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Evaluation of different microwave-assisted dilute acid extracting reagents on simultaneous coal desulphurization and demineralization

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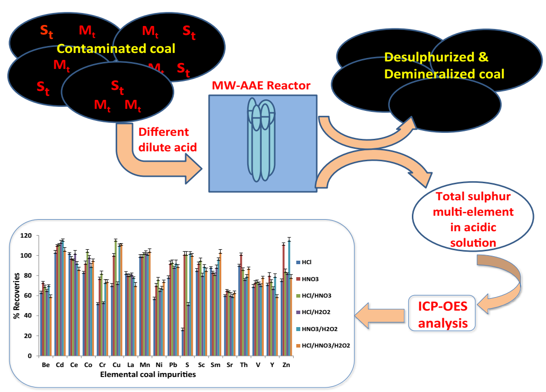
HIGHLIGHTS

- The method is rapid and cost-effective (dilute acids were used).
- The leachate solutions were easily analysed by ICP–OES for 18 multi-element.
- CHNS & ICP–OES results of HNO_3–H_2O_2 treated coal revealed sufficient coal desulphurization (102%).
- The HNO_3–H_2O_2 was selected as the potential extractant for the proposed MW-ADAE method.

GRAPHICAL ABSTRACT



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ABSTRACT

Coal combustion is one of the largest anthropogenic contributors to SO_x and some other volatile elemental emissions to the atmosphere. Therefore, the current study investigated the effect of different dilute acidic reagents (HCl, HNO_3, HCl–HNO_3, HCl–H_2O_2, HNO_3–H_2O_2 and HCl–HNO_3–H_2O_2) on simultaneous coal demineralization and desulphurization under microwave irradiation. The applied conditions for microwave-assisted dilute acid extraction (MW-ADAE) process were as follows: 180 °C, 5 min, 3 mol L^{-1}, 3 mol L^{-1}, 0.1 g and 2:1 for microwave temperature, extraction time, acid concentration, [H_2O_2], coal amount and acid-hydrogen peroxide volume ratios, respectively. The leachate solutions obtained from the MW-ADAE process were then analysed by using ICP–OES for multi-element determination. The ICP–OES analysis was performed in order to investigate the acidic reagent that resulted in highest extraction recoveries of the examined multi-element. All extracting reagents that contained HNO_3 showed accepted extraction efficiencies ($\% R \geqslant 80\%$) as indicated by the ICP–OES results. The proposed MW-ADAE procedure with HNO_3–H_2O_2 reagent showed excellent desulphurization efficiency parallel to the other literature reported methods. The raw and acid treated coals were then characterized by Elemental analyser (CHNS), FT-IR, SEM, P-XRD and TGA to examine the influence of different acids on the coal structure. The FT-IR, SEM and P-XRD results showed insignificant changes throughout all the studied acidic reagents. However, the CHNS results of HNO_3–H_2O_2 treated coal revealed sufficient coal desulphurization as compared to the other investigated acids. Alternatively, thermal studies of raw coal (A) showed high quantity of unburned mineral matter. In addition, most of the acid treated coals such as B (HCl), C (HNO_3), E (HCl–H_2O_2 and F (HNO_3–H_2O_2) indicated moderate removal of mineral matter while aqua-regia

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based extracting reagents (G (HCl–HNO_3–H_2O_2) and D (HCl–HNO_3)) caused drastic extraction of both carbon and mineral content. Therefore, the mixture of HNO_3–H_2O_2 was selected as the potential extracting reagent for the proposed simultaneous coal desulphurization and demineralization process as it showed moderate attack on the carbon content of the coal and sufficient desulphurization (102%) and demineralization (70–115%).

1. Introduction

Coal is the most abundant fossil fuel world-wide and it consists of many impurities. The latter include sulphur (sulphate, sulphide and organosulphur compounds) and mineral matter [1,2]. Coal impurities cannot be controlled or prevented as they occur naturally during coal genesis under a long period of microbiological and geological processes [2]. Therefore, the growth of coal utilization is limited by the liberation of sulphur and other elemental emissions to the atmosphere. For example, during coal combustion processes, sulphur participate in several reactions and is emitted from the coal framework mainly as SO_2 and SO_3 gases, while, coal gasification processes liberate sulphur as H_2S, CS_2 and COS gases [3–5]. The emission of S from anthropogenic sources has been related to the depletion of the Earth's ozone layer, acid rain incidence and chronic respiratory diseases [6,7]. Additionally, some of the multi-element in coal might be trapped inside the combustion boilers causing slagging, abrasion and fouling. Recently, the world is moving towards the implementation of renewable energy technologies (biomass, solar, wind and geothermal). However, in South Africa there is no evidence of commercially-viable alternatives that have been developed to significantly substitute fossil fuels such as coal [8,9]. Hence, coal still stands as the most trustworthy and sustainable energy with cost effective electricity generation. Therefore, the developments of more efficient, cost-effective, environmentally friendly and rapid methods are urgently required for coal purification to improve coal processing technologies.

Developments on removal of sulphur (desulphurization) and mineral matter (demineralization) from coal have been frequently practiced since the first coal mining sector [10–14]. However, most of these coal desulphurization and mineralization procedures have not reached widespread commercialization. The reason being, some of these methods have high cost, uncontrollable waste production, high complexity, tedious and environmentally unfriendly. Among all the developed coal desulphurization and demineralization methods, chemical leaching is well-established and it shows potential for industrial commercialization [15,16]. Recently, Hernandez and co-workers reported coal demineralization using organic solvents [17]. The latter are known to be environmentally unfriendly as they are carcinogenic agents; therefore, the study reported by Hernandez does not have potential of being industrial commercialized. Microbiological chemical leaching (MBCL) methods are also reported in literature [18,19] and are promising in terms of coal purification from an environmental point of view. However, MBCL methods are tedious and not so feasible for an industrial large scale purpose. Same applies to alkaline based extraction methods; they are reported as environmentally friendly but also cause a lot of waste which increase the overall costs of the method. For example, Wang et al. reported the utilization of $Ca(OH)_2$ followed by HCl for demineralization of Australian coals [10]. This method introduces more calcium to the coal which might cause slugging and fouling in the combustion reactors. To overcome challenges introduced by the utilization of $Ca(OH)_2$, Mukherjee and Borthakur investigated the use of KOH and HCl for simultaneous desulphurization and demineralization of Indian coal [11]. The same research group examined the desulphurization and demineralization of Indian coal using NaOH, KOH and mixed alkaline (KOH–NaOH) [13]. Recently, Saikia and co-workers presented ultrasonic-assisted extraction of sulphur and mineral matter in coal samples based on the use of aqueous mixed alkali media (1:1 KOH and NaOH) for industrial applications [20]. However, there are few attempts on coal purification using acidic reagents. Relay et al. reported a leaching process for coal desulphurization using 2 M HNO_3 followed by ICP–OES analysis to examine extraction efficiency of total sulphur [21]. Only 79% of total sulphur was extracted from coal. In 2011, Ambedkar and co-workers investigated the use of 2 M HNO_3–H_2O_2 for coal desulphurization and extraction efficiency of 87% was obtained under ultrasound assisted extraction [22]. Various acidic mixtures have been extensively studied for extraction of different elements in solid matrices [23–25]. Therefore, the current study aimed at evaluating the effect of different dilute acids (HCl, HNO_3, HCl–HNO_3, HCl–H_2O_2, HNO_3–H_2O_2 and HCl–HNO_3–H_2O_2) on simultaneous coal desulphurization and demineralization based on the use of microwave-assisted extraction followed by ICP–OES analysis. Subsequently, acid treated coal residues will be characterized (FT-IR, SEM, TGA, P-XRD and CHNS) to examine the influence of different extracting reagents on the coal structure. It is worth to mansion that, coal CRM (SARM 20) will be used throughout the study investigations.

2. Experimental section

2.1. Materials and methods

All chemical reagents used in the current study were of standard analytical grade and were utilized without any additional purification. Hydrogen peroxide (H_2O_2:30%) and nitric acid (HNO_3:65%) purchased from Sigma–Aldrich (Spruce St. Loius, MO, USA) were of Suprapur grade. Coal certified reference material (SARM 20) with particle size of $\leqslant$106 μm was obtained from Mintek (Randburg, RSA) and sampled from SASOLBURG with sulphur content of 0.51% (w/w). In order to minimize the risk of cross-contamination, all vessel materials were socked in HNO_3 solution (5 M) for a minimum of 24 h, thoroughly rinsed with Milli-Q water and then dried in the oven (Scientific series 2000, Lasec RSA) before use. The coal CRM was stored in a desiccator to prevent hygroscopicity.

The external aqueous calibration standards for ICP–OES sulphur analysis contained a known concentration of the target analyte (S) and were prepared by diluting standard certified elemental solution (10,031 mg L^{-1} total sulphur) to get the total sulphur concentration levels of 1, 3, 9, 12, 15, and 20 mg L^{-1}. External calibration method for ICP–OES multi-element analysis was performed by diluting commercially available 1000 mg L^{-1} stock solutions of Be, Cd, Ce, Co, Cr, Cu, La, Mn, Ni, Pb, Sc, Sm, Sr, Th, V, Y and Zn to two ranges (0.05–1 and 5–60 mg L^{-1}) of calibration standards. Two calibration standards were used for multi-element analysis due to different concentration levels of the elements in the coal CRM. Both sulphur and multi-element stock standard solutions