# Adsorption of Cobalt Ions by Activated Carbon Prepared from Agricultural Waste Residues and Treated with Magnetic Nanomaterials: A Review

# Adsorpsi Ion Kobalt oleh Karbon Aktif yang Dipreparasi dari Residu Limbah Pertanian dan Diolah dengan Nanomaterial Magnetik: Sebuah Tinjauan

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***Abstract*. General Background***: The study of heavy metal adsorption is crucial for environmental protection and industrial wastewater management.* ***Specific Background****: The adsorption of cobalt ions (Co2+) by activated carbon derived from agricultural waste, enhanced with magnetic nanomaterials, has garnered significant interest due to its potential for cost-effective and efficient wastewater treatment.* ***Knowledge Gap****: Despite numerous studies, there remains a lack of comprehensive research on the specific combination of agricultural waste-derived activated carbon and magnetic nanomaterials for Co2+ adsorption.* ***Aims:*** *This study aims to meticulously review the existing literature on the preparation of activated carbon from agricultural residues, the enhancement of its properties with magnetic nanomaterials, and its effectiveness in Co2+ ion adsorption.* ***Results****: The review demonstrates that activated carbon with a large specific surface area and diverse functional groups significantly improves Co2+ adsorption. The incorporation of magnetic nanomaterials further enhances this efficiency due to increased surface area and magnetic properties.* ***Novelty:*** *This research uniquely combines agricultural waste valorization with advanced nanotechnology, presenting a sustainable and innovative approach to heavy metal adsorption.* ***Implications****: The findings underscore the dual environmental benefits of recycling agricultural waste and mitigating industrial pollution, offering a cost-effective and efficient solution for cobalt ion recovery from wastewater. This study serves as a valuable resource for researchers and engineers focusing on sustainable environmental remediation technologies.*

***Keywords –*** *Cobalt Ion Adsorption, Activated Carbon, Agricultural Waste, Magnetic Nanomaterials, Wastewater Treatment*

***Abstrak*. Latar Belakang Umum***: Studi tentang penyerapan logam berat sangat penting untuk perlindungan lingkungan dan pengelolaan air limbah industri.* ***Latar Belakang Khusus****: Penyerapan ion kobalt (Co2+) oleh karbon aktif yang berasal dari limbah pertanian, yang disempurnakan dengan nanomaterial magnetik, telah menarik minat yang signifikan karena potensinya untuk pengolahan air limbah yang hemat biaya dan efisien. Kesenjangan Pengetahuan: Meskipun banyak penelitian, masih belum ada penelitian komprehensif tentang kombinasi spesifik karbon aktif yang berasal dari limbah pertanian dan nanomaterial magnetik untuk penyerapan Co2+.* ***Tujuan****: Penelitian ini bertujuan untuk meninjau dengan cermat literatur yang ada tentang persiapan karbon aktif dari residu pertanian, peningkatan sifat-sifatnya dengan nanomaterial magnetik, dan efektivitasnya dalam penyerapan ion Co2+.* ***Hasil****: Tinjauan tersebut menunjukkan bahwa karbon aktif dengan luas permukaan spesifik yang besar dan beragam gugus fungsi secara signifikan meningkatkan penyerapan Co2+. Penggabungan nanomaterial magnetik selanjutnya meningkatkan efisiensi ini karena peningkatan luas permukaan dan sifat magnetik.* ***Kebaruan:*** *Penelitian ini secara unik menggabungkan pemanfaatan limbah pertanian dengan nanoteknologi canggih, menghadirkan pendekatan berkelanjutan dan inovatif terhadap penyerapan logam berat.* ***Implikasi:*** *Temuan ini menggarisbawahi manfaat ganda lingkungan dari daur ulang limbah pertanian dan mitigasi polusi industri, menawarkan solusi yang hemat biaya dan efisien untuk pemulihan ion kobalt dari air limbah. Studi ini berfungsi sebagai sumber daya yang berharga bagi para peneliti dan insinyur yang berfokus pada teknologi remediasi lingkungan yang berkelanjutan.*

***Kata Kunci –*** *Adsorpsi Ion Kobalt, Karbon Aktif, Limbah Pertanian, Bahan Nano Magnetik, Pengolahan Air Limbah*

## I. INTRODUCTION

The attraction of activated carbon as an adsorbent occurs mainly due to the following properties: a large specific surface area which is effective in increasing the contact area and ensuring accessible sites for reaction; the presence of various functional groups such as hydroxyl, carbonyl, carboxyl, lactone, phenol, and quinone which act as ligands that bear electrons to react with a metal ion by chelation/complexation, electrostatic, and ion exchange to form an inner- or surface-carbon-metal complex; the presence of a large number of pores with different sizes, where some works have demonstrated that some types of pore structures such as micropores and mesopores can be used to direct metal ions into the carbon structure, and macropores are not involved in the process of metal adsorption. Therefore, the microporous structure is generally the most efficient in the adsorption process because it will condition a larger surface area to attach the added substances to it, and the largest open pores at the surface of the particles will undertake various processes such as reactant entrance and frontal in the samples [1][2][3].

1.1. Background and Significance

Analyzing the adsorption of heavy metals has been a topic of interest, and numerous inexpensive, simple, and environmentally friendly methods have been reported. Over the years, many researchers have turned their attention to these methods, particularly in order to determine a viable approach to eliminating toxic and hazardous heavy metal pollutants that are commonly found in industrial wastewater, in an effort to protect the environment and human health [4]. The presence of heavy metals in the environment is linked to environmental toxicity, which not only affects human health but also causes bioaccumulation in living organisms. The toxicity of cobalt generates various effects and symptoms on human health, depending on the route of exposure. In this sense, wastewater containing cobalt heavy metals must undergo rigorous treatment before being discharged [5]. An innovative approach to remove heavy metals involves sorption - which is defined as the process of removing heavy metals from liquid or gaseous waste via an adsorption stage aimed at concentrating the waste on solids. Various sorbents, especially agricultural waste, activated carbon, and magnetic nanomaterials, have served as the central attraction among researchers, and several researchers have recently reviewed the fabrication process of activated carbon from agricultural waste, modified its surface to boost its efficiency, and imbued it with magnetic properties [6]. While the potential use of these adsorbents to remove cobalt from wastewater is robust, an inclusive and intensive study in the public domain has yet to be conducted. In light of this, the review presented in this study focuses on the adsorption process of cobalt from aqueous solutions using activated carbon prepared from agricultural waste materials and treated with magnetic nanomaterials [7].

1.2. Objectives of the Review

Although expanded in some texts, no article has been specifically dedicated to the subject of our research. Therefore, the purpose of the review conducted by the team from which the article is extracted is to identify the main research lines in relation to the production and application of activated carbon and nanocomposites in the adsorption of cobalt, as well as to identify difficulties and gaps in the areas of production and application of materials derived from agricultural residues and nanotechnology in this area of research. The findings showed that both surface modifications of magnetic adsorbents and the use of adsorbate chelating modifiers can enhance the adsorption of cobalt by activated carbon, with 27 out of 35 articles obtained with these objectives [8]. The objectives of this review are to prospect these two lines of research to evaluate the state-of-the-art for the worldwide production of reviews and the scientific community's concerns for the manufacture and application of activated carbon in the removal of cobalt ions contained in liquid waste, as well as to analyze the prospects and demands of production articles and global agendas with agricultural residues used for the production of activated carbon from cobalt removal and modified with magnetic nanomaterials for cobalt adsorption. In terms of materials science, the modifications in carbon structures with the use of magnetic nanomaterials and the researches developed for the prospecting of elaboration of research articles about the modification of adsorbents with a magnetite modify the chemical interactions between the adsorbates until changing the main kinetic tables. Modifying the adsorbent surface with magnetic nanoparticles exerts control over the selectivity and increases the metal adsorption process, it is considered a good option for practical applications in large control operations [9].

2. Activated Carbon Preparation from Agricultural Waste Residues

Two different residues are produced from a single agricultural platform containing wood and food crops. Wood carcasses are currently widely used in commercial activities and represent a significant portion of industrial waste, whereas edible parts are largely consumed and their skin is often discarded. This research provides an efficient method for applying these residues. This method uses these residues for the preparation of activated carbon. The agricultural waste residues available from the food processing industry promise to generate value-added utilizable products. Therefore, in the present study, activated carbon was prepared from auxiliary tender coconut residue using various activating agents such as H3PO4, ZnCl2, and NaOH [10]. Activated carbon is a carbonaceous material that has been transformed to have an extensive, porous, highly developed internal surface area by using several activation techniques and methods that characterize the activation process, activation agents, and precursors. The preparation of activated carbon from agricultural waste preparations is instigated by the activation procedures, as the precursor or raw material can be used for the preparation of activated carbon through various activation methods and activation agents [11]. Major preparation methods, such as physical activation, cadmium glasses, direct activation procedures, organic precursor materials, inorganic chemical activating agents, and alkali activation agents, as well as hierarchical porous activated carbon materials for various applications with a numerical representation as a part of the results and discussion [2]. Agricultural residues include human food and animal feed, such as maize (corn), rice (rice bran), wheat, barley, oat, peanut, soybean, millet, and cottonseed husk. These forms of agricultural residues can be used for preparation of the most common methods of activated carbon preparation. High porosity was available in a significantly activated carbon preparation process such as surface engineering or modification [12].

2.1. Sources of Agricultural Waste Residues

Agriculture sector is the primary occupation in a developing country like India, Pakistan, Bangladesh, etc. and more than 80% of the residents—of these and other countries—direct or indirectly depend on agriculture for their living, food, clothing, etc. According to an estimate in India, 70 loads of agricultural waste are produced in 1 year. These residues are used for different purposes. A quarter of it is partly utilized as fuel, bedding for animals, whereas a major proportion of it is just burnt in open environment, causing environmental as well as health-related hazards. Therefore, processing and conversion of these residues into value-added products are of the utmost importance. This will not only lessen the chances of hazards but also cope with the demand for food, etc., which is increasing at a much larger rate [13]. The residues developed after processing can be transformed into activated carbon, which is a porous material widely used for removing impurities from the environment. Combustible part of these residues is burnt in an open environment, so the obtained activated carbon is for reducing environmental impurities. If in a case the residues are not entirely burnt and some part of it is in charcoal form, this can also be converted into activated carbon by treating it with the suitable oxidizing agent followed by heating on furnace for removing the moisture. This is due to the standardized composition requirements of agricultural waste charcoal, which brings into consideration the composition of ashes, organic volatiles, etc. The agricultural waste residues reported in the literature are discussed in the following section. These details are important for potential readers for utilizing it as feedstock and for the academician for scientific review. The potential residues can contain the following impurities, chemical formula, and composition [14].

2.2. Activation Methods and Techniques

The effective properties of carbon materials result from their textures and structures, as well as their surface chemical and functional groups. The porous texture, such as the surface area and nature of pores, is very important for carbon function. Pores can be characterized as macrosized pores with diameters greater than 50 Å, mesosized pores of diameters between 2 and 50 Å, and micropores with diameters smaller than 2 Å. Because of their diverse pore-distribution properties, the carbon material transforms highly active numerous functional groups on the surfaces of its internal pore walls and/or external surfaces. Thus, many publications have investigated the conversion of waste lignocellulosic agricultural into activated carbon using various activation methods and techniques for the effective uptake of heavy metal ions in their removal from wastewater. This literature maintains a focus on updating the efficient conversion of activated carbon prepared from various lignocellulosic agricultural waste residues using various activation techniques in their activation processes [15]. The processes of activating carbon and having proper surface area and pore volume must be considered for the material. In fact, there has been a vast amount of research on activated carbon materials, considering their main activating agents such as water steam, potassium hydroxide, and phosphoric acid. Thus, from previous research, the conversion of agricultural residues into activated carbon is used in many adsorptive applications concerning the removal of various impurities constituents such as dyes, heavy metal ions, and organic and inorganic materials. The focus on the uptake studies showed that these activating agents bring about differences in the development of surface area, surface bonding energy, particle adhesion, and capillarity of activated carbon [16].

3. Magnetic Nanomaterials for Adsorption Enhancement

There are many magnetic nanomaterials which are employed for the enhancement of the adsorption capacity, including magnetic nanoparticles, iron magnetic nanoparticles, iron oxides, magnetic nano composites, etc., which adopt different natures and have unique properties. These nanomaterials are comprised of magnetic dipoles which have the ability to provide these materials high magnetic susceptibility, high surface areas, and large surface-to-volume ratios. These magnetic nanomaterials are superparamagnetic in nature from an individual particle point of view and are quite stable in the absence of an external magnetic field. The process of adsorbing these magnetic nanomaterials along with an adsorbent offers possible usage for the heavy metal/other pollutants removal from wastewaters [17]. Several characterization techniques are followed to characterize magnetic nanomaterials, such as electron microscopy, transmission electron microscopy, scanning electron microscopy, X-ray diffraction, Mössbauer spectroscopy, nuclear magnetic resonance, etc. Preparation of magnetic nanomaterials can be done using several methods, such as microemulsion method, sonochemical technique, microwave irradiation, etc. There are many techniques which can be used to functionalize these materials. The magnetic nanomaterials, owing to their scientific advantages (discussed above), increase the adsorption capacity of the activated carbon in removing cobalt. Moreover, the use of various methods like initiation of HCl and ammonia, usage of ultrasonic agitation, large surface areas among others increase the effectiveness of the activated carbon prepared from the agricultural wastes for the removal of cobalt from aqueous solutions [18].

3.1. Types and Properties of Magnetic Nanomaterials

These materials can be divided into hard and soft nanomagnets. The major difference between the two is the coercivity. A hard nanomagnet is characterized by a single coercive field, such as Fe, Co, and FePt. They show an anisotropic behavior in particles and have the properties of a permanent magnet. On the other hand, soft nanomagnets have a very low coercive field and therefore they will not retain a magnetic alignment, such as Ni, CoFe. Single domain (SD) particles are the simplest magnetic state in magnetic nano-materials, also called superspins. Nanomagnetic particles with suitable magnetic properties can be used as a highly efficient adsorbent's carrier. Magnetic nanomaterials can be classified into two types according to the intrinsic nature of the interaction between them. Ferromagnetic materials have positive magnetization. Supermagnetic materials have both positive and negative values of magnetization in a uniform distribution, although the particle does not exhibit net native magnetization [19]. The magnetic properties of nanomagnets are targeted from the interactions of the magnetic moments within the system. These properties are mainly dominated by shape, size, composition, and fabrication of the material, among many factors. The most common materials used for magnetic nanoparticles are iron, cobalt, nickel, and their corresponding oxides. The metals and their oxides are commonly used and have giant magnetic moments, making them suitable for various uses including catalytic applications, ferrofluid preparation, magnetic fluid hyperthermia and clinical applications, and magnetic particles as sorbents, among many other uses. The general properties of iron, cobalt, and nickel, the three most commonly encountered elements, show that all have positive bulk moments [20].

3.2. Synthesis and Characterization Techniques

There are several chemical methods used to prepare MNMs for adsorption studies. The reactions involve the chemical characteristics of iron to synthesize various forms of nanomaterials. Co-precipitation, hydrothermal, sol-gel, microemulsion, and green synthesis are important techniques to fabricate MNMs. The characteristics are quite different, mainly with the size and abundance of the magnetic metal oxide and to coordinate with precursors for different metal oxides to form the precursor system structure that reveals the corresponding functional nature. All techniques used to prepare MNMs reported good results during adsorption studies due to the functional groups and the progress of the modification on the surface of the MNMs [21].

3.3. Characterization of magnetic nanomaterials

Several techniques can be used to analyze the structure and functional groups on the surface or inside the MNMs. The structural measurements describe many aspects of the MNM structure, such as morphology, composition, size, and during the thermal decomposition process or in both, the crystallography behavior and diffraction ability are related to the magnetic properties. In simpler terms, the techniques used for the evaluation of the MNM structure are divided into three main fields: morphological measurements, structural analysis, and surface groups of MNMs. The reports provide an explanation of which method was used during the characterization of the magnetic materials, and diagnostic indicators used for each characterization method. This step is essential for an in-depth study of the impact of MNMs on the process of adsorption of cobalt ions by the activated carbon [22].

4. Adsorption of Cobalt Ions by Treated Activated Carbon

This comprehensive review explores the direct adsorption of cobalt ions on activated carbon. It discusses the mechanisms of chemisorption and physisorption, as well as the factors influencing the adsorption. The use of magnetic nanomaterials enhances the efficiency of the activated carbon. Agricultural waste residues are used as the raw material for the activated carbon, making the process sustainable. The review also covers the successful adsorption and desorption of cobalt ions under optimized conditions. Various models are explored to understand and predict the behavior of cobalt ions. Overall, this review highlights the potential of treated activated carbon in cobalt ion recovery. It serves as a valuable resource for researchers and engineers in this field [23]. Activated carbon with multiple micro-pore sizes possesses favorable adsorption mechanisms. Research frequencies have shown an increasing concern about the behaviors of the adsorbent in comparison to the single influence, as a consequence of several difficulties encountered. However, the utilization of natural sources to act as adsorbent resorted to one particular weak point: the low attraction straight of the activated carbon. Enhanced activated carbon with complex shapes and sizes ascribe to the addition of various supports onto raw material. Additionally, the adsorbent was adequately immobilized and handled via ultra-modern technology. An intermediate in determining the changed physio-sorbent in removing cobalt ions will be essential to the said catalyst configuration. Almost all studies unanimously agreed with the essential determinants of the adsorption behavior of cobalt ions, correlating with the magnitude of cobalt ions removed [24].

5. Applications and Future Perspectives

All of the reported experiments in this paper favor the applications of COFACPs in the fields of environmental protection and industry. In the field of environmental protection, they can convert nontoxic agricultural waste (e.g., potato peel) into a highly efficient adsorbent for heavy ions (e.g., Co(II)). This is significant for economically underdeveloped countries, which are the main potato cultivation countries, the leading Co producer, and the countries with the highest heavy metal pollution. Of course, given the high cost of the research illustrated in these papers, most of the world is unlikely to use it; then, magnetization modification can be made for the activated carbon made from rich iron waste, and it can be used on a large scale after modification. After the exhaust is unqualified, the magnetite-activated carbon can be recycled and recycled due to being cheap and easy to prepare, and this has certain application value. Therefore, the extensive application of magnetite-activated carbon mainly has the following industrial value [25]. Some research studies have made progress in this field using better raw materials to prepare absorbers for metal cobalt ions utilizing activated carbon double-modified by Fe3O4 and cetyltrimethylammonium bromide and a trifunctional sol-gel inspired method. Despite these findings, it is an undeniable fact that research on single-component metal cobalt ion removal is relatively mature. The research status of mixed heavy metal adsorption needs to be further studied in subsequent research works. In terms of the treatment of practical domestic and industrial pollution sources, it is relatively mature to study adsorption of single-metal Co by activated carbon and magnetite-activated carbon, and it has reached the level of preparative adsorption. The adsorbers reported in these studies are based on modified low-cost activated carbon, which has great research and application value for different raw materials. In order to give full consideration to the research value of COFACPs from different angles, it is pointed out in the paper that, in addition to the application of environmental protection, making use of this paper's research perspective from the aspects of agricultural residues, activated carbon, and magnetite, we proposed the preliminary experimental research on the application of magnetization carbon in the industry. The results and practical value of the waste materials in the study were combined to give recommendations and put forward the development direction of this research [26].

### 5.1. Environmental and Industrial Applications

This part discusses the use of the prepared adsorbents for the removal of Co(II) ions from water and in other industrial applications. As previously mentioned, the adsorptive removal of Co(II) ions is necessary for environmental remediation. Metal Co(II) can be adsorbed from water using the magnetic nanomaterial-immobilized treated activated carbon. This assists in the reduction of health and environmental hazards. The simplicity and effectiveness of the process make it viable for drinking water applications. In addition to water demetallization, the prepared adsorbents can be used in other systems to remove Co(II) from closed industrial spaces. In battery production, catalysts, and electronic circuit board production, Co(II) is heavily used. Given the diverse industrial applications, there is a great need to develop strategies for the accumulation of Co(II) to protect the environment and human health. Additionally, metal-centered enzyme models containing Co(II) can be used to imitate all carbonic anhydrase activity [27]. The constructed biomimetic catalysts of Co-bound nano-MOF-5 can be used in all-CO2 electrochemical reduction. LopezP from the Durrani Research Lab showed that MOF-5-derived cobalt nanoparticles with diameters of 10 nm exhibited excellent selectivity towards CO. MOF-5-based catalysts demonstrate the highest CO Faradaic efficiency (89.3% ± 7.7%) and long-term stability at helium levels throughout a 24-hour operation. Co(II) complexes with Schiff base ligands can also be used as coordination compounds to produce important areas of chemical and enzymological interest. Consequently, adsorbents derived from treated waste materials transform valuable compounds from those typically considered pollutants [28].

### 5.2. Challenges and Future Research Directions

Challenges: The use of different agricultural waste residues as precursors for the production of AC can provide a wealth of materials with diverse surface properties: texture, surface chemistry, and ratios of surface oxygen-containing acidic or basic functional groups. In this context, the challenges associated with the adsorption of Co(II) using magnetic nanocomposite-assisted AC prepared from agricultural waste can be conceived via facile nanocomposites and residue materials from ubiquitous substances such as banana and orange fruit peel, coco fruit peels, and mango fruit stone.

Future Research Directions: (1) While diverse adsorbent materials from agricultural waste residues have been studied, further research on AC activated via a combination of chemical, thermal, and microwave routes is needed. (2) Although the initial experimental results indicate that orange peel activated carbon obtained from prize-winning destroyed oranges provides an additional layer of Co(II) adsorption, a detailed report on copper nanoparticle-assembly-assisted cobalt adsorption on orange peel residue samples is anticipated. (3) Various magnetic (nano) composites, including zero-valent iron, Fe3O4, and various diluted and undiluted composite ferrite formulations, were used for Co adsorption. These data offer an abundance of information on how various nanocomposites can optimize Co(II) removal and provide a basis for future experimental research on several magnetic nanomaterials including zero-valent iron (nZVI), sulfides, and cobangelated nanomaterials. (4) Adsorption of other metals, dyes, and phenolic materials on waste-derived magnetic activated carbons (ACs) can be used as future research perspectives. This direction is based on the availability of preliminary information relevant to the ACs used in this review.

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