

**POTENTIAL APPLICATION OF LIGNITE AS ADSORBENTS IN INDUSTRIAL WASTEWATER TREATMENT: A MINI REVIEW**  
**POTENSI PEMANFAATAN LIGNITE SEBAGAI ADSORBEN PADA INDUSTRI PENGOLAHAN LIMBAH: SEBUAH MINI REVIEW**

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**ABSTRACT**

Low rank coal (or lignite) is a low grade, wet, low cost and highly abundant coal. The high moisture content of lignite limits its application as high-heating value fuel and also creates barrier for its export as fuel. However, this property should not necessarily hinder its use in the water industry. Similar to activated carbons, lignite has the theoretical ability to treat the wastewater by adsorbing contaminants from aqueous solution. This review paper highlights the potential use of lignite in wastewater treatment industry.

**Keywords:** low rank coal, lignite, adsorbent, wastewater treatment.

**SARI**

*Di Indonesia Batubara peringkat rendah (lignit) adalah batubara dengan kadar air tinggi, relatif murah dan mudah didapat. Tingginya kandungan air dari lignit membatasi aplikasinya sebagai bahan bakar dan menjadikannya kurang disukai sebagai bahan bakar komoditas ekspor. Namun, berbagai sifat ini tidak harus membatasi aplikasi lignit dalam industri pengolahan air. Memiliki karakteristik yang mirip dengan karbon aktif, lignit memiliki kemampuan untuk mengadsorpsi berbagai kontaminan dari larutan limbah. Artikel mini-review ini menjelaskan mengenai potensi lignit sebagai material adsorben pada industri pengolahan limbah.*

**Kata kunci:** lignit, adsorben, pengolahan limbah cair.

**INTRODUCTION**

Activated carbon is the most common adsorbent used in wastewater treatment, but it is expensive - especially where large water volumes are involved. The current average bulk price of activated carbon is listed as US\$ 2.5 kg<sup>-1</sup> and forecasted demand of about 2.3 million metric tons by the year 2017 (Polat *et al.* 2006; Vepsäläinen 2012). The high demand for activated carbon and its high cost have become drivers in the search for cheaper alternative adsorbent materials.

Lignite, a low rank coal, has been widely used to prepare commercial

activated carbons via an expensive pyrolysis stage (Duggan and Allen 1997). However, raw lignite itself has been widely used as an adsorbent for metal and organics (Allen and Brown 1995; Duggan and Allen 1997). Being plentiful, cheap (priced at \$5 - \$8 t<sup>-1</sup>) and readily available in many parts of the world, raw lignite utilisation in industrial wastewater treatment would seem attractive. In principle, the used lignite may not require any expensive regeneration procedure or disposal requirements, since it may be simply consumed as fuel on site or, perhaps, disposed of as an agricultural aid (Qi *et al.* 2011).

**Lignite: properties and characteristics**

Coal is derived from a complex accumulation of plant debris. A definitive molecular structure of coal cannot be given due to its heterogeneous nature and any model is best considered as a 'statistical average'. For bituminous coals, the molecular structure is conceived to comprise aromatic structures in which clusters of aromatic groups are connected with various ether or aliphatic links. For low-rank coals, the molecular structure is more heterogeneous (Kidena *et al.* 2008).

The structural understanding of lignite is less developed compared to that of bituminous coal. A model by Hüttinger & Michenfelder ( $C_{270}H_{240}O_{90}N_3S_3M_{10}$ ) was developed from the results of elemental analyses, pyrolysis experiments and titration studies and from extrapolation of literature data for similar coals (Hüttinger and Michenfelder 1987). The model includes some important functional groups in the brown coal structure, such as carboxylic and phenolic groups, long chains and exchanged metal cations (Figure 1).

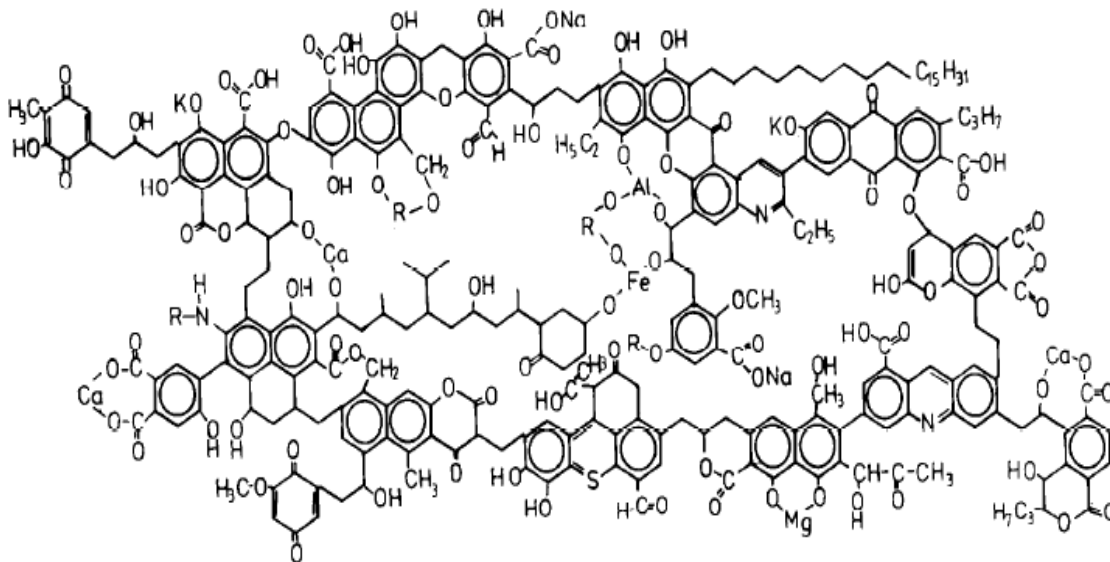


Figure 1. A model of low rank coal

Having properties between peat and bituminous coal, lignite is dark brown to black in colour when moist and light brown to black when dry. With density ranging from 1 to 1.3 g/cm<sup>3</sup>, lignite is typically amorphous and fibrous in texture (Pehlivan and Arslan 2007).

Various lignites mined from different parts of the world give very low surface areas when measured by the conventional BET N<sub>2</sub> method (see Table 1). This phenomenon is common for coals due to diffusion limitations at 77K that prevent the N<sub>2</sub> molecules from accessing the micropores in the coals (Pope 1984; Mahajan 1991). Due to this limitation, the surface area of coals is generally measured using CO<sub>2</sub> adsorption at higher

temperature, typically 273K. Carbon dioxide (3.3 Å) is a smaller molecule than nitrogen (3.65 Å) and has a critical temperature of 31.5°C (Mahajan 1991). The Dubinin-Radushkevich method is used to calculate surface area (Woskoboenko *et al.* 1991). The surface area of the lignite is now appreciable, but much lower than that of the activated carbon.

**Adsorption Mechanism**

The most prominent functional groups, phenols and carboxylic groups, give clear bands in the FTIR spectrum of the raw lignite (Figure 2.). The band at 1710 cm<sup>-1</sup> is the C=O stretching due to the carbonyl

and carboxyl groups. The absorption at 1630 cm<sup>-1</sup> is dominated by (C...C) stretching of aromatic rings, unsaturated olefinic bonds and poly-aromatic

structures, and C=O stretching of quinones bridged to acidic hydroxyl (Verheyen and Johns 1981).

**Table 1.** Surface area of various raw lignite samples measured by BET N<sub>2</sub> and CO<sub>2</sub> adsorption

No	Origin	Surface area (m <sup>2</sup> /g)	Method	Year/ Reference
1	Turkey	2.06 – 2.96	BET N <sub>2</sub>	2006 (Pehlivan and Arslan 2006)
2	Greece	11.40	BET N <sub>2</sub>	2011 (Aivalioti <i>et al.</i> 2010)
3	Serbia	1	BET N <sub>2</sub>	2012 (Milicevic <i>et al.</i> 2012)
4	Australia	298 – 395	DR CO <sub>2</sub>	2011 (Qi <i>et al.</i> 2011)
5	Indonesia	180 – 243	DR CO <sub>2</sub>	2006 (Artanto 2006.)
6	USA	116 - 134	DR CO <sub>2</sub>	2006 (Artanto 2006.)
7	India	202 – 204	DR CO <sub>2</sub>	2006 (Artanto 2006.)

<sup>\*)</sup> BET = Brunauer-Emmett-Teller and DR = Dubinin Radushkevich (Woskoboenko *et al.* 1991)

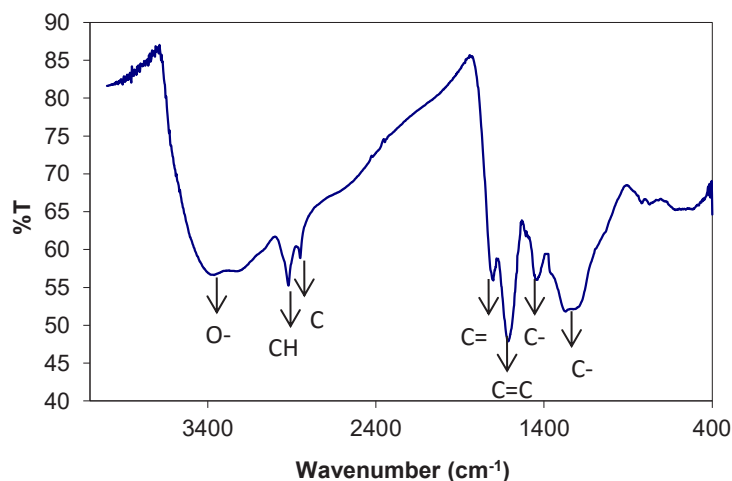
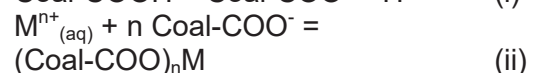


Figure 2. FTIR spectrum of lignite (Yuliani *et al.* 2012)

Among the heteroatoms in lignite, oxygen is the most abundant. The oxygen content of Victorian lignites varies from 25 to 30 percent (db) (Schafer 1991) and that of North Dakota lignites may be up to 20 percent (Harold 1995). The largest portion of the oxygen occurs in carboxyl and phenolic groups (Harold 1995). The carboxylate functional groups may exchange protons and facilitate the formation of carboxylate salts under appropriate pH conditions. These groups are the active sites that provide the ion exchange capability of lignite that enable its utilisation as a sorbent to remove heavy metals from aqueous solution. The detailed cation exchange mechanism of

the exchangeable groups on the coal (represented as Coal-COOH) and metal cations is as follows (Lafferty and Hobday 1990):



### Utilisation of lignite as an industrial sorbent

#### Lignite for metal sorption

Heavy metal contamination is a threat to humans, animals and plants. Many of these metals are not

biodegradable and may accumulate in the environment due to their solubility in aqueous solution (Arslan and Pehlivan 2008). Heavy metals known to be toxic and carcinogenic include Zn, Cu, Ni, Hg, Cd, Pb and Cr (Fu and Wang 2011). Many techniques have been trialled for removing heavy metals from process water; these include precipitation, coagulation, flotation, electrochemical treatment, adsorption and membrane filtration. Among these, adsorption is still considered to be the most effective and economic method. The adsorption method offers simplicity, flexibility in design and the possibility of regenerating the used sorbent (Fu and Wang 2011). Owing to its cation-exchange properties and availability, lignite has attracted significant interest as an efficient sorbent for metal removal from aqueous solution (Schafer 1970) (Lafferty and Hobday 1990).

Turkish Beypazari lignite was used to remove some heavy metals, namely Cd, Hg and Pb, from wastewater from mining operations. It was found that the solution pH was a crucial factor in determining the extent of removal of a particular metal species in the wastewater solution. The optimum pH was measured to be 4 for Hg and Cd, and 5 for Pb (Arpa *et al.* 2000).

Lignite mined in South Moravia, Czech Republic, has been utilised for the sorption of some metal ions ( $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$ ) in aqueous solutions. The sorption capacities of the raw lignite for two highly toxic metals, lead and cadmium, were relatively high compared with other lignite-derived sorbents such as humic acids, humin and oxihumolite (Janos *et al.* 2007; Havelcová *et al.* 2009).

Lignite obtained from Martin Lake, TX, USA, was used for the sorption of some metal ions from acid mine drainage. The sorption capacities for  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{3+}$  at 25°C were found to be 34.22 mg g<sup>-1</sup>, 25.84 mg g<sup>-1</sup> and 11.90 mg g<sup>-1</sup>, respectively. It was found that both Freundlich and Langmuir isotherms fit the adsorption data reasonably well (Mohan and Chander 2006; Mohan and Chander 2006).

Sulfonated lignite from Yunnan was used for Cr (VI) ion sorption with 1 h contact time. The adsorption capacity was 26.79 – 27.87 mg g<sup>-1</sup> when calculated using the Langmuir equation. The correlation coefficient ( $R^2$ ) was higher for the Langmuir isotherm compared to the Freundlich or Tempkin isotherms confirming better data fit for Langmuir model; hence suggesting a monolayer interaction (Zhang *et al.* 2010).

Four lignite samples mined from different areas in Greece were used for the removal of some metal ions ( $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$ ) from aqueous solutions. Based on mass uptake,  $\text{Pb}^{2+}$  appeared to have the strongest affinity. This conclusion was supported by competitive adsorption experiments using solutions containing several different metal ions. The Langmuir model again fitted the adsorption data better than the Freundlich model, supporting the model of monolayer interaction and the involvement of an ion exchange mechanism (Pentari *et al.* 2009).

## Lignite for organics removal

Organic pollutants are introduced into the environment by many industrial applications such as printing, leather, textile, petroleum, paint, pulp and paper, pesticide and rubber manufacture (Aksu 2005). Common organic contaminants include natural organic substances such as humic acids (HA), fulvic acids (FA), carbohydrates, proteins and carboxylic acids that are formed during decomposition of organic matter of vegetable origin (Schreiber *et al.* 2005; Aivalioti *et al.* 2010). There are also synthetic dyestuffs used extensively in textile and printing industries. Some of these compounds can be degraded by microorganisms in the activated sludge plant; however, a biorefractory portion of the effluent, which consists of high molecular weight oxidized organic compounds, is often an important fraction of the waste (Bijan and Mohseni 2005; Pöykiö *et al.* 2008).

Raw lignite from Soma, Turkey, having moisture content of 21%, has been used as an adsorbent for phenol removal from wastewaters. The adsorption capacity of lignite ( $10 \text{ mg g}^{-1}$ ) was much lower compared to that of activated carbon ( $300 \text{ mg g}^{-1}$ ) (Polat *et al.* 2006). When normalized for the surface area (lignite BET surface area of  $4.79 \text{ m}^2 \text{ g}^{-1}$ ), the adsorption capacity was reported to be much larger for lignite ( $1.3 \text{ mg m}^2$ ) than for activated carbon ( $0.05\text{-}0.3 \text{ mg m}^2$ ) (Polat *et al.* 2006). However, as described in section 2.2.2, the surface of lignite when measured using  $\text{N}_2$  adsorption does not represent the actual surface area of the coal due to the limited access of  $\text{N}_2$  to the coal micropores at 77K (Mahajan 1991). The low capacity of the coal for phenol was more likely due to the fact that phenol cannot adsorb via a cation-exchange mechanism.

An adsorbent bed of Loy Yang lignite from Victoria, Australia, was used to treat wastewater that resulted from a non-evaporative lignite dewatering technique called Mechanical Thermal Expression (MTE). This method achieved 60% reduction in COD and also removed about 25% of the total cations. The lignite adsorption capacity for dissolved organic carbon (DOC) was around  $30 \text{ mg g}^{-1}$  (Butler *et al.* 2008).

Lignite mined from Fushun, China, was utilized to adsorb an extracellular enzyme secreted by a fungus that was isolated from decaying wood. The maximum adsorption capacity for this enzyme was  $2.0 \text{ mg g}^{-1}$ . The Langmuir equation was applied to the experimental data giving a correlation coefficient of 0.98 (Yin *et al.* 2009).

Three Turkish lignite samples were used to adsorb a non-ionic dispersant, polyoxyethylene sorbitan monooleate (Tween-80) in the presence of sodium lauryl ether sulfate as a wetting agent. The Çayirhan-Ankara lignite exhibited particularly high adsorption of Tween-80, it was suggested, due to the high content of carboxylic groups on its surface. It was also noted that acidic to neutral conditions were favourable for the adsorption of the

Tween-80 dispersant by the lignites (Karatepe 2003). In this case the high adsorption cannot be due to cation exchange. Since, Tween-80 has a high concentration of polar (OH) groups, it is likely that it is the H-bonding of these groups with the polar carboxylic groups at the coal surface that leads to the high adsorption capacity.

Two Turkish lignite samples were also used to adsorb Pellapur B69 dispersant. It was reported that the adsorption capacity decreased from  $7 \text{ mg g}^{-1}$  to  $4 \text{ mg g}^{-1}$  when the lignite sample was oxidized. It was suggested that this was due to the changes at the lignite surface that made it more hydrophilic due to the formation of acidic functional groups (Yavuz and Küçükbayrak 2001). However, since the oxidation of the lignite sample was carried out at 473 K for 48 h, the loss of moisture and pore volume of lignite upon drying may have been a more dominant factor.

Loy Yang lignite was utilized to remove colour, total phosphorus and organics from wastewaters of a magnesium bisulphite pulp and paper mill. The coal exhibited multi-component adsorption of colour, organics and phosphorus from the solution. The coal showed an ability to remove phosphorus from the wastewater, which could not be achieved with activated carbon; yet it had significantly lower adsorption capacities for colour and organics than did activated carbon. The low capacity of the coal was due to the nature of organics and colour that carried negative charge in the wastewater and the absence of cation-exchange mechanism (Yuliani *et al.* 2012). The adsorption capacity of lignite for dyes varied depending on the nature of the dye and the charge carried by the dye molecules in aqueous solution. For basic and cationic dyes, the adsorption capacities were quite high and were comparable to those for activated carbon (Allen *et al.* 1994; Qi *et al.* 2011).

Various lignites and a coal-derived active carbon were investigated for cationic and anionic dye adsorption from aqueous solution. Coal-derived active

carbon showed consistent performance in adsorbing both cationic and anionic dyes with high adsorption capacities, due to its high surface area and pore volume. The adsorption capacity of the lignites for the anionic dye was only 15% of that for the cationic one, suggesting that a cation-exchange mechanism is the dominant mechanism involved. The study also demonstrated a loss of adsorption capacity of lignite upon drying which was attributed to pore collapse in the lignite structure (Yuliani *et al.* 2012).

## Summary

Lignites have reasonably high adsorption capacities for some metal ions and dye solutions. The efficiency of lignites in adsorption processes is attributable, in most cases, to their cation exchange properties. Some of the lignite properties that influence the cation exchange properties include moisture content and the concentration of more strongly acidic (pKa~5) functional groups. The use of raw (wet) lignite as adsorbent without drying is advisable and makes it even more attractive as an alternative to expensive activated carbon.

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