

Enrichment of Indonesian Low Rank Coal'S Surface Oxygen Compounds (SOCs) Using Hydrogen Peroxide and Its Adsorptive Properties

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Abstract. Cheap and highly abundant low rank coal from Banten, West Java, Indonesia, was utilized as an adsorbent for a cationic dye. The previous reports show that raw low rank coal has low adsorption capacity when compared to activated carbon. It is also indicated that the coal's surface oxygen compounds played a major role in the adsorption mechanism. This research aimed to enrich the oxygen compounds on the coal's surface by a straightforward oxidation process using hydrogen peroxide and to investigate the adsorption capacities of raw and treated coals using cationic dye solutions. The oxidation process was conducted by adding the raw coal in hydrogen peroxide solutions having concentrations of 5%, 10%, and 20%, followed by stirring for 10 minutes to 60 minutes. After a serial of washing processes and air-drying, the adsorption capacities of the treated coals for a cationic dye were investigated using batch tests. The batch tests were conducted by adding 0.1 to 0.3 g of coals to 50 mL of methylene blue solutions followed by stirring the solutions for 5 hours. The experimental data were plotted using Langmuir adsorption isotherm model. The adsorption capacity of a treated coal when plotted using Langmuir isotherm was found to be 103 mg/g, significantly higher than that of the raw coal, which was only 52 mg/g. The FTIR spectra showed new absorption of carboxylates at 1700 cm^{-1} indicating increases in the oxygen containing groups, whilst the surface area measurement indicated an increase in surface area from $0.097\text{ m}^2/\text{g}$ to $0.232\text{ m}^2/\text{g}$. It is concluded that the treatment using hydrogen peroxide solution has significantly improved the surface oxygen compounds of the low rank coal, increased its surface area and also its adsorption capacity for a cationic dye.

Introduction

Due to their high surface area, microporous structure and high degree of surface reactivity, activated carbons have been the most used adsorbents in water treatment processes. Activated carbons are commonly utilized in purification, decolorisation, deodorisation, dechlorination and separation processes. However, the increasing price of activated carbons and the difficulty in regenerating used activated carbons have become major problems for their application [1]. In the search for alternative adsorbents, numerous naturally occurring materials have been investigated. These materials include various kinds of fly ash [2], chitosan [3], raw and modified zeolites [4], and low rank coal (brown coal) [5].

Deposit of low rank coal in many parts of the world is exceptionally large [6] and this has become the basis for low rank coal application as fuel. Being a plentiful, inexpensive and locally available material, other applications of low rank coal are explored. Currently, low rank coal from many parts of the world has been used as adsorbent for heavy metal and organics [7], and has been applied in wastewater treatment processes [8].

The oxygen containing groups are considered as the active sites that provide the ion exchange capability of low rank coal, hence augmenting its ability to adsorb cationic species in aqueous solution [9]. Therefore, this research aimed to enrich these oxygen compounds on the coal's surface via a straightforward oxidation process using hydrogen peroxide. Both treated and untreated low rank coals were then analyzed for their adsorptive properties toward a cationic dye via batch experiments. The Langmuir isotherm model was utilized to plots the experimental data

achieved. The adsorption capacities of the treated coals were then compared to that of the raw low rank coal.

Experimental

Oxidation of Low rank coal. Two grams of low rank coal originated from Banten, West Java, Indonesia, were added to 50 mL of H₂O₂ solution. To investigate the effect of H₂O₂ concentration, various H₂O₂ solutions having concentrations of 5% (v/v), 10% (v/v), and 20% (v/v) were used. The mixtures were stirred for 10 minutes to 60 minutes. The mixtures were then filtered and air-dried. Raw and treated low rank coals were analyzed using elemental analysis (CHONS), FTIR and surface area. The elemental analysis of the coals before and after treatment was provided in Table 1.

Table 1. Elemental analysis of low rank coal before and after treatment

| Property | Raw coal | Treated Coal (20% of H ₂ O ₂) |
|---|----------|---|
| Calorific value (cal/g) | 4,954 | 4,898 |
| Ash (%) | 5,59 | 4,38 |
| Carbon (%) | 55,07 | 55,18 |
| Hydrogen (%) | 5,68 | 5,43 |
| Oxygen (%) | 31,34 | 32,71 |
| Nitrogen (%) | 0,92 | 0,91 |
| Sulphur (%) | 1,40 | 1,39 |
| Surface area (BET, N ₂) (m ² /g) | 0,097 | 0,232 |

Batch Adsorption . Known amount of adsorbents were added to methylene blue solutions in a 100 mL Erlenmeyer flask and were shaken for 5h. The aqueous phase was passed through a filter and was analyzed for residual concentration of dye using a UV/VIS spectrometer at 665 nm. The absorbance measured using spectrometer was converted to concentration using linear calibration curve built for methylene blue (the calibration curve not shown)

Results and discussion

Oxidation of Low rank coal. The oxidation processes using various concentrations of H₂O₂ solutions yielded low rank coals with darker color compare to that before oxidation. The filtrate produced upon oxidation had yellow colour. The higher the concentration of H₂O₂ solution used, the resulted filtrate solution was becoming darker yellow. This indicated a more severe organic leaching; presumably lignin compounds predominated from the coal structure. However, from the CHONS analysis (Table 1), the decrease of carbon content from the oxidized coal was not observed. This was probably due to the simultaneous leaching of inorganics and other contaminants from the coal structure that compensated the percentage of organic being leached.

Additionally, the oxidised coal has higher surface are than the raw one (Table 1). This was probably due to the change in the coals' surface structure as a result of oxidation. The oxidation of the coal using hydrogen peroxide solution caused the organic and inorganic leaching and presumably alter the surface structure of the coal. The increase in surface area may positively contribute to the adsorption capacity of the treated coal.

As expected, the oxidation process improved the oxygen content of the low rank coal (Table 1). To investigate the nature of oxygen compounds promoted upon oxidation, the FTIR analysis was conducted (Fig. 1). The FTIR spectra clearly indicated the increase in carboxylic acid groups supported by the increases in the absorption at 1750 cm⁻¹ (C=O), 1250 cm⁻¹ (C-O) and 3400 cm⁻¹

(O-H). It is also evident that the oxidation also promoted the formation of alkenes groups as indicated by the absorption at 1680 (-C=C-).

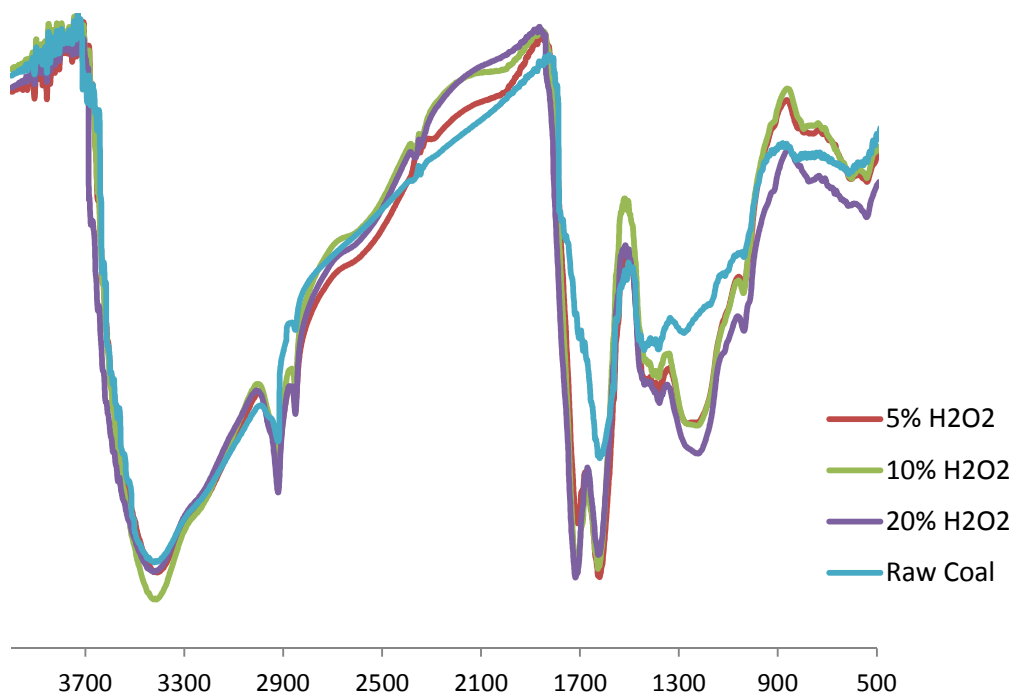


Fig. 1. FTIR Spectra of raw and treated low rank coal

Adsorption capacity. The adsorption capacities of treated low rank coals were calculated using Langmuir isotherm adsorption model. The result is tabulated in Table 2. Oxidation of the coal was able to significantly increase its adsorption capacity. The more concentrated the hydrogen peroxide used, the increment of the adsorption capacity was more evident. In addition to the increment of surface area that directly related to adsorption capacity of the coal, increases in the oxygen containing groups of the treated coals seemed to enhance the reactivity of the coals' surface to interact with the cationic dye molecules, possibly via a cation exchange mechanism (Eq.1). Additionally, the R^2 values showed that the data fits the Langmuir isotherm, hence the monolayer interaction between the adsorbent and the adsorbate was indicated. This result also supported the cation exchange mechanism in the adsorption processes since this mechanism required a monolayer interaction [8,9].



Table 2. Langmuir isotherm constants of raw and treated coals

| Adsorbent | Isotherm Langmuir | | |
|-------------------------------------|-------------------|-----------|-------|
| | q_m (mg/g) | K_{ads} | R^2 |
| Raw low rank coal | 52 | 0.9 | 0.92 |
| Treated, 5% H_2O_2 | 62 | 0.4 | 0.99 |
| Treated, 10% H_2O_2 | 77 | 2.9 | 1 |
| Treated, 20% H_2O_2 | 103 | 0.3 | 0.99 |

Summary

The oxidation process of Indonesian low rank coal using hydrogen peroxide solution has successfully conducted. The resulting coals have higher surface areas and oxygen containing groups contents than the raw coal. When tested using cationic dye solutions through batch experiments, the adsorption capacities of treated coals when calculated using Langmuir isotherm were significantly higher than that of the raw coal. It is concluded that the increase in the surface oxygen compounds (SOC's) enhances the coals'ability to interact with the positively charged dye molecules, hence improving its adsorption capacity. The result also supported the role of oxygen containing groups and cation exchange mechanism in the adsorption processes involving low rank coal.

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