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RESEARCH ARTICLE

Treatment of Spent Merox Caustic Waste in Industrial Ecology Frames

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Abstract
Possible treatment options of spent Merox caustic waste have been explored for the sake of recommending a neutralization scheme that is not only affordable but promises modest profit and provides an environmentally benign technique that meets criteria of industrial ecology. We concluded to recommend a system in which two waste streams are co-processed and in addition to efficient neutralization the potential of a renewable energy resource is also produced. Colloid chemical specifics of the waste in question have been shown to have influence on processing this hazardous and otherwise difficult to treat waste of petroleum refining.

Keywords
desulfurization, waste to energy, Merox treatment, colloid chemistry

1 Introduction

The spent Merox caustic waste (***SMC***) in question is a by-product of desulfurization of light hydrocarbon fractions and products in petroleum refinery operations. Removal of sulfur is necessary because of environmentally driven product specifications for protecting life and safety of living organisms. The term of industrial ecology is used by answering simple questions, like a) are all of the resources, mass and energy flows in the system rational and harmonized? b) was the production planned and operated without adverse effect on our environment, resources and cannot interfere with food chains [1]. Light hydrocarbon fractions and products can be desulfurized by extraction or by chemical conversion. In extractive treatment a solvent that can be regenerated transfers sulfur compounds into polar phase. This phase does not mix with the apolar hydrocarbon phase and can easily be separated by settling. NaOH is a convenient agent for this. Low molecular weight acids are also separated into the water phase. The action of converting the sulfur compound reveals that the mechanism is a reactive extraction:

$$RSH_{[oil]} + NaOH \rightarrow RSNa_{[water]} + H_2O$$
$$2RCOOH_{[oil]} + 2NaOH \rightarrow 2NaOOCR_{[water]} + 2\,H_2O$$

For the sake of recycling the caustic salts and soaps and other sulfur compounds are oxidized in catalytic oxidation. Disulfides are the determinant products of oxidation. These oil soluble components are transferred into an apolar phase by the use of a light hydrocarbon solvent and the separated polar phase caustic is recycled to the reactive extraction operation:

$$4NaSR_{[water]} + O_2 + 2H_2O \rightarrow 2RSSR_{[oil]} + 4NaOH$$

The overall process from the viewpoint of desulfurization is characterized by **MER**captane**OX**Idationand has therefore been designated accordingly as MEROX unit:

$$2\,RSH_{[oil]} + \tfrac{1}{2}\,O_2 \rightarrow RSSR_{[oil]} + H_2O$$

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Along the reactive extraction step most of the polar compounds of the light hydrocarbon fractions submitted to desulfurization are accumulated into the water phase. This separation is challenging, because of the slight difference in density and boiling points, in comparison to characteristics of water, as illustrated in Table 1. To improve efficiency of separation, that is most probably influenced by colloid chemical interferences, the use of a mercaptane-free re-extraction technique was recommended [2].

Table 1 Most probable di-sulfides present in oxidized MEROX stream [3]

component		specific density g/cm^3, 15^{o}C-on	normal boiling point, ^{o}C
di-methyl-disulfide	CH_3SSCH_3	1,057	114
di-ethyl-disulfide	$C_2H_5SSC_2H_5$	0,992	152
ethyl-propyl-disulfide	$C_3H_7SSC_2H_5$	0,964	142

Components with stubborn resistance to oxidation (phenols, thiols[1], hydrocarbons, etc.), diluent water and catalyst residuals are held either dissolved or dispersed forms [4] in the solvent and are circulated between extraction and oxidation cycles as long as the caustic becomes depleted and SMC must be discarded. Difficult to meet environmental and safety rules must be observed in neutralization of SMC.

Some experts think that not the active Merox catalyst, but the support causes decisive depletion of the catalyst and caustic, through adsorption of polars and transfer of these into the bulk of caustic [5]. Regeneration procedures of the Merox catalyst are also contributing sources of difficult to degrade components. In addition to desorbed polar components ammonia, used for catalyst impregnating agent and iron-chelates appear in the inventory of the waste caustic.

Accumulation of these highly reactive components that are difficult to degrade in biological treatment systems make that spent caustic is categorized hazardous waste and any disposal method must respond to relevant regulatory prescriptions. This is why majority of articles dealing with the subject start with analyzing high cost consequences associated to disposal. The actual practice of disposal of this waste is done by incineration, catalytic oxidation [6] or by deposition. The reason for temporary deposition is a hope for less expensive, affordable and environmentally more benign neutralization technique to become available. Neutralization of the highly alkaline Merox caustic is not preferred at industrial scale because of evolvement of objectionable, toxic and odiferous gases (hydrogen sulfide, mercaptanes) [7]. The former practice of dilution and discharge into the sea cannot be accepted today. Because of expenses and associated environmental impacts petroleum refineries are considering to explore wet air oxidation (WAO), that was first commercialized for the production of artificial vanilla flavoring and later for the destruction of sludge streams in paper-mill and biological treatment technologies. Today, application of WAO provided benefits in successful treatment of industrial wastes such as the caustic solution from scrubbing towers, and for treatment of powdered activated carbon [8].

Employing a proper catalyst and proper technology severity of reaction conditions can be significantly reduced to possible decomposing refractory pollutants at lower operational pressure and temperature in catalytic wet air oxidation (CWAO). There are reports, that capital and operational cost can be significantly reduced in addition to much higher oxidation efficiency in CWAO in comparison to WAO [9]. Although, because of interactions of the support of the catalyst and the caustic media it is difficult to operate the catalytic technique at industrial scale [10]. A particular problem consists in dissolving the support of aluminium-oxide that is the preferred support material of industrial catalysts. Our efforts in this field resulted in developing a novel technique for treating the said waste. It has been claimed in a submitted patent document [11] that the following range of catalytic conditions can neutralize difficult to oxidize waste streams: pressure: 10-80 bar, temperature 150-280 °C, hourly space velocity 0,4-3,6 1/h, and waste to oxygen rate: 5-500:1 (vol:vol). However, even CWAO technique benefits of pretreatment of the SMC. Our aim in the present work was to test possible treatment options that makes the neutralization treatment less challenging. A number of ideas have been considered in shaping the project, the main ideas were the followings:

a) Colloid characteristics of the waste have not been addressed before. Oprea reported, that neutralization of SMC with 10% sulfuric acid resulted in a curve that is typical to base-acid neutralization curve [12]. Our results lead to different conclusion.
b) Research conducted by Behin and Zeyghami [13] motivated our research to look for converting this waste in a co-processing scheme. The addition waste was of biomass origin. The target frame was to convert waste into commodity product and energy. Our results showed that SMC can be used in paper processing, in an industrial ecology system that produces added value in financial and environmental terms alike.
c) It has been known that the 10-35% lignin content of biomass [14] can be converted into biogas in anaerobic treatment. High organic content of the SMC oriented our attention to explore conversion of this content into renewable energy resource.
d) It has been published that CWAO improves bio-methane potential of distillery waste streams [15], but none of the above listed attempts structured and focused observations into an industrial ecology frame.

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[1] Thiols and mercaptanes are the same terms for *organosulfur compounds* that contains a carbon-bonded *sulfhydryl* (-C-SH or R-SH) group, the former name comes from Greek, the later from Roman.

e) Whatever is known about the waste streams designated for disposal, whatever is known about possible treatment options there is a need to develop a structure of industrial symbiosis. This approach, that is also referred as industrial ecology makes efforts to reduce specific consumptions and to explore byproducts as feedstocks for associated operations and this is why there is a need to assess and provide means for potential linkages [16]. The experimental work of the present article is being dedicated for possible exploration of these efforts.

2 Experimental

Materials: The SMC was provided by Danube Refinery of MOL, Százhalombatta. Chemicals used in technology exercises were of technical grade and reagent grade for analytical tests. Straw was provided by experimental station of St. Istvan University, Gödöllő. Straw stalks have been broken and crushed into pieces of 1-2 mm in average diameter by the use of a cutting mill. Characteristic properties of the SMC are given in Table 2. Chemical oxygen demand (COD) was assessed by the use of COD test mixtures and test procedure of Hach with a thermal cycler and a visible spectrophotometer according to ISO 15705:2002. BOD was tested by the use of 5 day tests in Oxytop flasks, according to MSZ EN 1899-2:2000. Sulphide constituents were quantified by ISO 10530:1992.

Neutralization: SMC waste was chemically neutralized in a beaker. Stirring was provided by a magnet stirrer. Titration curves were registered by the use of a combined pH electrode with temperature compensation. The reagent was dispensed manually, in aliquots. Temperature was maintained by placing the beaker in water bath.

Adsorption: SMC streams were percolated over a bed of adsorbent placed in elution chromatography column, made of glass, with a PTFE valve on the bottom and a feeding bulb on the top. The effluent was submitted to analysis. Commercial fuller earth, aluminum sulfate and petroleum coke were the selected adsorbents. Fuller earth and petroleum coke are present in refinery operations, while aluminium sulfate was chosen to demonstrate solubility characteristic of the SMC. Chromatography columns were filled with 20 g adsorbent. 2 l of SMC was percolated through the adsorbent bed at room temperature. pH and COD values have been recorded.

Coagulation: SMC waste was stirred in a beaker into which the coagulant was weighed on analytical balance, pH apparatus, equipped with combined pH electrode and thermometer were attached to it. Stirring was provided by a magnet stirrer at about 300 rpm. Temperature was maintained by placing the beaker in water bath. Separation was done by filtration. The filtrate was submitted to analysis.

Steam explosion: SMC waste was weighed over a weighed amount of crushed straw and magnet bar in a high pressure autoclave of 400 ml in capacity. Pressure was adjusted after the reactor was flushed two times with and pressurized to preset value by loading with nitrogen from cylinder. Time on stream was measured from the moment the temperature reached the preset value. Upon completion the preset time on stream the heat isolation jacket was removed, the reactor cooled under water flow and the pressure was released from the reactor at room temperature. The content of the reactor was transferred onto a filter. The filter cake was washed with distilled water. The liquid stream was submitted to analysis and to anaerobic digestion.

Biogas system: neutralized SMC and effluents of the above presented treatment exercises were brought to anaerobic treatment at 37 °C with or without pH adjustment and with added NPK nutrients. Facultative microorganisms were provided by the Northern-Budapest Waste Water Treatment plant. The gasometer was filled with 10% NaOH solution to read only the developed amount of methane. Some improvements to the gasometer system was also needed and executed. The completeness of CO_2 absorption by the gasometer system was confirmed by gas chromatography, by the use of a thermal conductivity detector and a short – 2m - packed (Al_2O_3) column in HP5890 system.

3 Results and Discussions

Neutralization:

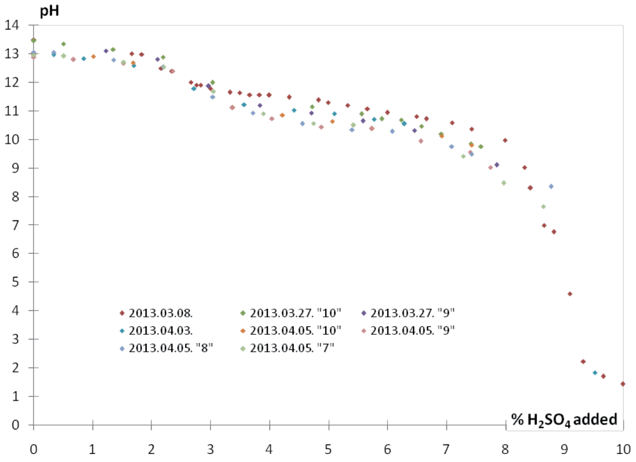

Fig. 1 Collected neutralization curves of SMC

A number of titration readings of the SMC in question with sulfuric acid have been collected in Fig. 1. Labels indicate dates of execution of the test. There is no need to perform an ANOVA analysis for obvious observations. Initial pH values of SMC are between 13 and 13,6. In contrary to findings of Oprea et al. there are two inflection points in neutralization curve. The first, at close to pH=12.5 and another, at neutralization range of pH 5. From our point of view to conclude to treatment options, the first of these inflection points is of special interest. This inflection point is sending a signal for change in colloid structure of the solution titrated. The colloid character is also indicated by the spread of neutralization points in the range of alkaline pH, even though the SMC has a clear appearance of a solution (Fig. 2). Upon completing the titration a narrow supernatant hydrocarbon layer can be distinguished that can be decanted. It revealed that the amount of this oil phase, after acidifying the waste to pH 2 was below 2%. Appearance of SMC, dilution test with water and pattern of neutralization indicated that the SMC incorporates finely dispersed organic compounds. From industrial ecology principles the following potentials are to be mentioned:

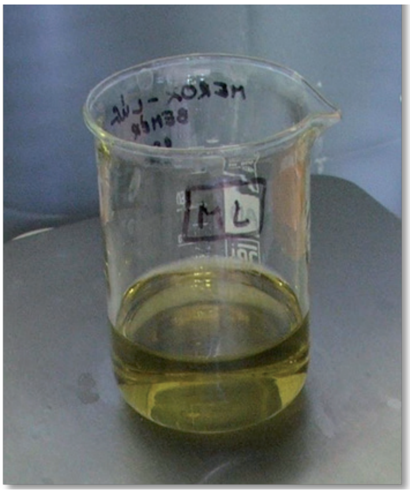

Fig. 2 SMC in a beaker appears clearly as a solution

a) The finely dispersed hydrocarbon droplets bear with energy resource potential. This can manifest either in reducing the specific energy demand in incineration or in providing nutrient for biogas producing microorganisms in anaerobic degradation;

b) It is possible that if these droplets are separated from the continuous phase, by employing a suitable physical treatment, the caustic can probably be recycled into the core process of reactive extraction;

c) It is also possible that if these droplets are separated by a suitable treatment there can be found a number of applications in which disulfides can be used as process or product additives.

The second inflection point truly responds to acid-base neutralization of the waste. In case of SMC was dumped into the pool of refinery waste water this inflection point serves to calculate the amount of acid necessary, with the conditions of not causing any harm to organisms and environment in contact with the said waste along processing and discharge.

4 Adsorption

a) Bleaching earth did efficiently reduce the content of components that contribute to COD. A COD removal efficiency of 55-60% was recorded from 114 g/l to 46 g/l. We concluded, that fuller earth can be an element to use in a complex treatment of SMC.

b) The aluminium containing adsorbent collapsed, the column was plugged as a result of dissolving into the SMC.

c) Petroleum coke did not reduce the COD value of SMC. COD values showed that there was no removal of COD components from SMC. Apolar components must have been remained as solubilized fine droplets. However, percolation with SMC presented a typical elution chromatography pattern (Fig. 3) SMC desorbed hydrocarbon layers that adhered onto the surface in petroleum coke processing. Upon completion of elution of this adhered petroleum derived layers SMC effluents showed no change in COD.

d) Neither pH values of effluents showed significant change, this proves that COD components were finely dispersed within the continuous caustic phase.

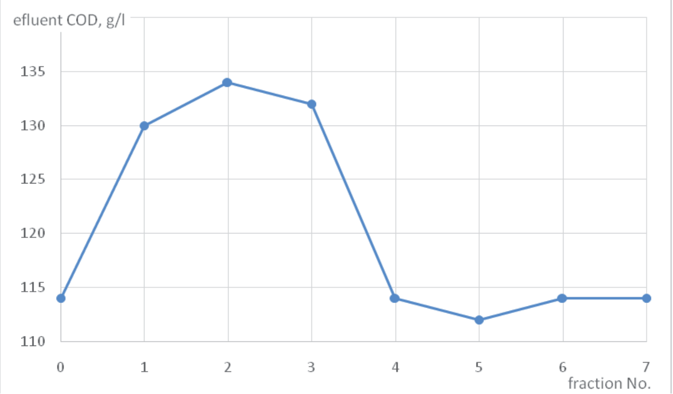

Fig. 3 COD values of petroleum coke effluent fractions

Coagulation:

Aluminium sulfate and ferric chloride were both effective in coalescing and separation of the finely dispersed droplets (Fig. 4). The amounts needed for treatment with acceptable efficiency are much too high to consider this treatment attractive.

a) Because of the short contact time coagulation experiments could have been completed with aluminium sulfate at low treatment range. The chemical collapsed at higher range, similar to what was observed along adsorption tests.

b) Ferric ions clearly showed moderate efficiency, approaching the efficiency of fuller earth at rather high rate of coagulant added.

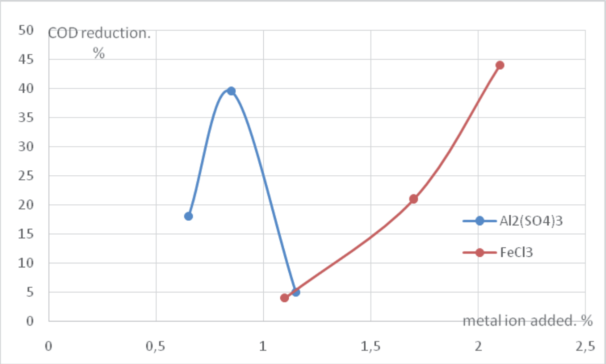

Fig. 4 COD reduction by coagulation

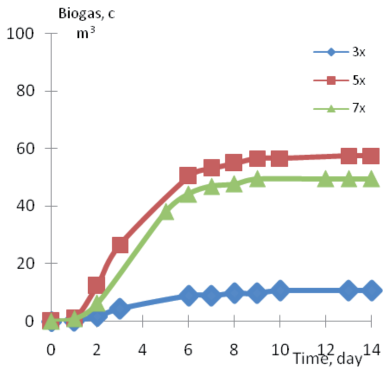

Fig. 5 Anaerobic degradation of effluent of steam explosion of 100 g straw with NaOH *(legends indicate rate of treatmentNaOH:straw, [g:g])*

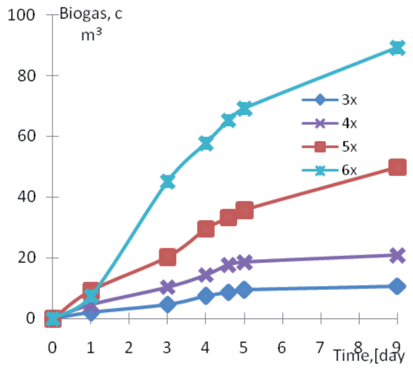

Fig. 6 Anaerobic degradation of effluent of steam explosion of 100 g straw with SMC *(legends indicate rate of treatmentSMC:straw, [g:g])*

Steam explosion and biogas processing:

Experimental data showed that alkali and COD contents of the SMC was almost halved by steam explosion treatment. This was achieved by chemical oxidation of components in the process of digestion (Table 2). The pulping process consumed significant amount of caustic reserves of the SMC. The treatment of steam explosion reduces significantly the amount of acid needed for neutralization, because of bringing the SMC to a state in which neutralization response is intensive (see also Fig. 1).

Table 2 Steam explosion of straw

rate of treatment SMC:STRAW, g:g	pH, filtrate	COD, filtrate, g/l	COD reduction, %
initial (no treatment)	13.5	170	n.a.
3	10.8	80.5	52.7
4	11.8	89.6	47.3
5	12.3	80.5	52.7
6	12.4	85.0	50

Without entering into details of processing specifics, biogas yields were significantly higher for those digestates that were pretreated with SMC, in comparison to digestates treated with NaOH. (Fig. 5 and 6). It can be concluded that

- for efficient steam explosion there is a need for a rate of NaOH:straw of 5-7 [g:g],
- the amount of components that can be anaerobically degraded originates not only in pulping of the straw. Additional amount of gas must have been formed from degradation of constituents of the SMC.
- Figures 1 and 6 have in common a pattern specific to colloid chemical response to release of dispersed droplets.

5 Conclusions

There are potential benefits in treatment of hazardous waste SMC if basic principles of industrial ecology are considered. The foreseen and recommended sequence is given in Fig. 7.

- Two waste streams were taken into consideration to get processed in a sequence to have two added value products. Net benefit of the scheme consists in biogas and cellulose products. Beside economic merits of resource management the scheme meets majority of industrial symbiosis criteria to use low value byproduct or waste output of a process to provide feedstock for a downstream process. SMC waste of petroleum refinery operation provided digestion, pulping agent for cellulose production on straw basis.

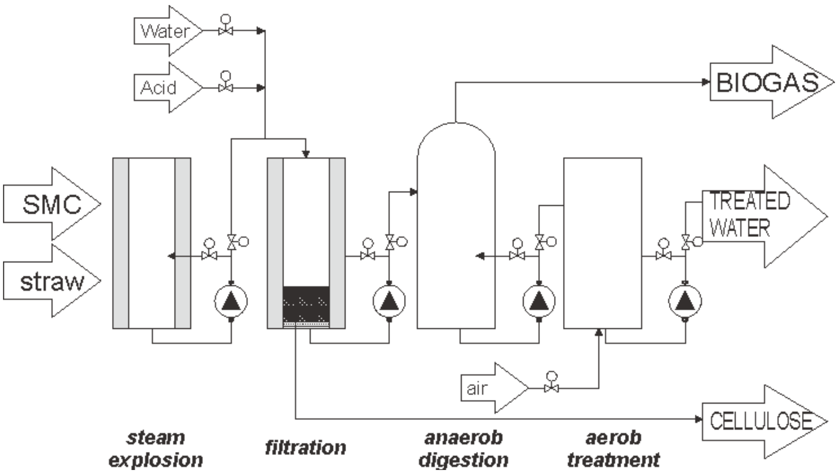

Fig. 7 Simplified SMC treatment technology

- This symbiosis resulted in synergetic improvement of process yields. With straw and neat alkali the potential of biogas was inferior to biogas yield if the symbiotic sequence.
- Activity record in biogas system provided a safe reference to downstream processing of biogas effluent. On this basis it can be expected that facultative aerobic microorganisms in waste water treatment will not be poisoned by the stream that leaves an active anaerobic microbial system.
- By treatment of straw with SMC it not only can be submitted to biological treatments, but the amount of acid necessary for neutralization can be reduced significantly.
- The solid fraction produced in digestion represent a potential and available cellulose basis for further processing.
- There are a number of perspective routes to explore for making SCM disposal more environmental benign by taking into considerations and conducting studies of the series of observations concluded in the present screening tests.

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