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ADSORPTION OF Cr, Fe, Cd, Co IONS ONTO RAW AND TREATED INDONESIAN SUB-BITUMINOUS COAL

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ABSTRACT

Efforts have been made to improve low rank coal adsorption capacity, such as acid washing and reaction with oxygen to enhance its active sites. In this research, the coal was subjected to oxidation using hydrogen peroxide solution. After treatment, the coal was subjected to elemental and FTIR analyses. The treated and untreated coals were then applied for adsorption of divalent and trivalent metal cations such as Cr^{3+}, Fe^{3+}, Cd^{2+}, and Co^{2+}. The adsorption experiments were carried out in batch tests, applying constant temperature and constant stirring speed. The result showed that treated coal possessed better adsorption capacity than that of raw coal. It was also indicated that trivalent cations were adsorbed better than divalent ones signifying better interaction of trivalent ions with coal surface.

Keywords: adsorption, low rank coal, metal cations.

INTRODUCTION

Until now, activated carbons are considered as the most utilized adsorbents in water treatment processes due to their surface area and high degree of surface reactivity. Activated carbons have been extensively used in purification and separation processes [1]. There are, however, some drawbacks associated with their use, such as high activation and regeneration costs. To overcome this, many cheap materials have been explored as alternatives for activated carbons [2].

Numerous industrial by-products and naturally occurring materials have been investigated as substitutes for activated carbon. Various kinds of fly ash offer a low cost option and have been utilized to remove organics, dyes and heavy metals from water [3]. Chitosan, a naturally occurring biopolymer extracted from crustacean shells, has been used for metal and organic adsorption from aqueous solutions [4]. Raw and modified zeolites have ion exchange properties and large surface areas allowing them to adsorb heavy metals from wastewater [5]. Like zeolites, brown coal, a low rank coal, is characterized by its considerable surface area and also has high oxygen and carboxylic group content, which may facilitate adsorption of some organics and cations from aqueous solution [6,7].

Low rank coals deposits in many parts of the world are plentiful, but their application in power generation industry is limited due to its high water content. Therefore, alternative uses of low rank coal was critically needed [8]. Low rank coal was commonly converted to activated carbon via an expensive pyrolysis stage. There are also many reports that utilized raw low rank coals for organics, dyes and metal removals from aqueous solutions [9-13].

Brown coal mined in South Moravia, Czech Republic, has been utilized for the sorption of some metal ions (Pb2+, Zn2+, Cu2+ and Cd2+) in aqueous solutions. The sorption capacities of the raw brown coal for two highly toxic metals, lead and cadmium, were relatively high compared other brown coal-derived sorbents such as humic acids, humin and oxihumolite [14]. It is commonly accepted that high adsorption capacities of brown coal for metal ions and dyes are mainly due to the cation-exchange mechanism of some oxygen containing groups on the coal surface [11]. Despite its sizeable deposit, reports on Indonesian low rank coal as adsorbent are lacking. This study reported the use of raw and treated Indonesian low rank coals and adsorbents for Cr3+, Fe3+, Cd2+, and Co2+ ions from aqueous solutions. The treatment of raw low rank coal employed the enrichment of oxygen containing groups method using hydrogen peroxide solution reported before [15].

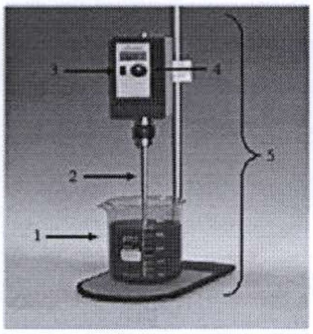
METHOD

Preparation of treated low rank coal

An amount of low rank coal originated from Banten Indonesia were treated using 20% (v/v) of hydrogen peroxide for 30 min employing a method reported by Yuliani [15]. The mixtures were then filtered and air-dried. Raw and treated low rank coals were analyzed using elemental analysis (CHONS), FTIR (not shown) and surface area. The elemental analysis of the coals before and after treatment was provided in Table-1.

Batch adsorption

Known amount of adsorbents were added to 50 mL of 25 ppm of metal solutions in a batch reactor illustrated in Figure-1 and were shaken for 2h under constant stirring speed of 200 rpm. The metal solutions used were Cr(NO3)3, Co(NO3), Fe(NO3)3 , Cd(NO3)2 purchased from Merck. The aqueous phase was passed through a filter and was analyzed for concentration using a Perkin Elmer AAS. The absorbance measured using spectrometer was converted to concentration using linear calibration curve built for each solutions (the calibration curve not shown). The initial pH for the metal solutions was 3.8 to 4.0.



1. Beaker glass
2. Stirrer
3. On/Off button
4. Speed adjustment
5. Full set

Figure-1. Batch reactor for adsorption study.

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

Parameter	Raw coal	Modified coal	Basis
	Proximate analysis		
Moisture	2.99 %	3.09 %	adb
Ash	15.28 %	19.55 %	adb
Volatile	30.98 %	28.76 %	adb
Fixed Carbon	50.75 %	48.60 %	adb
	Ultimate analysis		
C	81.54 %	81.22 %	daf
H	6.18 %	6.25 %	daf
N	3.43 %	2.79 %	daf
Total S	1.46 %	0.97 %	daf
O	7.39 %	8.77 %	daf
Calorific value	6,752 Cal/g	6,322 Cal/g	adb
Surface Area	3.658 m^2/g	8.651 m^2/g	N_2 adsorption (BET)

RESULTS AND DISCUSSION

Oxidation of low rank coal

The oxidation processes using H_2O_2 was expected to reduce the carbon content and increase the oxygen content and the surface area. Treatment using H_2O_2 solutions may be followed with organic leaching; presumably lignin compounds predominated from the coal structure.

From the CHONS analysis (Table-1), the slight decrease in carbon content from the oxidized coal was observed. Unexpectedly, the increase in the ash content of the modified coal was observed. This was probably due to the deposition of some inorganic on the coal surface. As expected, the oxidation process improved the oxygen content of the low rank coal. Additionally, the oxidized coal has higher surface are than the raw one. The oxidation of the coal using hydrogen peroxide solution caused the organic and inorganic leaching and presumably altered the surface structure of the coal [15].

Adsorption study

The treatment of the coal was able to increase its adsorption capacity (Figure-2). Presumably, the increment of surface area and the increase in the oxygen containing groups of the treated coals enhanced the reactivity of the coals' surface to metal cations. Additionally, the adsorption capacities of raw and treated coals for trivalent cations (Cr^{3+} and Fe^{3+}), calculated using Langmuir isotherm models, were significantly higher than divalent cations (Co^{2+} and Cd^{2+}).

The adsorption capacities of raw coal for Fe^{3+}, Cr^{3+}, Co^{2+}, and Cd^{2+} ions were 0.83, 0.24, 0.02, 0.01 mg/g, respectively. On the other, the adsorption capacities of treated coal for Fe^{3+}, Cr^{3+}, Co^{2+}, and Cd^{2+} ions were 0.92, 0.54, 0.06, 0.1 mg/g, respectively. The trivalent cations were considered to have stronger affinity to negatively charged coals' surface.

The mechanism of ion adsorption onto the coal surface may proceed via physical and chemical interaction. The increase in surface are of the coal as a result of oxidation treatment played a role in enhancing the interaction between metal ions and coal via physical adsorption. However, the ion exchange mechanism operated via the negatively charge oxygen containing groups is presumed to play a significant role. Pehlivan reported the possible ion-exchange mechanism as follows [16, 17].

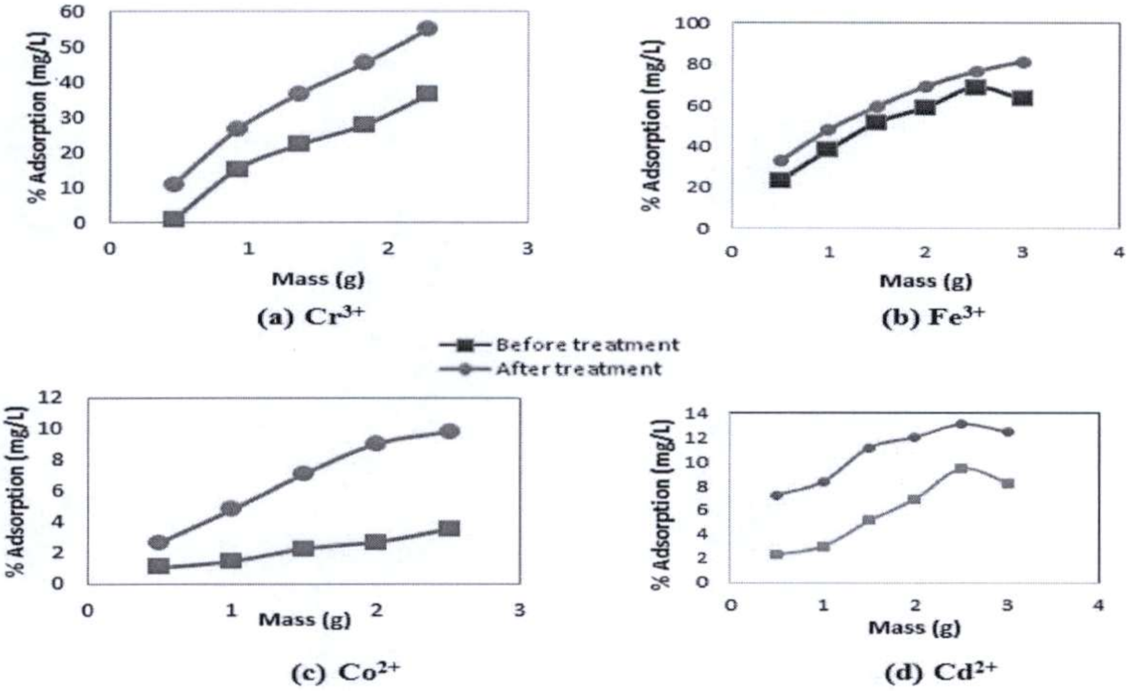
$$\text{Coal–COOH} \rightleftharpoons \text{Coal-COO}^- + H^+_{(aq)} \quad (1)$$

$$M^{2+/3+}_{(aq)} + n\text{Coal–COO}^- \rightleftharpoons (\text{Coal–COO})_n \quad (2)$$

$$M^{n+}_{(aq)} + n\ OH^- \rightleftharpoons M(OH)_n \quad (3)$$

These equations explain the strong observed pH dependence of the adsorption capacity for metal ions, as discussed by Lafferty and Hobday [18]. At a high concentration of H^+ (pH~2), the equilibrium in Equation. (1) lies primarily to the left where the ion exchange sites are mainly protonated, thus less available for metal ion exchange. At a solution pH between 2 to 5, the carboxylic acid sites can be appreciably deprotonated allowing Equation. (2) to proceed further to the right and enabling metal ion removal to predominate via the ion exchange mechanism. At a pH above 5 (Equation. (3)), the formation of metal hydroxide can become significant, thus allowing the metal removal processes via metal hydroxides precipitation [18].

The adsorption isotherm analysis was also conducted using Langmuir and Freundlich isotherms. From the adsorption data, only the trivalent cations (Cr^{3+} and Fe^{3+}) fitted both isotherm models. The adsorption capacities for divalent cations (Co^{2+} and Cd^{2+}) were too insignificant and could not fit the models. The adsorption isotherm data were tabulated in Table-2. It was indicated from the R^2 value that the data followed the Langmuir isotherm, supporting the monolayer interaction and the cation exchange mechanism.



(a) Cr^{3+} (b) Fe^{3+}

(c) Co^{2+} (d) Cd^{2+}

Figure-2. Adsorption of metal cations onto raw and treated low rank coals.

Table-2. Adsorption isothermal data for trivalent ions adsorption on treated and untreated coal.

Metal Ion	Adsorbent	Isoterm Langmuir			Isoterm Freundlich		
		Q_m (mg/g)	b	R^2	Kf (mg/g)	n	R^2
Cr^{3+}	Coal	0.24	0.27	0.99	0.12	5.81	0.91
	Treated Coal	0.54	0.11	0.98	0.11	2.51	0.95
Fe^{3+}	Coal	0.82	0.07	0.90	5.48	2.57	0.96
	Treated Coal	0.92	0.12	0.96	8.32	1.53	0.96

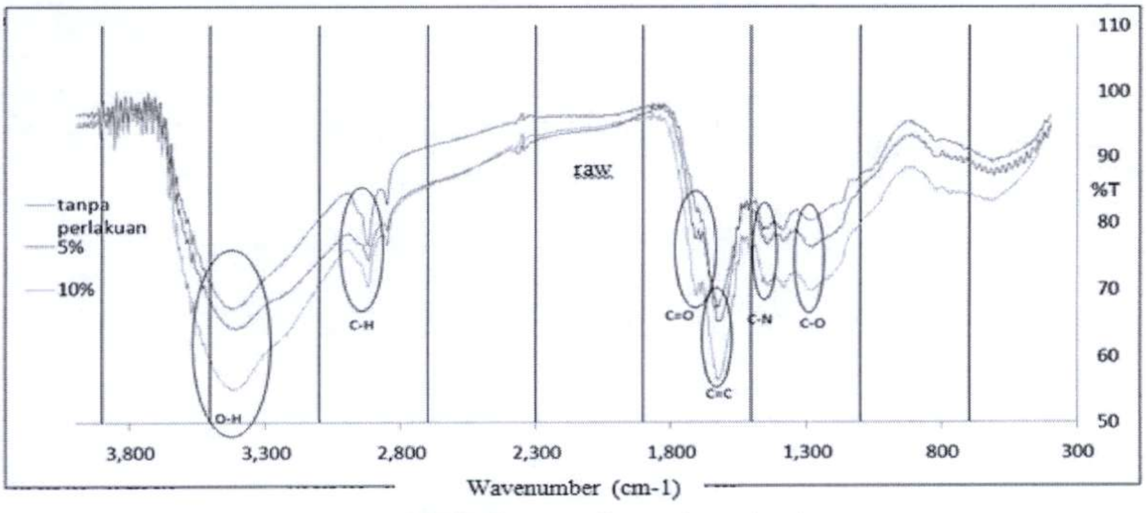


Figure-3. FTIR Spectrum of raw and treated coal.

CONCLUSIONS

The application of raw and treated Indonesian low rank coal for the adsorption of divalent and trivalent metal cations has been conducted. The resulting treated coal was characterized to have higher surface areas and oxygen containing groups than the raw one. In the batch experiments, the adsorption capacities of treated coals when calculated using Langmuir isotherm were significantly higher than that of the raw coal. The trend for adsorption capacities of raw and treated low rank coal was: Fe3+> Cr3+>Co2+~ Cd2+. It is believed that the increase in the surface oxygen compounds (SOC's) upon treatment enhanced the coals' ability to interact with the metal cations. It is also concluded that the trivalent cations established better interaction with the coal presumably due to their higher affinities.

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