



## Review

## Coal-based adsorbents for water and wastewater treatment



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## ABSTRACT

Coal, just like other fossil fuels such as oil and natural gas, is mainly used as a non-renewable source of energy. It is a physically unique mineral resource almost totally composed of organic matter (carbon), and a smaller percentage of elements such as hydrogen, oxygen, sulphur, and nitrogen. It is believed that underground coal deposits formed about 250–300 million years ago, when much of the Earth was a swamp covered with thick forest and plant growth. This review explores the use of coal, not as an energy source used for generating electricity, but as a low cost adsorbent in water and wastewater treatment processes. In fact, today, coal-based adsorbents still attract considerable interest in their usage. The review critically analyses the chemical composition, ion-exchange and sorption properties of coal. The use of the as-received coals, demineralized coals, sulphonated coals, calcium-loaded coals, chitosan-doped coals, activated carbon, coal fly ash, and coal fly ash derived-zeolite has also been extensively discussed. It is evident from this review that although the pollutant exchange capacities of various types of coal-based adsorbents are significantly lower in comparison to other forms of adsorbents, the substantially lower cost of coal shows a great potential for the utilization of coal as a means to remove a range of pollutants from water and wastewater effluents. However, due to the scarcity of consistent cost information, cost comparisons are difficult to make, and consequently, in this review, such comparisons were not done for the coal-based adsorbents.

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## 1. Introduction

Coal has the longest history of use amongst the fossil fuels, with its use as a fuel dating back to 3000 BC in China and Wales [1], and undoubtedly, it still remains the largest and cheapest source of solid fuel across the globe [2]; and there is an estimated 861 billion tonnes of coal reserves worldwide [3]. Broadly speaking, coal is a complex combustible sedimentary rock, composed chiefly, but not exclusively, of helophytic ( $\pm$ aquatic) plant debris and plant derivatives [4]. It is predominantly made of carbon, but also features other elements such as hydrogen, oxygen, sulphur and nitrogen [5]. In other words, coal is a very heterogeneous organic rock in which organic matter has inclusions of mineral matter [6]. In fact, organic material typically represents 85–95% (wt/wt) of a dry coal [7].

In recent past, various types of coal have been increasingly used not only as fuels, but also as valuable materials in several remediation and pollution control processes [8,9]. This is because besides being inexpensive and abundant in many countries, coal possesses very exciting characteristics that make it an effective adsorbent for the removal of various organic and inorganic pollutants. In this regard, this review paper critically analyses the use of coal-based adsorbents in the treatment of water and wastewater. In terms of the paper organization, following this introductory section, Section 2 briefly discusses the classification and composition of coal. This is followed by the surface characteristics of coal in Section 3. The analyses of production and activation of some of coal-based adsorbents are discussed in Section 4. Subsequently, Section 5 discusses applications of coal-based adsorbents. Finally, Section 6 summarises the paper and highlights future prospects of the usage of coal as an adsorbent.

## 2. Classification and composition of coal

Coal is an extremely complex and a heterogeneous combustible sedimentary rock [4,7,10]. In a broader sense, coal is essentially composed of plant remains, which are coalified organic matter formed by exposure to high temperature and pressure during burial [11]. Three main parameters are considered when classifying coals, i.e., type, rank, and grade [10]. Coal types typically fall into two categories: humic coals, developed from peat, and sapropelic coals, developed from organic mud [4]. Either type may be allochthonous or autochthonous, and within the different types, further refinement of depositional environment can also be made [4]. Coal rank refers to the level of maturity in coal [12]. Broadly speaking, coal rank refers to the changes in geochemistry and resultant changes in reflectance caused by increasing thermal maturity of the coal, thus providing an overprint of maturity on existing coal types [4]. In other words, during coalification, physiochemical changes occur under conditions of high temperature and

pressure over time, thereby giving rise to the process of maturation and metamorphosis (changes) in the various plant fragments (macerals). For example, the high temperatures and pressures result in the transformation of the original peat swamp plant materials through progressive stages of brown coal (lignite), sub-bituminous and bituminous coals to anthracite and meta-anthracite [4,13]. The end-point of this continuum is graphite, which occurs only rarely in nature as a result of intense pressure and temperature in some coalfields of the world [13]. In summary, the level to which a coal has reached in this coalification series is referred to as rank or level of maturity [13]. On the other hand, coal grade refers to the amount of inorganic matter content [10].

## 3. Surface characteristics of coal

It is known that the surface properties of coal, such as surface area, pore volume, and surface chemical structure, affect the physico-chemical behaviour of coal in many applications [14] including adsorption. In fact, it is on the surface of coal where it initially interacts with the rest of the world, and under many circumstances, the initial contact is totally controlled by the area, geometry, and chemical nature of the surface [15]. Therefore, this particular section explains the general physical and chemical characteristics of the surface of coal and why they are important.

Coal particles are extremely heterogeneous, comprising of various heteroatoms and functional groups along with inorganic impurities within the hydrocarbon matrix [6]. These surface sites exhibit various characteristics, which all contribute to the overall adsorption capacity of coal. For example, coal surface electrochemical properties stem from the presence of oxygenated surface functionalities, such as carboxylic acid and phenolic groups [16]. There are also other forms of oxygen that are buried as heteroatoms in aromatic or naphthenic rings or as bridges between the nuclei as ethers or, to a lesser extent, as esters [7]. All these types of oxygen functional groups strongly influence coal reactivity [7,17], and their relative numbers vary significantly as a function of coal rank [7,18]. Furthermore, chemically, coals become progressively more aromatic with increasing coal rank, and the cross-link density in the macromolecular system is considered to decrease with increasing coal rank to coals of about 87 wt% of carbon and then progressively to increase again to the most mature anthracites [19].

In aqueous solution, the acidic protons on the oxygenated surface functional groups on coal dissociate, leaving negatively charged sites on the coal surface [16]. The dissociation is enhanced in basic solution, whereas the surface groups are protonated in strongly acidic solution, reducing the negative charge density and the surface can even become positively charged in highly acidic solution. Positively charged sites can also develop from proton adsorption by chromene and pyrone-type structures on coal [16].

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