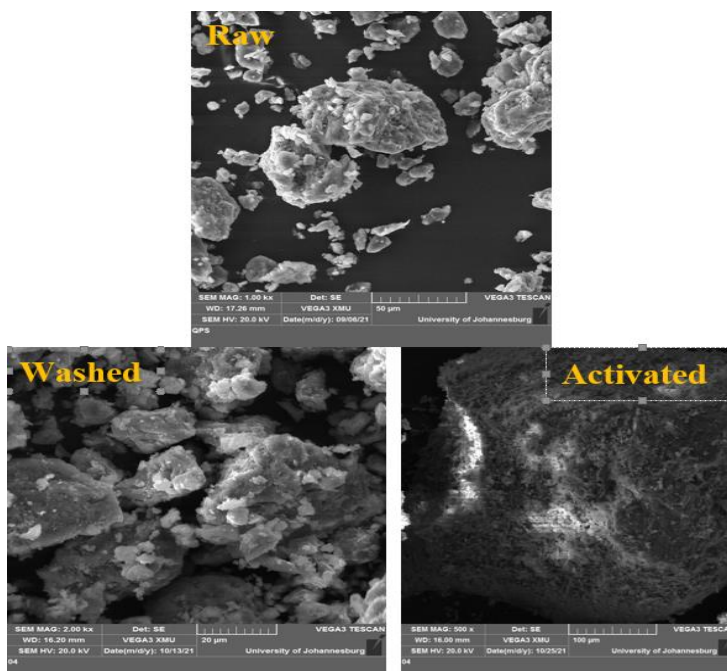

Fig. 3: Surface morphology of raw, purified and activated clay

In comparison to the activated, there is a significant change in the clay structure, resulting in a large surface with punctual pores, indicating a rise in surface area, which will enhance the processed clay's absorption capacity.

3.5. Clay functional group changes

The results of the comparison of the activated to both the as-received and the washed is shown in Fig. 4. As a result of the vibration magnitude being impacted, the spectrum intensity altered. The FTIR pattern shows that the clay structure had been altered. The activated clay showed disappearances of M-X, M-O, and CO_3^{2-} functional groups at frequencies of 467, 529, and 1384 cm^{-1}, but the washed and as-received clays did not.

3.6. Characterization of spent and regenerated organic solvent

The comparison of the three types of solvents is represented in Fig. 4. Results revealed that the degraded or spent solvent was structurally modified compared to the fresh solvent. Therefore, it is characterized by a considerable change in the intensities of all the characteristic peaks. Besides the above, spent solvent was characterized by the disappearances of a peak at 1541 cm^{-1} (=C-H) and appearance of a peak at a frequency of 1587 cm^{-1} (C-H) representing an aromatic vibrational group. Further comparison was done with the regenerated sample and results demonstrated an appearance of a characteristic peak at about 2347 cm^{-1}, indicating the Si-H vibrational group. This situation may be due to the presence of the silicon Si from the activated clay.
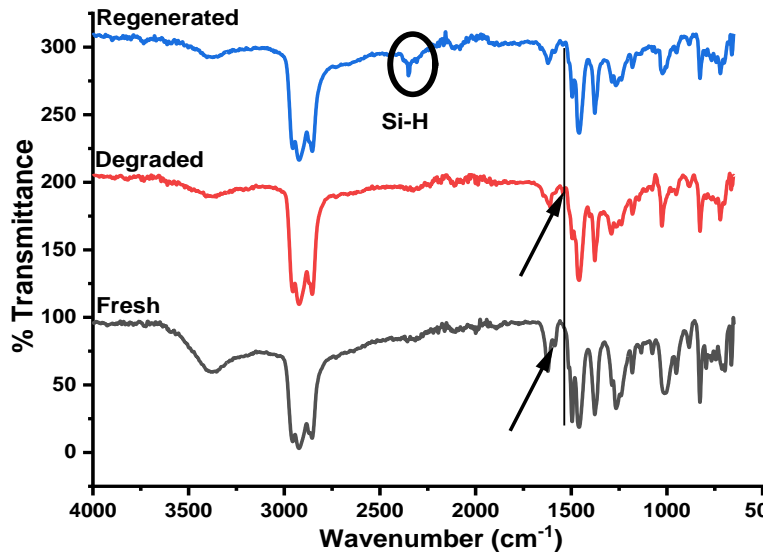
Fig. 4: FTIR comparison of fresh, spent and regenerated solvents

3.7 Performances of the regenerated organic phase

The performances of the regenerated solvent consisted of the evaluation of the selectivity of the solvent. Therefore, the current investigation assessed the fresh, spent, and regenerated solvents based on the ratio Cu/Fe in the raffinate. Outcomes are presented in Table 4.

The results revealed that the ratio Cu/Fe in the fresh, spent and regenerated were about 740, 218 and 495, respectively. This shows that the selectivity was improved after regeneration. The loading of Fe in the organic degradation phase increased from 0.003 g/l to 0.007 g/l, resulting in a reduction of the selectivity Cu/Fe from 740 to 218. This might be due to loading of considerable amount of iron on the organic charge of impurities leading to poor copper selectivity.

Table 4: Cu/Fe selectivity

Organic phase	Cu loading (g/l)	Fe loading (g/l)	Cu/Fe selectivity
Fresh	2.22	0.003	740
Degraded	1.52	0.007	218
Regenerated	1.98	0.004	495

However, the iron is extracted less by regenerating the organic phase, raising the Cu/Fe selectivity from 218 to 495. This result demonstrates that the organic regenerate's performance was improved. Since the selectivity of the regenerated cannot reach that of the fresh solvent, in practice, the spent solvent must be mixed with the fresh to improve its activity. However, this practice contributes to alleviating the cost during solvent extraction.

3.8 Kinetic extraction

Likewise, in all metallurgical processes, kinetics play a determinative role since it directly impacts the production cost. The effect of time on the extracting of copper from a synthetic Cu solution using the fresh, spent and regenerated organic solvent was investigated and the results are shown in Fig. 5. The extraction rate decreased when comparing the behaviour of the fresh organic and the spent curve. After 300 seconds, the extraction rate decreases from 91.3 to 79.2 %, indicating that the degradation of the organic solvent reduces the kinetics.
After the regeneration stage, the organic regained its efficacy and enhanced the extraction rate from 79.2 to 87.8%.
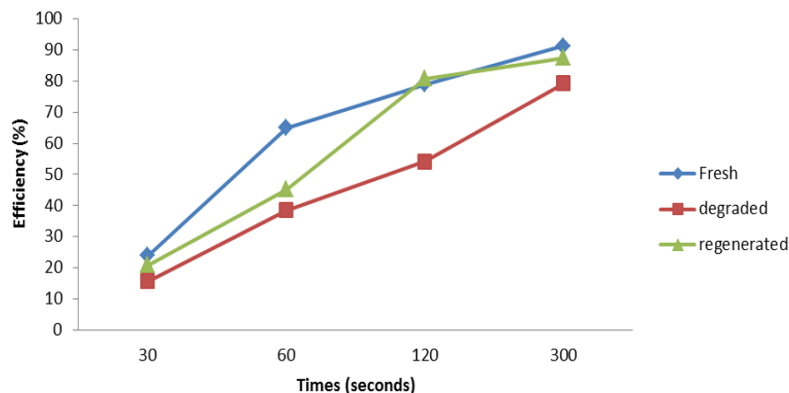
Fig. 5: Extraction kinetics of fresh, spent and regenerated solvents.

3.9 Phase disengagement time (PDT)

The average time required for 90 % phase disengagement for the fresh, spent and regenerated organic was 90, 113 and 88 seconds. The increase in phase disengagement time 90 to 113 seconds might be due to surfactants, which cause a slow separation of phases, generating an interface issue. The effect of organic pollutants adsorbing on the active clay reduces the phase separation time after regeneration from 113 to 88 seconds.

4. Conclusion

The impact of the activated clay in the regeneration of the spent organic solvent was investigated at a laboratory level. The clay mineral was characterised, washed and optimized under conditions determined using the DoE through the Taguchi method while considering concentration, time and temperature as variable parameters and copper yield efficiency as response. NaOH can be used to activate bentonite clay which can be used for regeneration of spent solvent during solvent extraction of copper. The removal efficiency of Cu from a synthetic solution could range between 77.2 and 97.3 % using the regenerated solvent. The kinetics investigation in the removal of Cu from synthetic solution using the fresh, spent and regenerated solvent showed that the removal rate order was fresh > regenerated > spent solvent. The selectivity followed the same order. The disengagement process was faster in the fresh than the spent organic spent.

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