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Algal Lipids as Biocollector for Recovery of Coal from Fine Coal Waste by Froth Flotation

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Abstract: Raw algal lipids (RALs) and their derivatives (fatty acid methyl esters; FAMES) were investigated as biocollectors for the recovery of coal from ash-rich fine coal waste by froth flotation. Testing was done on fine coal discards from two South African sites—a high ash (50%), high sulphur (5.7%) sample and a lower ash (26%), low sulphur (0.91%) sample. The yield and recovery of combustibles on using biocollectors was similar to, or better than, with oleic acid, a polar collector demonstrated as a good collector in previous research. The RALs and FAMES reduced the ash and sulphur content of the combustible fraction of the high ash-high sulphur sample to between 23–28% and 1.9–3.3%, respectively. The chemical modification of RALs to FAMES provided potential for improving the selectivity of the recovery of combustibles. It also resulted in a change of the optimum operating pH, with RALs yielding better results at the natural pH of the sample (pH 2.7), while FAMES performed best at pH 7.

Keywords: flotation; biocollector; algae; lipids; coal; tailings; waste; valorisation

1. Introduction

At the current rate of coal extraction, South Africa generates around 60 million tonnes of coal waste annually, with over a billion tonnes of coal waste already accumulated [1]. This waste has a large footprint on land that could be used for other productive purposes. Furthermore, studies have shown that most mined coals contain pyrite as the main impurity. Coal cleaning results in a greater proportion of this impurity reporting to the waste stream, being termed discards [2–4]. For example, a study by Chugh and Behum [5] in the United States showed that some coal wastes that were produced from the cleaning process had as high as 6.85% sulphur (sulphur is a proxy for pyrite content in coal characterisation). For a coal mine in Tula, Russia, characterisation studies on the waste discards that are produced from the beneficiation process showed that there was as much as 13.5% sulphur [6]. South African coal wastes have been reported to contain sulphur, typically ranging from 2–5% [7]. Through biological and chemical activity, this pyrite is unintentionally leached over time from the deposited wastes, which results in the formation of acid mine drainage [8,9].

A two-stage desulphurisation flotation process has been developed to valorise ultrafine coal wastes [8,10]. The first stage of the flotation process, the focus of this paper, recovers clean coal from the waste while the second stage recovers pyrite into the small volume concentrate fraction, which results in a high volume, low-sulphur tailings that has reduced or no risk of acid generation; both these fractions can be re-purposed for other applications [9,11–14]. This minimises or entirely avoids the waste formation.

The addition of a collector is required for improving the coal floatability. Much research has focussed on suitable collectors for fine coal flotation [15–18]. Standard fuel oil or kerosene is the most

commonly used coal flotation reagent. For oxidised coals, which are difficult to float while using conventional non-polar reagents, like diesel, oleic acid, and biodiesel produced from waste cooking oil, have been found to be effective [14,17–20], although the results are not necessarily optimal for fine coal flotation from fine waste fractions with a high ash content. Kazadi Mbamba et al. [21] established that oleic acid (an ionic collector) in conjunction with methyl iso-butyl carbinol (MIBC) as frother was best suited for the flotation of a South African ultrafine coal waste, compared to dodecane and kerosene collectors. A techno-economic evaluation of the two-stage desulphurisation process while using this collector-frother condition showed that it was technically feasible [13,14,22]. However, the economics of the process were highly sensitive to coal prices and operating cost. The reagent costs contributed to the high cost of operation, with oleic acid contributing approximately 80% to the overall reagent cost and 36% to the total operating cost for the two-stage process. Thus, the objective of this work was to look for cost-effective alternatives to oleic acid for the first flotation stage.

Algal lipids were identified as potential replacements of oleic acid, because they have similar physical and chemical properties, which classes them as polar collectors. Microalgae have been shown to have higher oil yields (litres per acre of land) when compared to conventional oil crops, such as soya beans or corn [23], and they can accumulate higher amounts of lipids, up to 80% of their dry weight [24]. Algal lipids consist of neutral lipids (up to 97%), glycolipids (31–56%), and phospholipids (10–20%) [25,26]. Neutral lipids are made up of di- and triglycerides, sterols and sterol esters, and hydrocarbons. Triglycerides are the most abundant of the neutral lipids and they are easily extracted while using non-polar solvents, such as hexane [27]. Processes for lipid recovery from algal cultures without the need for solvent extraction are currently being investigated.

Algal lipids can be chemically modified to produce fatty acid methyl esters (FAMES) by a process that is known as transesterification. This process is currently used at an industrial scale to produce biodiesel (FAMES being the main constituent) from vegetable oils. FAMES from waste vegetable oils have been successfully used in flotation of fine coals [17,18]. However, the waste cooking oil market in South Africa is faced with challenges [28], and it is not located near the coal mining regions, leading to transportation costs. Thus, the use of raw algal lipids as the source of FAMES is more attractive.

In this paper, raw algal lipids and their derivatives are evaluated for their performance as biocollectors for the recovery of fine coal from fine coal waste by flotation and compared to traditional collector types. Further, their potential for concomitant desulphurisation is assessed.

2. Materials and Methods

2.1. Algal Cultivation

Scenedesmus sp. (University of Cape Town microalgal culture collection) was used as the source of algal lipids, because it has a relatively high lipid content (18–36% dry wt.) and productivity (36–150 mg/L/day) [29,30]. The subculturing of *Scenedesmus* sp. was done in 500 mL Erlenmeyer flasks (aerated and illuminated) for a period between 10 and 15 days before inoculating the 3.2 L batch airlift photobioreactors that were described in Langley et al. [31]. Modified 3N BBM was used as a growth medium with the nitrogen content reduced to 150 mg/L to enhance lipid productivity [32]. The photobioreactors were sparged with air enriched to 1% carbon dioxide. The reactors were maintained for at least 25 days, at the end of which the harvested algal culture was dewatered by centrifugation at 10,000× g for 15 min while using a Beckman Avanti® J-E centrifuge (Beckman Coulter, Indianapolis, IN, USA) with a JA-10 rotor.

2.2. Algae Lipid Extraction

Raw algal lipids (RALs) were extracted from the dewatered algal pastes while using the total lipid extraction method that was developed by Axelsson and Gentili [27]. Hexane-methanol at a volume ratio of 2:1 was used instead of chloroform. The hexane-methanol solution was added to the algal paste and the mixture was vigorously shaken until being well mixed. Subsequently, 0.8 vol. 0.73%

sodium chloride solution was mixed with the algal suspension in 2:1 hexane-methanol. The mixture was allowed to settle and the phases were then separated by decanting. The lipids in the hexane phase were recovered by solvent evaporation (lipids are less volatile than hexane).

A portion of the dewatered algal lipid paste was used to produce FAMES by direct transesterification. The detailed transesterification protocol is found in Griffiths et al. [33]. The transesterification process used hexane as the solvent, 0.5 N sodium hydroxide in methanol as the basic catalyst, and 5% hydrochloric acid in methanol as the acid catalyst. Deionised water was used to quench the reaction. The recovery of RALs and FAMES from the hexane solvent was achieved while using a Heidolph Hei-VAP Value rotary evaporator (Heidolph, Schwabach, Germany).

Lipid content analysis was completed while using gas chromatography (Varian 3900 GC with a flame ionisation detector, ZB-WAXplus column (30 m long, 0.25 mm thick with a 0.25 μm film thickness) (Zebron, South Africa), while using nitrogen as the carrier gas) [33,34]. Peaks on the chromatogram were identified while using Supelco 37 Component FAME and C14:0 to C22:0 FAME reference standard mixtures. The area under each peak on the chromatogram was used to quantify the identified lipids and the sum of the total area gave the total lipid content in mg/L or percentage dry-cell weight.

2.3. Waste Coal

Two samples from different geographical locations were used to assess the performance of the raw algal lipids and the fatty acid methyl acids on fine coal flotation. The first sample, which was identified as Site 1 discards, was from a site in the Waterberg area and the second sample, identified as Site 2 tailings, was sourced from a coal mine in the eMalahleni area, both being located in South Africa. The Site 1 discards represented a high-ash, high-sulphur sample with 49% ash and 5.71% total sulphur, while the Site 2 tailings contained 26% ash and 0.91% total sulphur.

Particle size reduction was done on both samples while using a laboratory scale rod mill with 10 rods ($\Phi 25 \times 288 \text{ mm}$), such that at least 75% of particles were less than 150 μm . Figure 1 shows the size distributions, determined using a Malvern Mastersizer 2000 (Malvern Instruments, Worcestershire, UK).

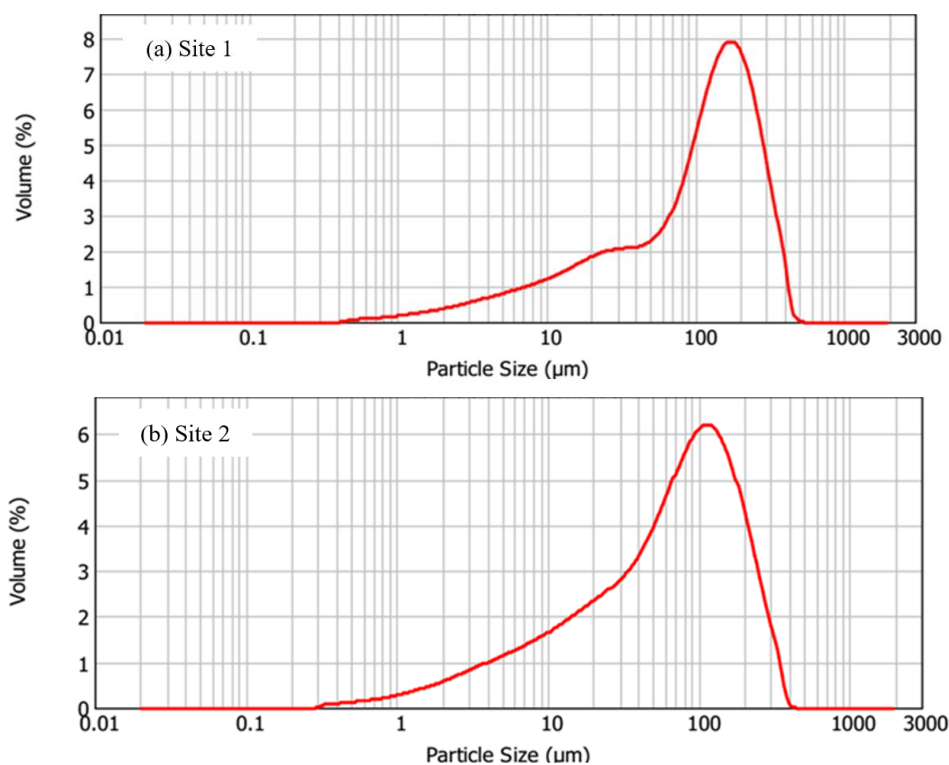


Figure 1. Particle size distributions for the (a) Site 1 sample [$d(0.1)$: 10.37 μm , $d(0.5)$: 116.47 μm , $d(0.9)$: 272.50 μm] and (b) Site 2 sample [$d(0.1)$: 6.34 μm , $d(0.5)$: 67.77 μm , $d(0.9)$: 199.37 μm].

2.4. Flotation Experiments

The flotation experiments were performed in a batch 500 mL Leeds-type sub-aerated flotation cell. The cell was charged with 34 g of solid feed to achieve 6% solids loading. The flotation cell was operated at a 5 L/min. (10 vvm) aeration rate and 170 rpm agitation speed. Following appropriate collector addition, a conditioning time of five minutes was allowed. Methyl isobutyl carbinol (MIBC) frother was then added to all of the tests at a dosage of 0.28 kg/t, with a subsequent conditioning time of one minute. A 2 mL aliquot of the feed sample was collected before the start of flotation, after which the concentrates were collected at 0.5, 1, 2, and 5 min.

The following variables were experimentally tested: Biocollector type (RALs or FAMES); biocollector concentration at fixed dosages of 1.20, 2.00, 2.79 (baseline concentration), 3.20 and 3.70 kg/t; and, pH between 2.7 (the natural pH of the coal waste sample) and 7.0. All of the flotation experiments were done in triplicate. Concentrated sodium hydroxide was titrated into the pulp until the desired pH was achieved, with a concentrated sulphuric acid being used when the pH was a point or two above the desired value, since the coal sample used for pH tests was naturally acidic. A Metrohm 704 pH meter and probe, calibrated at pH 1.0, 4.0 and 7.0 before use, was used for measurements. Concentrated solutions were used to avoid the over-dilution of the pulp. Oleic acid and dodecane were used as positive control reagents, being dosed at 2.79 kg/t [8].

The mass of each concentrate fraction was determined by filtering using standard grade qualitative filter paper of a known mass, drying at 80 °C for at least 24 h in a Memmert UM500 oven and weighing.

The combustible matter content of the feed samples, concentrates and flotation tailings was determined gravimetrically while using an ashing test. A pre-weighed 1 g sample was placed in a crucible and heated in a furnace (Carbolite High-Temperature Box Furnace) at 850 °C for a period of three hours. The ash that remained in the crucible was cooled in a desiccator and then weighed to determine the ash and combustible matter percentages of the sample.

The total sulphur of the samples was measured while using LECO analysis.

Equations (1) to (5) detail the standard performance indicators used to evaluate the fine coal collection by flotation using RALs and FAMES as biocollectors. They were determined while using the wt. % data for ash content (C_A —concentrate ash content, T_A —tails ash content, and F_A —feed ash content) and sulphur content (C_S —concentrate sulphur content and F_S —feed sulphur content).

The overall percentage yield (Y), which was equivalent to the overall percentage mass recovery, was calculated as the ratio of the total mass of the concentrate (M_C), relative to the mass of feed (M_F). The floatability of the different feed components was assessed by calculating percentage recovery of the combustibles, ash, and sulphur (R_C , R_A , and R_S) to the concentrate relative to the feed. Finally, a flotation efficiency index (FEI) was used to quantitatively describe the separation efficiency of a collector, i.e. its ability to separate the valuable material from gangue material. This was calculated as the difference between combustibles recovery and ash recovery, with alternative calculation mechanisms also given.

$$\text{Overall yield: } Y (\%) = 100 \times M_C/M_F = 100 \times (T_A - F_A)/(T_A - C_A) \quad (1)$$

$$\text{Combustibles recovery: } R_C (\%) = Y \times (100 - C_A)/(100 - F_A) \quad (2)$$

$$\text{Ash recovery: } R_A (\%) = Y \times (C_A)/(F_A) \quad (3)$$

$$\text{Sulphur recovery: } R_S (\%) = Y \times (C_S)/(F_S) \quad (4)$$

$$\text{Flotation efficiency index: FEI (\%) = } R_C - R_A \quad (5)$$

3. Results

3.1. Site 1 Sample—Flotation Results

3.1.1. Effect of Collector Type

While using the sample from Site 1, no significant difference in flotation performance was observed between RALs, FAMEs, and oleic acid with regards to overall yield and combustible matter recovery, as shown in Table 1. The two bioflotation reagents present the same collecting ability as oleic acid at the standard dosage. It is hypothesised that this similarity in performance is attributed to similarities in chemical structures. Oleic acid has a polar head ($-\text{COO}^-$) and a hydrophobic or non-polar hydrocarbon chain ($-\text{C}_{17}\text{H}_{31}$). RALs are mainly made up of triglycerides and they are non-polar and hydrophobic, even though they have polar carbonyl groups ($-\text{C}=\text{O}$). Hydrolysis of the triglycerides by transesterification produces fatty acid methyl esters that also have a polar carbonyl group easily accessible to oppositely charged polar sites on coal surfaces and a hydrophobic or non-polar tail. Dodecane, which is a non-polar collector, resulted in the lowest total mass recovery and combustibles recovery at the same dosage as oleic acid or the two bioflotation reagents under investigation. This result is in agreement with Kazadi Mbamba et al. [21] and Iroala [7], who observed that non-polar collectors require higher dosages to achieve the same yield as polar collectors.

The FEI results showed that the RALs were less efficient than FAMEs at separating the combustible material from ash material. No significant difference was observed between the FEI for the FAMEs and oleic acid. The FEI of 12.6% when dodecane was used showed that pure non-polar reagents are the least efficient at concentrating coal waste when compared to RALs (27.8%), FAMEs (31.7%) and oleic acid (34.0%).

When comparing the resultant product quality, as given in Table 2, it is seen that the lower FEI for RALs corresponds to a product of a lower quality in terms of the ash content (26.1%). This might be attributed to the fact that RALs are a mixture of lipids, with different molecular weights (saturated (C12 to C22), mono- (C17:1, C18:1 and C19:1) and poly-unsaturated lipids (C18:2 and C18:3)), with different collecting abilities. It is recognised that selectivity is a weak function of hydrocarbon chain length, while yield is a strong function of this. Hence, low molecular weight collectors, while slightly more selective, are less effective when compared to high molecular weight collectors, so their presence in RALs might reduce the overall effectiveness of the RALs as compared to use of a pure lipid collector of higher molecular weight. This is in agreement with the discussion by Han [35], where higher yields are obtained, without compromising the selectivity, when higher molecular weight collectors are used. The product quality that was obtained while using FAMEs was equivalent to that obtained using oleic acid ($24.1 \pm 0.1\%$ ash for FAMEs and $23.5 \pm 0.7\%$ ash for oleic acid). The dodecane results confirmed that purely non-polar reagents are not suitable for enhancing the flotation separation of particles that do not have great natural hydrophobicity, which is typical of coal waste [19,20].

Table 1. Performance results from Site 1 batch flotation experiments using raw algal lipids (RALs) and fatty acid methyl esters (FAMEs) compared to oleic acid and dodecane controls at a fixed dosage of 2.79 kg/t and at pH 2.7.

Collector Type	Overall Yield (%)	Combustibles Recovery (%)	Ash Recovery (%)	Sulphur Recovery (%)	Flotation Efficiency Index (%)
RALs	34.1 ± 1.2	47.1 ± 1.6	19.2 ± 0.7	25.3 ± 3.4	27.8 ± 1.8
FAMEs	35.3 ± 0.7	50.3 ± 1.4	18.4 ± 0.6	24.1 ± 2.4	31.7 ± 1.6
Oleic Acid	34.3 ± 0.6	50.7 ± 1.2	16.7 ± 0.6	18.9 ± 1.7	34.0 ± 1.3
Dodecane	15.4 ± 0.1	21.4 ± 0.2	8.8 ± 0.1	11.1 ± 0.6	12.6 ± 0.3

Table 2. Quality of coal recovered from Site 1 discards using RALs and FAMEs when compared to oleic acid and dodecane controls at a fixed dosage of 2.79 kg/t and at pH 2.7.

Collector Type	Ash Content (%)	Sulphur Content (%)
(Feed)	(49.0)	(5.71)
RALs	26.1 ± 0.3	2.6 ± 0.3
FAMEs	24.1 ± 0.1	2.8 ± 0.3
Oleic Acid	23.5 ± 0.7	2.4 ± 0.2
Dodecane	27.0 ± 0.3	2.6 ± 0.1

3.1.2. Effect of Collector Dosage

Increasing the biocollector dosage was shown to result in an increase in the overall yield (overall mass recovery) and combustibles recovery (Figure 2). It was also observed that increasing the biocollector dosage did not have a significant effect on the product ash content. The slight increase in product ash content could have been due to the increased flotation of material with a low degree of liberation between the combustible material and ash material or to the increased entrainment of ash-bearing materials.

When comparing performance across collectors presented in Figure 2, FAMEs as biocollector gave consistently better yield and combustibles recovery than RALs, especially at lower reagent concentrations. FAMEs resulted in a product with lower ash content than that obtained while using RALs at the same dosages. For example, at a dosage of 1.20 kg/t RALs lipids produced a product with an ash content of 25.3%, while FAMEs gave a product with an ash content of 23.1% at the same dosage.

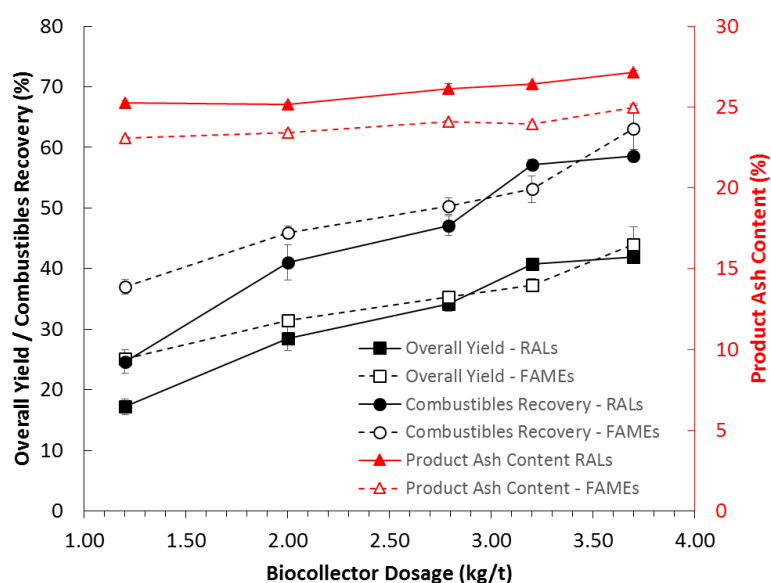


Figure 2. Overall yield, combustibles recovery and product ash content for Site 1 flotation experiments as a function of RAL and FAME dosage at pH 2.7.

Figure 3 shows the calculated FEI values that were achieved while using RALs and FAMEs at different dosages. For RALs, the FEI increased as the reagent dosage was increased from 1.20 kg/t to 3.20 kg/t. A further increase of the RAL dosage to 3.70 kg/t did not significantly increase the separation efficiency. For FAMEs, the FEI increased throughout the whole range of biocollector dosages tested. When comparing the biocollectors, FAMEs and RALs gave similar FEI values with FAMEs showing potential for slightly improved FEI, except at 3.20 kg/t. However, RALs resulted in a product with a higher ash content at this dosage when compared to that obtained while using FAMEs.

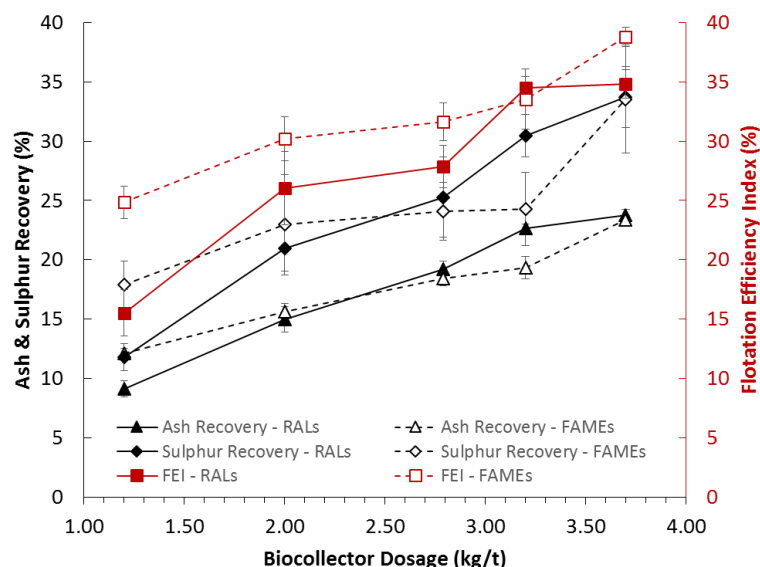


Figure 3. Ash recovery, sulphur recovery and FEI for Site 1 flotation experiments as a function of RAL and FAME dosage at pH 2.7.

3.1.3. Effect of pH

Figure 4 shows the overall yield on varying the flotation pH between 2.7 to 7.0. The best yield was achieved at pH 4.0 for RALs, FAMEs, and oleic acid and at pH 7.0 for dodecane. The behaviour of oleic acid at different pH conditions has been extensively reported in literature [36–39]. At a pH near the pKa (4.8 for the carboxylic group), there is an equal concentration of the protonated and deprotonated form of the oleic acid [36]. Deprotonation is enhanced at a pH below the pKa, while increasing the pH beyond the pKa results in the protonation of all available deprotonated molecules, which results in the formation of lamellar or liquid-crystalline aggregates. Similarly, for the coal surface, there is a pH at which a balanced concentration of protonated and deprotonated coal particles is found. At this pH, flotation is optimum [40]. At pH 4.0, there is anticipated to be a higher concentration of deprotonated carboxylic groups, which easily hydrogen bond or associate with oppositely charged groups on coal surface particles by Van der Waals forces, hence the high yield that is observed in Figure 4. The decrease in performance above pH 4 could be due to one or both of two reasons. Firstly, the lamellar or liquid-crystalline aggregates that formed at higher pH results in a fewer molecules available for easy attachment to coal surface particles, which results in a drop in yield as the pH is increased beyond 4.0. Secondly, an increase in pH was shown to result in the precipitation of iron ions on coal particle surfaces [40]. This precipitation has a depressing effect on coal flotation, without affecting selectivity. The same response observed in oleic acid flotation tests is expected since FAMEs are a mixture of fatty acids of different chain lengths.

Dodecane, which is a low molecular weight non-ionic collector, is not affected by pH, hence the performance that is observed in Figure 4 is only due to the effect of pH on the coal sample. Increasing pH results in an accumulation of protons on the coal particles surface, decreasing the electrical charge (coal particles become more hydrophobic as pH increases). This causes more hydrophobic interactions between the coal particles and the dodecane molecules, which results in an increase in yield as more hydrophobic coal particles becomes available.

The trend for combustibles recovery (Figure 5) followed that of overall yield across all of the pH values tested. The bioflotation reagents outperformed oleic acid at pH 4.0. Further, good flotation performance in terms of both yield and recovery of combustibles was maintained with FAMEs across the pH range 4.0 to 6.0, whereas, with RALs and oleic acid, the yield decreased some 50% on increasing pH from 4.0 to 6.0. The FEI results given in Figure 6 confirm the flotation performance. It was observed that pH had no statistically significant effect on the product ash content for all of the reagents tested

(Figure 7a), but significantly affected the product sulphur content (Figure 7b). Figure 7b shows that the best pH with respect to sulphur content reduction was 2.7 for RALs and 7.0 for FAMEs.

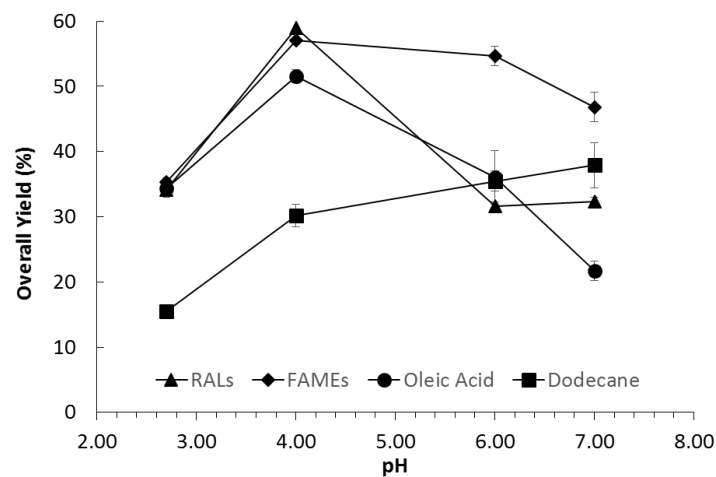


Figure 4. Overall yield as a function of pH for RALs, FAMEs, oleic acid, and dodecane collectors at a fixed dosage of 2.79 kg/t.

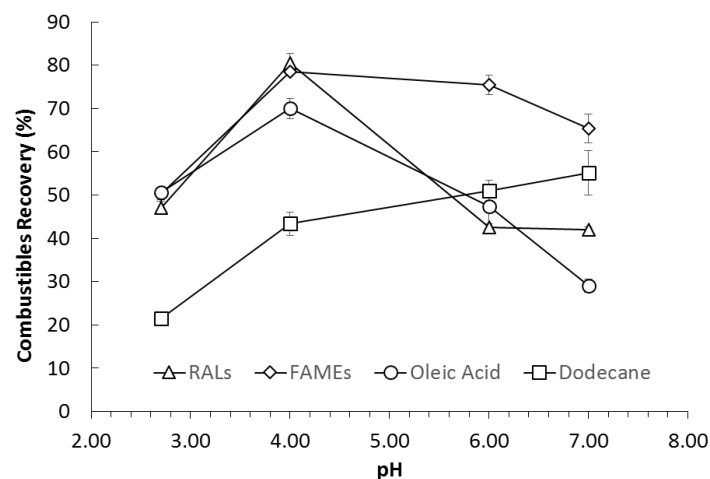


Figure 5. Combustibles recovery as a function of pH for RALs, FAMEs, oleic acid, and dodecane collectors at a fixed dosage of 2.79 kg/t.

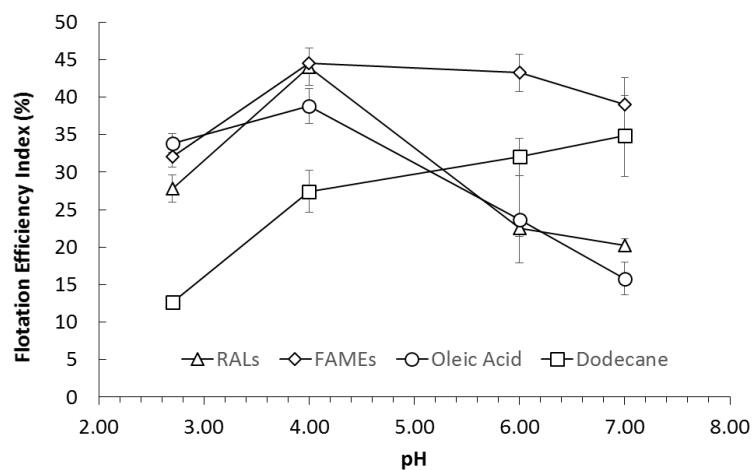


Figure 6. FEI as a function of pH for RALs, FAMEs, oleic acid, and dodecane collectors at a fixed dosage of 2.79 kg/t.

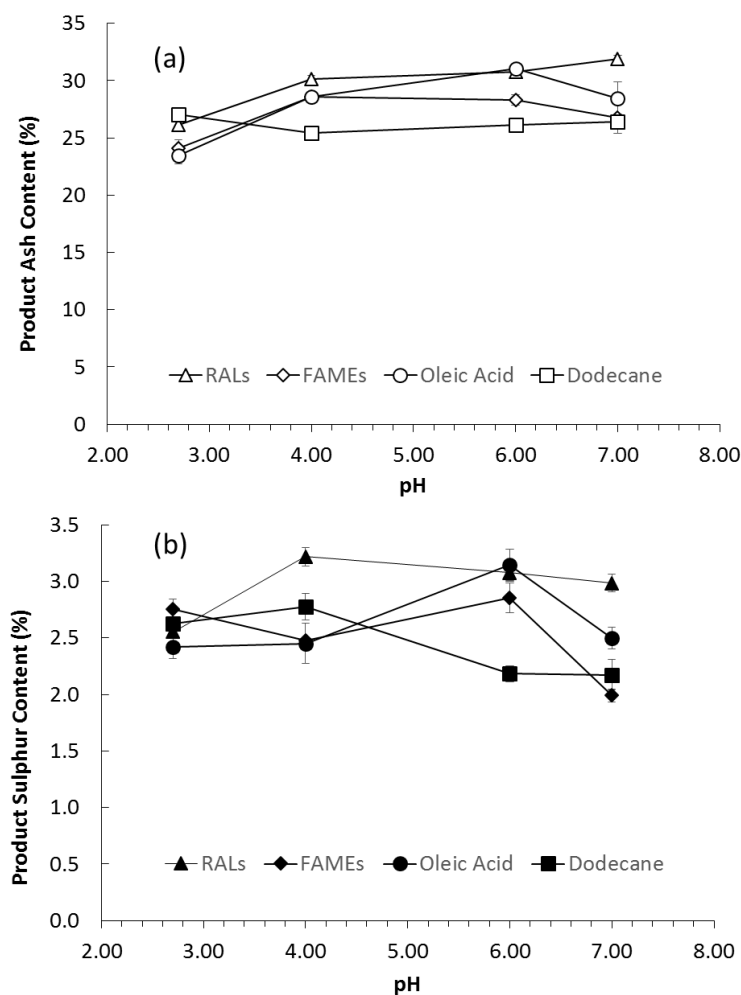


Figure 7. The (a) ash and (b) sulphur content of the product obtained using RALs, FAMEs, oleic acid, and dodecane collectors at a fixed dosage of 2.79 kg/t.

It was observed that the best operating pH for RALs was 2.7 while taking all of the performance indicators into account (the natural of the sample), as this gave the cleanest product with respect to sulphur content, while pH 7.0 was found to be the best operating pH for FAMEs, based on the same reason.

3.2. Site 2 Sample—Flotation Results

3.2.1. Effect of Collector Type

Tables 3 and 4 show the results of the Site 2 tailings flotation analyses. The Site 2 tailings, which were low in ash and sulphur when compared to the Site 1 discards, gave a significantly higher overall yield (Table 3) than the Site 1 flotation tests (Table 1). This is in agreement with the observations presented by Han [35], in which the high ash content, associated with high pyrite content, resulted in low floatability of coal, owing to hydrophilic gangue material. The biocollectors performed significantly better when compared to oleic acid and dodecane at the same fixed dosage of 2.79 kg/t. Thus the data show that biocollector performance is strongly dependent on coal waste type. However, ash recovery and, thus, resultant ash content of the product was higher while using the biocollectors than for oleic acid, which resulted in a lower FEI for the biocollectors (Table 3) and limited improvement in coal quality in the concentrate (Table 4).

Table 3. Performance results from Site 2 batch flotation experiments using RALs and FAMEs compared to oleic acid and dodecane controls at a fixed dosage of 2.79 kg/t and at pH 2.7.

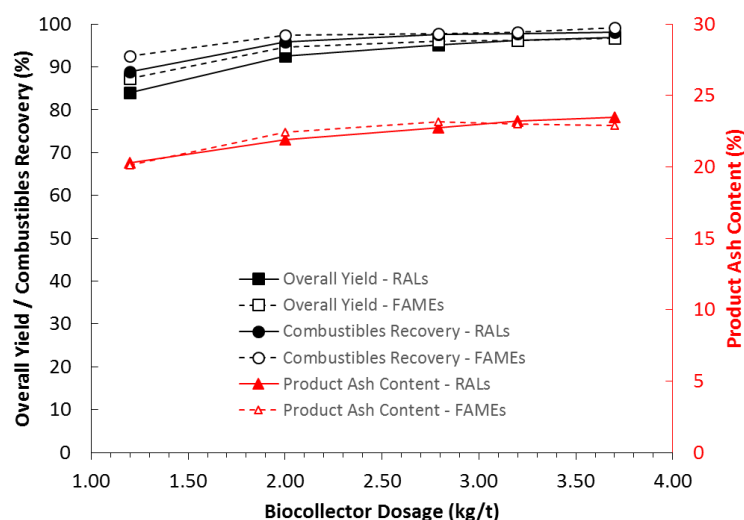
Collector Type	Overall Yield (%)	Combustibles Recovery (%)	Ash Recovery (%)	Sulphur Recovery (%)	Flotation Efficiency Index (%)
RALs	95.2 ± 0.1	97.6 ± 0.2	87.8 ± 0.4	86.7 ± 5.3	9.8 ± 0.5
FAMEs	96.0 ± 0.1	97.8 ± 0.2	90.3 ± 0.4	97.7 ± 5.3	7.5 ± 0.01
Oleic Acid	86.2 ± 0.3	91.0 ± 0.3	71.3 ± 0.4	73.5 ± 11.1	19.7 ± 0.01
Dodecane	61.7 ± 0.9	68.9 ± 1.1	40.0 ± 1.2	-	28.9 ± 0.03

Table 4. Quality of coal recovered from Site 2 tailings using RALs and FAMEs compared to oleic acid and dodecane controls at a fixed dosage of 2.79 kg/t and at pH 2.7.

Collector Type	Ash Content (%)	Sulphur Content (%)
(Feed)	(26)	(0.91)
RALs	22.8 ± 0.1	0.8 ± 0.04
FAMEs	23.2 ± 0.1	0.7 ± 0.04
Oleic Acid	20.2 ± 0.1	0.7 ± 0.05
Dodecane	16.1 ± 0.4	-

3.2.2. Effect of Collector Dosage

Increasing the biocollector dosage beyond 2.79 kg/t did not significantly increase the yield for the Site 2 tailings (Figure 8). At biocollector dosages of 1.20 and 2.00 kg/t, FAMEs outperformed RALs by 3.3% and 2.1% in overall yield, respectively. The best biocollector dosage was in the 1.2 to 2.79 kg/t range on the basis of overall yield and product ash content.

**Figure 8.** Overall yield, combustibles recovery and product ash content for Site 2 flotation experiments as a function of biocollector dosage at pH 2.7.

However, the FEI significantly decreased as biocollector dosage increased from 1.20 kg/t to 3.70 kg/t (Figure 9). Thus, the biocollectors became less selective for the combustible fraction with increasing collector dosage. This is likely because the combustibles recovery was already very high at low dosages (>90%), such that more of the gangue material was floated with increasing collector. The FEI trend for the Site 2 tailings flotation experiments was, thus, opposite to the Site 1 discards flotation experiments. For RALs, the FEI reached its minimum at a biocollector dosage of 3.70 kg/t while the minimum FEI for FAMEs was reached at 2.79 kg/t. In both cases, the maximum FEI was at a collector dosage of 1.20 kg/t, suggesting this as the maximum collector dosage to be used, owing to the small impact of increased collector on combustibles recovery, but large impact on ash and sulphur recovery.

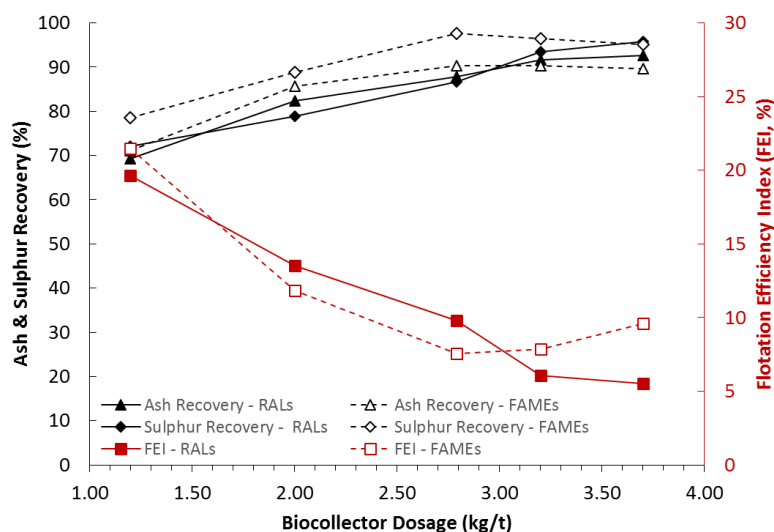


Figure 9. Ash recovery, sulphur recovery and FEI for Site 2 flotation experiments as a function of biocollector dosage at pH 2.7.

Figure 10 shows the ash and sulphur content of the concentrates. The ash content of the concentrate floated with the RAL and FAMEs was significantly higher than that recovered in the control experiments, an undesirable result. The product sulphur content was found to be independent of the biocollector dosage.

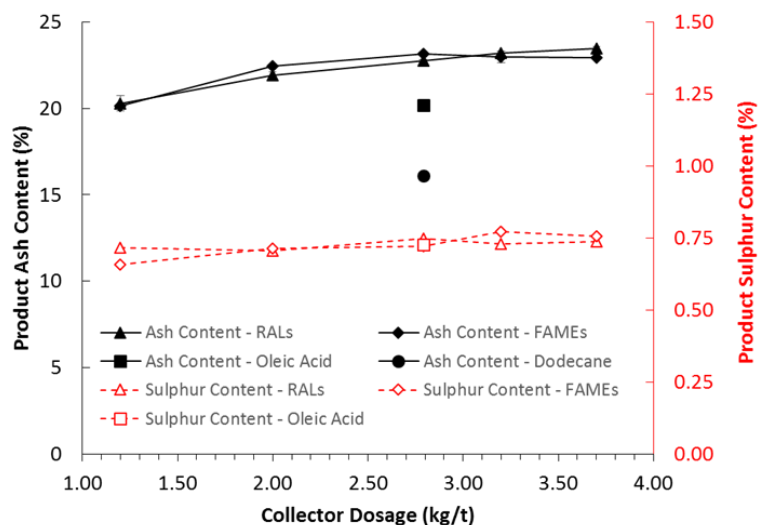


Figure 10. Site 2 flotation experiment product ash and sulphur content using RALs and FAMEs compared to oleic acid and dodecane controls at a fixed dosage of 2.79 kg/t.

4. Conclusions

Raw algal lipids proved to be a good biocollector for the flotation of both high-ash, high-sulphur and low-ash, low-sulphur fine coal waste from two different geographical locations in South Africa. Their performance matched that of oleic acid, which has been demonstrated to be a suitable collector in the desulphurisation of fine coal waste by froth flotation. Chemical modification of the raw algal lipids to fatty acid methyl esters showed the potential to improve specificity as a collector, as exemplified by the flotation efficiency index.

Bioflotation reagents both successfully reduced the ash content of the Site 1 discards from 49% to below 28%, with the lowest recorded ash content at about 23% while using FAMEs. The ash content of the Site 2 tailings was reduced from 26% to below 23%, with the lowest recorded ash content of 21%. The recovered product sulphur content was reduced from 5.7% to between 1.9% and 3.3% for the

feed for Site 1 tailings and from 0.9% to 0.7% and 0.8% for Site 2 tailings. These results show how the performance is dependent on both collector and specific coal waste.

The choice of best flotation conditions for the Site 1 tailings (high ash, high sulphur) requires a trade-off between higher overall yield, combustibles recovery and FEI (whose trends corresponded), and maximum permissible ash or sulphur content in the final product. For example, the best FEI while using RALs was found at pH 4.0, but the lowest ash and sulphur recovery values occurred at pH 2.7. For waste coals similar to Site 2 tailings (relatively low ash, low sulphur) where high combustible recovery is achieved at low collector dosages and decreasing FEI found with increasing biocollector dosage, use of the lowest dosage that maintains a reasonable combustibles recovery is recommended to maximise product quality.

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