

Mini-Review: Removal of pharmaceuticals and dyes pollution from wastewater using modified agriculture wastes

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Abstract. The seepage, discharge or uncontrolled disposal of pharmaceuticals, antibiotics, and/or dyes into water bodies is a growing environmental and health concern. These substances, emanated from medical, agriculture, domestic and industrial activities, contaminate water and adversely impact ecosystems and human health. Traditional treatment methods, such as adsorption, bio-degradation, advanced oxidation, photo-catalysis, coagulation, ozonation and filtration are commonly used. Among these, adsorption using agricultural waste is preferred due to its cost-effectiveness, simplicity, practicality and availability/ease of bio-wastes processing. To enhance the performance of agricultural wastes for organic pollutants removal, modification(s) is (are) performed on the raw materials, either physically or chemically, to increase porosity/surface area, carbon content, surface functionality and (or) hydrophilicity.

1. Introduction

The production/use of pharmaceuticals, including anti-inflammatories, antibiotics, and analgesics, have surged in recent decades, with over 3,000 compounds produced annually in quantities exceeding hundreds of tons [1]. Antibiotics, widely used to strive bacterial infections, have drawn significant attention lately due to their persistence in the environment and their potential risks to physical and mental well-being and ecosystems [2]. Most drugs are not fully metabolized by living organisms (human/animals), leading to the excretion of active pharmaceutical compounds. Pharmaceutical compounds enter surface and groundwater from various sources. Urban wastewater is a primary contributor, carrying pharmaceuticals from human wastes and improperly discarded drugs. Agriculture and cattle-related activities also play a significant role as drug-laden animal feed and excreta (used as soil amendments) can leach into groundwater. Additionally, effluents from pharmaceutical industries, particularly in regions with loose regulatory enforcement, contribute high concentrations of pharmaceuticals [1].

Dyes, as persistent pollutants, contribute significantly to global water pollution, altering the physico-chemical properties of water and impeding light penetration. This impacts aquatic vegetation by hindering photosynthesis, which in turn disrupts the aquatic food chain [3].

Physicochemical and biological methods such as adsorption, biodegradation, advanced oxidation, photocatalysis, coagulation, ozonation, and filtration are commonly used to treat contaminant effluents as shown in Fig. 1. However, many of these methods are costly and generate sludge. Adsorption stands

out for its simplicity, efficiency, cost-effectiveness, and scalability [4]. Activated carbon is highly effective for contaminants removal in wastewater due to its excellent adsorption capacity. However, its high cost limits its widespread use, prompting the exploration of cheaper alternatives. Agricultural and industrial wastes, natural materials, and bio-sorbents are emerging as cost-effective and efficient substitutes for active carbon in adsorption [5]. Untreated agricultural wastes may have low adsorption capacity and can increase chemical oxygen demand (COD), biological oxygen demand (BOD), and total organic carbon (TOC) levels by releasing soluble organic compounds [6]. Therefore, modifying these wastes is crucial before their use as adsorbents. By Modifying the wastes physically and (or) chemically, porosity, surface area, carbon content, surface functionality, and/or hydrophilicity can be improved [7].

The goal of this mini-review paper is to bridge the major studies on agricultural wastes-based adsorbents for pharmaceuticals and dyes elimination from wastewater. The paper presents critical discussion of various agricultural wastes, pristine and modified, used to remove pharmaceuticals, focusing on adsorption as mechanism for wastes removal. A summary of adsorption efficiency, kinetics, equilibrium thermodynamics are included. Also, the influence of raw material treatment (physical/chemical) on adsorption efficiency is explained in terms of structure modification.

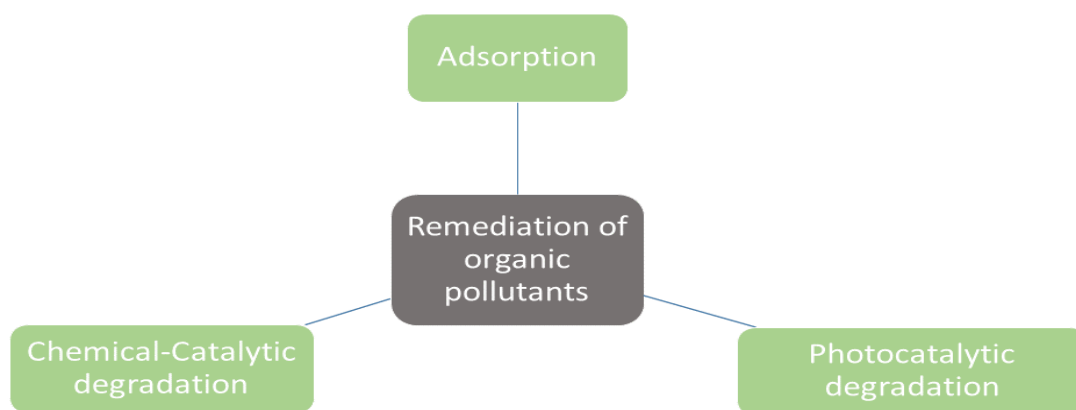


Figure 1. Overview of different treatments for the remediation of organic pollutants in wastewater.

2. Remediation from Pharmaceuticals

Pharmaceuticals pose significant environmental concerns due to their ability to induce physiological effects on humans and animals even at low concentrations. They enter the environment primarily via human and animal wastes. Despite adsorption is an effective wastewater treatment method, the high cost of commercial activated carbon has driven interest towards low-cost, sustainable alternatives like agricultural wastes. These materials are abundant, eco-friendly, and effective for adsorbing pharmaceutical contaminants [8].

2.1 Removal of Pharmaceuticals by adsorption

Research by O. Bello investigated the use of phosphoric acid-modified bean husk for removing ibuprofen from water. The FTIR showed the material had significant number of functional groups, including the -OH of alcohols and phenols (3402 cm^{-1}), C-H of alkanes (2929 cm^{-1}), C=O of ketones, lactones, and carboxylic anhydrides (1705 cm^{-1}), and C=O of carboxylic acids (1618 cm^{-1}), which

were useful for ibuprofen adsorption. The SEM images of both raw and treated bean husk showed that raw sample had an uneven surface with irregular pores, while after acid activation, a prominent regular pores have developed. Optimal adsorption occurred at pH of 4.75, with a maximum capacity of 50.0 mg/g. The adsorption process was well described by the Langmuir isotherm and adhered to pseudo-second order kinetics. Thermodynamic analysis indicated that the process was both spontaneous and endothermic [9].

In another study, O. Bello evaluated the phosphoric acid-modified kola nut husk as a non-conventional adsorbent for removing ibuprofen from water. EDX analysis showed that the activated sample contained less oxygen content and lacked some elements that were present in the raw sample, primarily due to the activation process. SEM revealed that activation significantly enlarged the pores from 1.56 nm to 2.91 nm. Experimental results showed that the maximum adsorption was achieved at 50 °C with initial drug concentration of 50 mg/l. The experimental data aligned with the pseudo-second order model, while Langmuir isotherm provided the best fit with a maximum adsorption of 39.22 mg/g. A negative Gibbs free energy and a positive enthalpy values suggested a spontaneous endothermic process [10].

2.2 Removal of Pharmaceuticals by Photocatalytic degradation

A Zn-pillared composite (Zn@CU/BEN), synthesized using bentonite modified with curcumin-derived chemicals, was evaluated as a cost-effective photocatalyst for ibuprofen removal from water. The catalyst achieved complete ibuprofen (25 mg/l) oxidation in 80 minutes and total mineralization after 160 minutes. The study showed that the maximum degradation efficiency (52.6%) of the hybrid catalyst was achieved at pH of 6, attributed to the enhanced solubility and retention of ibuprofen in slightly alkaline environment. Beyond pH of 6, degradation efficiency declined due to repulsive interactions between deprotonated ibuprofen groups and the negatively charged catalyst. The reaction pathway involved hydroxylation, decarboxylation, and ring-opening steps, with hydroxyl radicals as the key oxidizing agents. Following the ring-opening, the resulting intermediate products underwent further oxidation, ultimately leading to mineralization. This means that the complex drug molecule was completely broken down into simple, inorganic molecules, such as water (H₂O), carbon dioxide (CO₂), and possibly other basic minerals [11].

2.3 Concluding Remarks and Perspectives

The studies collectively highlighted the effectiveness of using modified agricultural wastes as low-cost, sustainable adsorbents for pharmaceuticals extraction from water as displayed in Table 1. Acid-modified banana stalks, bean husks, cocoa shells, algae as well as tea leaves show high adsorption capacities for drugs like Lumefantrine, ibuprofen, tramadol, and aspirin. These materials exhibit favorable adsorption kinetics, with most processes being spontaneous and endothermic. Future research should focus on optimizing the adsorption conditions for these materials and exploring new modifications in attempt to maximize the contaminants uptake. Meanwhile, investigating their reusability should be considered. Catalytic oxidation has not been widely applied to agricultural wastes for pharmaceuticals degradation. Currently, only activated carbons and biochars are utilized in pharmaceuticals catalytic degradation, highlighting the need to modify raw agricultural wastes for this purpose. Researchers should explore the potential of impregnating these wastes with metals/metal oxides to drive catalytic degradation to occur in line with adsorption.

3. Remediation from Antibiotics

Antibiotic residues in sewage treatment plants pose a risk to human health through promoting the development of antibiotic-resistant microorganisms when present in sub-lethal concentrations. Proper wastewater treatment is crucial before discharge into rivers, lakes, or sewage systems to prevent the spread of bacteria resistant to antibiotics and resistance genes being introduced into the environment [12].

3.1 Removal of Antibiotics by Adsorption

A study by T. Pham and T. Vu investigated the elimination of ciprofloxacin with protein-functionalized nanosilica. The protein was extracted from Moringa seeds, using petroleum ether and ammonium sulfate, while nanosilica was synthesized from rice husk. The FTIR spectrum of the extracted protein showed peaks relevant to C=O group (1643.35 cm^{-1}) and –NH group (amide I and II) at 1409.96 cm^{-1} . After nanosilica modification, the ciprofloxacin removal efficiency increased from 56.84% to 89.86%. Maximum adsorption was met at pH of 7.0 for 90 minutes using 10 mg/ml adsorbent dosage and 1 mM KCl ionic strength. Adsorption followed a pseudo-second order kinetics and the maximum adsorption capacity was 85 mg/g. The protein-modified nanosilica demonstrated strong electrostatic interactions with the drug, thanks to C=O and –NH groups. The adsorbent maintained high removal efficiency after three regeneration cycles [13].

Table 1. Summary of modified agricultural wastes employed for pharmaceuticals removal.

Adsorbent	Modification(s)	Drug	Removal mechanism	Uptake (mg/g) Removal %	Ref.
Bean husk	phosphoric acid	Ibuprofen	Adsorption	50.00	[9]
Kola nut husk	phosphoric acid	Ibuprofen	Adsorption	39.22	[10]
Curcumin	Incorporating curcumin into bentonite	Ibuprofen	Photocatalytic	52.6%	[11]

Another study explored the use of Indian almond leaf biomass, activated with concentrated sulfuric acid, for removing dicloxacillin from pharmaceutical wastewater. Maximum adsorption (86.93% removal) was achieved using optimal experimental conditions of pH=6.0, biomass dosage of 0.1 g/l, initial concentration of 20 mg/l, contact time of 24 hours and at 10 °C. The process followed pseudo-second order kinetics and was best described by the Langmuir isotherm giving adsorption capacity of 71.4 mg/g. The process was spontaneous and endothermic as demonstrated by thermodynamic study. The adsorption mechanism included physical interactions (hydrogen bonding and Van der Waal's forces) [14].

Rice straw was alkaline-modified to create an efficient biosorbent for removing ciprofloxacin from water. The maximum adsorption capacity of the NaOH-modified rice straw fiber was 93.5 mg/g, with adsorption equilibrium reached within 35 minutes. The biosorbent reached its highest adsorption capacity at a neutral pH and lower temperatures. The removal mechanism included hydrogen bonding. The adsorption process adhered to the pseudo-second order kinetics, the isotherm was properly described by Langmuir model [15].

3.2 Removal of Antibiotics by Photocatalytic degradation

The grafting of alkali-modified rice straw with TiO₂-gel layer remarkably enhanced ciprofloxacin removal, especially under UV exposure, achieving 153 mg/g removal. The adsorption and photo-degradation processes were collectively better described by the pseudo-second order model compared to the Langmuir-Hinshelwood model [15]. A recent study developed a novel bio-based photocatalyst using polymeric microspheres made by incorporating biomass-derived phenylpropenes onto the surface of amino-modified TiO₂ nanoparticles. These microspheres effectively degraded tetracycline, achieving a degradation efficiency of 97% [16].

3.3 Concluding Remarks and Perspectives

The aforementioned studies revealed that various mechanisms, including electrostatic interactions, hydrogen bonding, and π - π interactions have important roles in the removal of antibiotics. Photocatalytic process, combined with adsorption, were effective for antibiotic degradation, with

radicals, such as hydroxyl and superoxide, contributing to the photo-degradation as shown in Table 2. Adsorption kinetics generally adhered to the pseudo-second order model, suggesting that the removal rate is dependent on the adsorption sites. The Langmuir isotherm model best described the adsorption in most cases. Biomass modifications using, for example, TiO₂ gel or nanoscale zero-valent iron, significantly raised the removal capacities by increasing the adsorptive and catalytic properties of the bioadsorbent. Additional studies could aim at improving the regeneration and reusability of these adsorbents, as some materials exhibited promising removal efficiency even after multiple cycles. Last, researchers should investigate the outcome of impregnating agricultural wastes with metals/metal oxide in attempt to increase uptake by coupling adsorption with redox process.

4. Remediation from Dyes

Industries, especially paints sector, release around 10-15% of the 0.8 million tons of dyes, produced globally every year, into the environment. The dye industry is expected to grow by 2-3% annually due to increasing global production and consumption. Dyes often possess intricate aromatic structures, which contribute to their stability and resistance to biodegradation. Additionally, many dyes are toxic to microorganisms, disrupting or prohibiting their functions [4]. This underscores the ongoing need for effective, cost-efficient, and environmentally sustainable methods to remove such contaminants from wastewater.

4.1 Removal of Dyes by Adsorption

A study explored the use of dehydrated peanut hull, treated with sulfuric acid, as an adsorbent for removing methylene blue from water. The FTIR spectrum showed that the decreases in the -COOH peak intensity (1700 cm⁻¹) is attributed to the esterification reaction after acid treatment. Adsorption increased with increasing temperature (up to 50 °C) and dye concentration (up to 400 mg/ml), and when using smaller particle sizes (below 100 meshes). Adsorption data were best described by Langmuir model, which gave a maximum adsorption of 161.3 mg/g. The pseudo second order kinetics best fitted the experimental data, with the observation that the intra-particle diffusion process became the rate-controlling step at higher dye concentrations. During the dehydration of peanut hull with sulfuric acid, the carbohydrate hydroxyl groups were converted to esters. This created cation-exchanger functional groups; the cationic methylene blue was attracted and adsorbed by the anionic carboxylate groups formed during the treatment [17].

Table 2. Summary of modified agricultural wastes employed for antibiotics removal.

Adsorbent	Treatment	Antibiotic	Removal mechanism	Uptake (mg/g) Removal %	Ref.
Moringa seeds + rice husk	Extraction + grafting	Ciprofloxacin	Adsorption	85	[13]
Indian almond leaf	Sulfuric acid	Dicloxacillin	Adsorption	71.4	[14]
Rice straw	Sodium hydroxide	Ciprofloxacin	Adsorption	93.5	[15]
Rice straw	TiO ₂ gel + NaOH	Ciprofloxacin	Photocatalytic + adsorption	153	[15]
Bio-phenylpropenes	Extraction + grafting	Tetracycline	Photocatalytic degradation	97%	[16]

The phosphoric acid-activated coconut husk was evaluated as an adsorbent for removing Rhodamine-B dye from water. The changes in the intensities and positions of FTIR peaks revealed a

reduction in hydroxyl groups number and disappearance of phenolic and ether groups. Moreover, the activation process resulted in an increase in pores area and volume. These changes enhanced the material's adsorptive properties, which was reflected in a high monolayer adsorption capacity of 1666.67 mg/g (obtained by Langmuir isotherm), indicating strong affinity for the dye. Kinetics conformed to the pseudo-second order model and the thermodynamic analysis showed the process was spontaneous and endothermic ($\Delta H^\circ = 62.77$ kJ/mol) [18].

A study optimized the adsorption-based elimination of two dyes, methylene blue and acid red 73, using a chemically-modified oak wastes, applying experimental design technique. The experimental variables included pH (2-10), initial dye concentration (10-90 mg/l), contact time (20-200 min), and adsorbent dosage (0.5 to 2.5 g/l). The surface of the adsorbent was modified with different chemicals, with sodium hydroxide proving the highest performance for dye removal. With NaOH treatment, the removal efficiencies were 96% and 29% for methylene blue and acid red 73, respectively. The optimization showed that the best conditions for dye removal were a pH of 6.2, a contact time of 160 minutes, an adsorbent dosage of 2.0 g/l, and a dye concentration of 70 mg/l achieving 85.36% and 41.27% removal for methylene blue and acid red 73, respectively [19].

4.2 Removal of Dyes by Photocatalytic degradation

A novel bio-based catalyst was synthesized by grafting bio-phenylpropenes on amino-modified TiO₂ nanoparticles. The microspheres were effective in degrading Rhodamine-B dye, achieving degradation rate of 95%. The photocatalyst showed high stability, recyclability and followed pseudo-first order kinetics. The degradation process was driven by superoxide and hydroxyl radicals [28].

Table 3. Summary of modified agricultural wastes employed for dyes removal.

Adsorbent	Modification(s)	Dyes	Removal mechanism	Uptake (mg/g) Removal %	Ref.
Peanut hull	Sulfuric acid	Methylene blue	Adsorption	161.3	[17]
Coconut husk	Phosphoric acid	Rhodamine-B	Adsorption	1666.7	[18]
Oak waste	Sodium hydroxide	Methylene blue; Acid red 73	Adsorption	96 % 29 %	[19]
Bio-phenylpropenes	Grafting on TiO ₂	Rhodamine-B	Photocatalytic	95%	[16]
Sugar beet pulp; quinoa husk	Acid hydrolysis- Fe ₂ O ₃ impregnation	methylene blue; crystal violet; Congo red	Catalytic	98%; 96%; 62%	[20]

4.3 Removal of Dyes by Chemical-Catalytic degradation

A novel bio-based Fenton-like catalyst was synthesized by incorporating Fe₂O₃ nanoparticles into biomass-derived nanocellulose (NC). The NC samples were synthesized via acid hydrolysis of sugar beet pulp (SBP) and quinoa husk (QH) using various H₂SO₄ concentrations. The SBP-based NC (under conditions of 60% H₂SO₄, 1 hour at 50 °C) showed superior properties including higher crystallinity, larger surface area (13.9 m²/g) and greater surface charge. The SBP-based catalyst outperformed the QH-based one in removal efficiency due to its larger surface area and higher Fe content (6.7%). Under optimal experimental conditions (2 g/l catalyst, 30 mM H₂O₂, neutral pH, 30 min contact), Fe/NC composite achieved removal efficiencies of 98%, 96%, and 62% for methylene blue, crystal violet and Congo red, respectively. Kinetic studies indicated pseudo-first order. Increasing temperature from 15 °C to 35 °C improved dye removal. The catalyst demonstrated good reusability, retaining about 80% efficiency after ten cycles [20].

4.4 Concluding remarks and Perspectives

The dye adsorption behavior of agricultural wastes generally followed Langmuir and Freundlich isotherms, suggesting monolayer and multilayer adsorption, respectively. Kinetic studies predominantly adhered to the pseudo-second order model, indicating chemisorption processes. Future studies should focus on optimizing the modification processes (e.g. the concentration of modifying agents) and activation conditions, to maximize the adsorption capacity. Many of the reviewed research has concentrated on the removal of single dyes and future work should explore the simultaneous removal of multiple dyes from mixed wastewater streams, which is more reflective of real-world scenarios. Though many studies highlighted the regenerability of adsorbents, more work is still needed to understand the prolonged stability and reusability of these materials under practical conditions. Integrating chemical-catalytic degradation with adsorption could be a promising direction for future research, as well as the combination of adsorption and biodegradation process, where adsorbed dyes are biologically degraded, leading to a more sustainable and efficient treatment method.

5. Conclusions and Recommendations

The previously mentioned studies evaluated the effectiveness of modified agricultural wastes as for its an affordable cost and sustainable adsorbents for removing of pharmaceuticals, antibiotics and dyes from wastewater. Electrostatic interactions, hydrogen bonding, and π - π interactions were critical to adsorption. Langmuir and Freundlich isotherms predominantly described their adsorption behavior along with pseudo second order model for kinetics. Most papers used chemical treatment (acid/base), which removed the lignin, wax and (or) hemicellulose content, increasing porosity and surface area with little or no influence on the surface functionality. Surface grafting or impregnation of agricultural wastes with active ingredients (such as metals/metal oxides/organic ligands) has the potential to improve organic waste uptake by introducing additional removal mechanism(s) besides adsorption, such as chemical catalytic degradation and (or) photocatalytic degradation. As such, these approaches should be considered for future work. To enhance efficiency and reduce the time spent on waste removal, future research should work on optimizing operating conditions regarding chemical modification processes (grafting/impregnation/activation) and adsorption experiments using experimental design tools. Last but not least, efforts should be directed towards testing the performance of these adsorbents in continuous systems, mixed wastewater streams and real-world pharmaceutical wastewater scenarios. By addressing these recommendations, future research can improve the practical applications of agricultural wastes for wastewater treatment and assist in promoting sustainability and cost-effective environmental remediation strategies.

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