IOSR Journal of Applied Chemistry (IOSR-JAC)
e-ISSN: 2278-5736. Volume 18, Issue 7 Ser. 1 (July 2025), PP 01-13
www.iosrjournals.org

Agricultural Waste and Minerals based Adsorbents for the Elimination of Heavy Metal Ions from Wastewater – A Review

[1]Ashok Kumar, [2]Dr. Veerender Sharma[#] & [3]Dr. D. Singh Raghuwanshi
[1]ashokahim@gmail.com, [2]chemi.veeru@gmail.com & [3]rdrdeependrasingh@gmail.com
[1&3] Department of Chemistry, Govt. Madhav Science College, Vikram University, Ujjain, Madhya Pradesh
[2]Department of Textile & Fibre Engineering, Indian Institute of Technology,
Hauz Khas, New Delhi, 110016, India
#Corresponding author's contact: mail Id, ashokahim@gmail.com

Abstract: *Researchers today exhibit great enthusiasm for utilizing agro-waste and mineral-based adsorbents to eliminate heavy metal ions from aqueous solutions as well as industrial effluents. Adsorbents, which are solid materials, play a crucial role in eliminating impurities such as heavy metals from water—substances hazardous to both human state as well as the environment. The environment is a precious gift from God to all living beings, and safeguarding the earth's natural resources through careful planning and management is essential for the well-being of present and future generations. However, the growing population and unregulated exploitation of natural resources have led to severe pollution problems, posing significant hazards to life. Modern societies face critical challenges in wastewater management due to high population densities and large-scale industrialization. On a routine basis, wastewater from industries and domestic sources contributes to effluents that heavily pollute receiving water bodies, placing an immense burden on water quality management systems. Based on a review of the literature, future perspectives and conclusions have been presented, along with proposed directions for further research to address these pressing issues.*

Keywords: *Agricultural waste, minerals, Adsorbents, wastewater treatment*

Date of Submission: 02-07-2025 Date of Acceptance: 11-07-2025

I. Introduction:

The discharge from various industries contains both inorganic and organic hazardous waste, including heavy metal ions that are highly toxic and oncogenic, posing significant risks to humans and other living organisms [1,2,3]. Common heavy metal ions found in industrial waste include nickel, cadmium, lead, zinc, arsenic, copper, chromium, and mercury [4]. Heavy metals are defined as a class of metals or metalloids with atomic weights ranging from 63.50 to 200.60 g/mol and densities exceeding 5.0 g/cm^3 [5,6]. Examples include arsenic, lead, nickel, mercury, chromium, cadmium, silver, zinc, platinum, iron, palladium, and copper. Water contamination by heavy metals is primarily caused by industrial activities such as fuel combustion, mineral processing, mining, metallurgical operations, explosive manufacturing, electroplating, paper production, paint manufacturing, battery production, pigments, and photographic materials [7,8].

In India, the permissible limits (ppm or mg/mL) for hazardous metals like arsenic, mercury, lead, zinc, cadmium, chromium, nickel, and copper are 0.050, 0.00003, 0.006, 0.80, 0.01, 0.05, 0.20, and 0.25, respectively [9]. Various treatment technologies are employed to remove heavy metals from wastewater, including adsorption [10], nanofiltration, electrodialysis, membrane separation [11], reverse osmosis, ultrafiltration, chemical precipitation, reduction, ion exchange, oxidation, and ion flotation [12]. Among these, adsorption stands out as the most effective method due to its cost-effectiveness and eco-friendly nature. Other methods often generate large amounts of mud, have low yield, require critical operative provisions, and involve high disposal costs. Adsorption is particularly attractive because cost-effective adsorbents can be synthesized from agricultural waste. Consequently, adsorption has emerged as a viable, economical, and environmentally friendly alternative for wastewater treatment. Heavy metals are non-biodegradable and can bioaccumulate through food chains, causing severe impacts on living organisms [13]. This process is advanced, adaptable, and reversible, allowing for the regeneration and reuse of adsorbents.

The efficiency of adsorption determined by the number of active sites on the surface, which are attributed to the presence of potential functional groups such as hydroxyl (-OH), carboxyl (-COOH), amino (-NH_2), and sulfonyl (-SO_3H) on the adsorbent surface [14]. The toxicity and permissible limits of specific heavy metals, as defined by the International Organization, World Health Organization (WHO), are summarized in Table I.

Table-I: Heavy metal ions, permissible limits and their adverse effect according to World Health Organizations

S. No.	Toxic Metals	Acceptable Limit (mg/L) (WHO)	Health Hazards
1.	Cobalt (Co)	0.100	Harmful to the thyroid as well as liver, respiratory issues, Asthma like allergy, carcinogenic, injurious to the heart [15].
2.	Lead (Pb)	0.050	Increased risk of high blood pressure, neurological problems, hematological effects, renal effects, vomiting, cardiovascular effects [16].
3.	Chromium (Cr)	0.050	Headache, liver and kidney disease diarrhoea, internal bleeding, Nasal septum perforation and ulceration, vomiting, lung and skin cancer [17].
4.	Arsenic (As)	0.010	Cardiovascular diseases, lung, Skin, kidney, and bladder cancer, skin lesions, neurological disorder, nervous system disturbances, muscular weakness and nausea etc. [18].
5.	Zinc	5.000	Reduced immune functioning, Depression, Dizziness and headaches, lethargy, anemia, neurological problems, dehydration and loss of apetite [19].
6.	Mercury (Hg)	0.001	Kidney damage, Neurological problem, eye staining, paralysis, digestive problems, rheumatoid arthritis, lungs and skin damage and anorexia [20].
7.	Copper (Cu)	2.500	Wilson disease (autosomal recessive disorder), Insomnia, neurodegeneration, Liver problems, [21].
8.	Cadmium (Cd)	0.003	Respiratory problems, Kidney damage due to formation of kidney stones, renal disorder, risk of lung cancer, emphysema [22].
9.	Nickel (Ni)	2.000	Kidney and cardiovascular diseases, Dermatitis, skin irritation, nausea, gastrointestinal problems, chronic asthma, and cancer [23].
10.	Iron (Fe)	0.300	Aesthetic based problems, harmful to pancreas, liver and heart., Brittle nails, Tinnitus, Gastrointestinal problems [24].
11	Manganese (Mn)	0.500	Nervous system damage, motor disfunction, permanent brain damage, Parkinson disease and respiratory effects [25]

The elimination of heavy metals or ions has consistently been a challenging task for researchers or inventors, as potential adsorbents are essential for their removal. Agricultural-based adsorbents offer several advantages over conventional chemical-based sorbents in water treatment processes. These include biodegradability in natural and environmental settings, large surface area, abundance in nature, high affinity to adsorb hazardous metal ions, suitable pore dimensions, increased mechanical strength, and compatibility. Additionally, they are easily accessible, recyclable, low-cost, eco-friendly, and have simple synthesis processes. Their structures possess a excessive surface area-to-volume ratio and multifarious active binding sites, such as –NH$_2$, –COOH, –SH, and –OH groups, which enable effective adsorption of heavy metals under specific conditions [26, 27].

Adsorption primarily depends on the interaction of amino, hydroxyl, and carboxylic groups on the adsorbent's surface with hazardous metal ions, including lead (Pb^{2+}), chromium (Cr^{3+}), and copper (Cu^{2+}) cations [28, 29].

Currently, there have been a improved interest in naturally occurring non-conventional biomass as well as organic adsorbents and low-cost materials derived from agricultural wastes. Examples include rice husks, sugarcane bagasse, cotton, kapok fibers, and various types of fruit wastes or peels such as apple pomace, banana peels, and orange peels. These materials have been effectively used in environmental remediation [30, 31, 32], as summarized in Table II. They are derived from sustainable sources and are cost-effective, non-toxic, non-corrosive, and fully active in recycling processes

Table-II: Different Types of Agriculture Waste Based Adsorbents immersed for the exclusion of Heavy Metals or Ions from Wastewater or Industrial effluent

S. No.	Sorbents	Adsorbent site	Adsorbent Mode	Adsorption Capability (mg/g)	References
1.	Coconut exterior shell	Cellulose	Modified/Transformed	2.48	[33]
2.	Rice based husk	Cellulose	Modified/Transformed	6.0–9.0	[34]
3.	Wool based fibre	Keratin	Natural/Raw + Modified/Transformed	12.0	[35]
4.	Corn cob	Cellulose	Modified/Transformed	4.21–7.80	[36]
5.	Green macroalgae	Cellulose	Modified/Transformed	19.38–23.08	[37]
6.	Hazelnut shells	Cellulose	Modified/Transformed	41.3	[38]
7.	Coconut fibre	Cellulose	Modified/Transformed	13.2–14.0	[39]
8.	Pineapple leaf waste	Cellulose	Modified/Transformed	37.9	[40]
9.	Wheat straw	Cellulose	Modified/Transformed	41.84	[41]
10.	Sunflower stalk	Cellulose	Modified/Transformed	39	[42]
11.	Papaya seed	Cellulose	Modified/Transformed	55.6 37.43	[43]
12.	Sugar beet pulp	Cellulose	Modified/Transformed	73.53	[44]
13.	Palm shell	Cellulose	Modified/Transformed	83.33	[45]
14.	Wheat bran	Cellulose	Modified/Transformed	62	[46]
15.	Chicken feathers	Keratin	Modified/Transformed	6.1	[47]

16.	Sunflower stalk	Cellulose	Modified/Transformed	182.90 69.80	[48]
17.	Palm ash	Cellulose	Modified/Transformed	61	[49]
18.	Mango peel	Cellulose	Modified/Transformed	46.09 39.75 28.21	[50]
19.	Cotton fibre	Cellulose	Modified/Transformed	25–75	[51]
20.	Orange peel	Cellulose	Modified/Transformed	200	[52]
21.	Sugarcane bagasse	Cellulose	Modified/Transformed	38.03	[53]
22.	Cashew nutshell exterior	Cellulose	Modified/Transformed	22.11	[54]
23.	Rice husk	Cellulose	Modified/Transformed	15.0	[55]
24.	Paper waste	Cellulose	Modified/Transformed	29.67	[56]
25.	Bamboo powder from leaf	Cellulose	Modified/Transformed	28.1	[57]
26.	Vegetable based fibres	Cellulose	Natural/Raw	85.0	[58]
27.	Silk based fibre	Cellulose	Modified/Transformed	46.83	[59]
28.	Wastepaper	Cellulose	Modified/Transformed	24.4	[60]
29.	Hazel nutshell	Cellulose	Modified/Transformed	28.18	[61]
30.	Kapok fibre	Cellulose	Modified/Transformed	46.9–58.8	[62]
31.	Banana	Cellulose	Modified/Transformed	5	[63]
32.	Wheat straw	Cellulose	Modified/Transformed	6.91	[64]
33.	Banana peel	Cellulose	Modified/Transformed	32.40 68.92 99.09	[65]
34.	Rice husk	Cellulose	Modified/Transformed	6.22	[66]
35.	Sugarcane bagasse	Cellulose	Modified/Transformed	13.72	[67]
36.	Chicken feathers	Keratin	Modified/Transformed	50.0	[68]
37.	Pigeon feathers	Keratin	Modified/Transformed	30.0	[69]
38.	Rice husk	Cellulose	Modified/Transformed	19.66	[70]
39.	Corn stalk	Cellulose	Modified/Transformed	21.37	[71]

Different Types of Agriculture Waste Based Adsorbents Employed for the Elimination of Heavy Metals or Ions from Sewer water or Industrial effluent

There are several types of Agriculture Waste Based adsorbents that are employed for the elimination of heavy metals or ions from sewer water/wastewater or industrial effluents. Some of them are explained as follows:

A variety of agricultural wastes or residues have been transformed or impregnated using surfactants [72–75]. Surfactants are the substances that are amphipathic in nature and contains both lyophobic (water-repelling) and lyophilic (water-attracting) groups, enabling them to form self-assembled or self-involved clusters. Based on such type of hydrophilic groups that they possess, surfactants are categorized in three types: (i) cationic surfactant that have positive charge, (ii) anionic surfactant that have negative charge, (iii) non-ionic that have no apparent charge and generally called zwitterion (exhibits both positive and negative charges). These unique properties make surfactant-transformed or modified adsorbents more advanced in elimination efficiency and effective for selective adsorption [76,77].

Transformed Sugarcane Bagasse as an adsorbent:

Sugarcane bagasse is a residual product of agricultural waste, is made up of primarily of 23% lignin, 50% cellulose, and 27% polyoses. It is the solid residue or fibrous material left after the extraction of sugarcane juice. Due to its biological polymeric components, sugarcane bagasse is well abundant in phenolic as well as hydroxyl groups. Such types of functional groups can be transformed chemically to enhance its adsorption capability [78].

The sugarcane bagasse was analyzed for X-ray diffraction (XRD) and this analysis exhibits a minimum intensity at the shoulder peaks ($2\theta = 16°–18°$), corresponding to the amorphous part of cellulose, and a prominent peak at $2\theta = 19°–25°$, which indicates the crystalline nature of cellulose. Sugarcane bagasse is obtained from both the external rind and internal pith [79] and can be utilized in its natural form or chemically transformed form.

Sugarcane bagasse is widely used as a inexpensive biosorbent for the elimination of heavy metal ions or dyes from sewer water/wastewater and industrial effluents. However, it has certain limitations. Fresh sugarcane bagasse has relatively low adsorption capacity and must be purified and pretreated to remove surface impurities. Chemical treatments with various reagents can significantly improve its adsorption performance, although these treatments increase the overall cost of the process.

Ahmad et al. (2013) demonstrated the elimination of chromium metal ions using chromium-resistant bacteria as well as Acinetobacter haemolyticus, embedded in sugarcane bagasse. This bacterium transforms toxic Chromium (VI) into less toxic and less soluble Chromium (III), achieving over 90% elimination [80].

Chemical Modifications for Improved Adsorption

Chemical reagents used for modifying sugarcane bagasse include:

Acids- Nitric acid, sulfuric acid, phosphoric acid, and pyromellitic anhydride.

Chelating Agents- Ethylenediamine tetraacetic acid dianhydride (EDTAD), succinic anhydride, citric acid, and xanthate.

Other Chemicals- Ethylenediamine and sodium bicarbonate.

These chemicals function as excellent chelating agents. When chemically bound or polymerized with sugarcane bagasse, such types of transformations maximize the active adsorption sites, facilitating the removal of hazardous metals or ions from wastewater. Garg et al. treated residuals of sugarcane with 1,4-butanedioic acid and achieved 92% chromium removal with reference to optimal pH of 2 [82]. Cronje et al. reported over 87% chromium removal via treating sugarcane bagasse using $ZnCl_2$ (zinc chloride) with reference to optimal pH of 8.58 [83].

Table-III: summarizes the potential applications of sugarcane bagasse as adsorbent, particularly for the elimination of chromium from sewer water/wastewater.

Adsorbent	Metal Ions Concentration (mg/L)	Ideal pH	Adsorbent dose (g/L)	Adsorbent Capability (mg/g)	Elimination percentage (%)	References
Acinetobacter haemolyticus bacteria present in the interior of sugarcane bagasse	10-100	7	-	-	> 90	[80]
1,4-Butanedioic acid transformed sugarcane bagasse	50.0	2.0	20	-	92.0	[81]
Sugarcane bagasse activated by the use of zinc chloride	77.5	8.58	6.85	-	> 87	[82]

Transformed Orange Peel Residue or Waste as Adsorbent

Orange peel as an adsorbent has been effectively employed for the elimination of chromium ions from sewer water or industrial effluent. This is attributed to its composition, which primarily includes lignin, cellulose (22%), polyphenols (28%), hemicellulose (11%), and pectin (galacturonic acid) (25%) [84]. These components impart various functional groups and coordinating sites, such as carboxylic (-COOH) and phenolic acid groups, that facilitate the adsorption of hazardous metals. Additionally, residual orange peel is considered pleasant adsorbent due to its abundant availability, inexpensive and eco-friendly nature [83]. The Orange peel has not fixed chemical composition which depending on factors such as variety, weather, soil properties, location, ripening time, maturity level as well as planting conditions [84]. According to Mafra, orange peel predominantly contains 97.80% organic content, including oxygen, carbon, starch, hydrogen, fiber, nitrogen, sulfur as well as sugars, along with minor amounts of ash and cellulose chloride [85].

Bampidis validated these findings, revealing that the dehydrated part of residual orange peel is primarily composed of organic content [86]. It contains small chains of acids as organic with not more than four number of carbons, as well as proteins. Other studies have proposed that residual orange peel comprises of dissolved sugars, cellulose, starch as well as fiber, hemicellulose, lignin, pectin, ash, protein, fat, and about 1% organic acids [87]. As summarized in Table IV, the chemical components of residual orange peel indicate that it is primarily composed of organic matter, making it a valuable material for adsorption applications.

Table-IV: Elemental Chemical constitution of orange peel

Chemical Constitution	Mass (%) [87]	Mass (%) [88]	Mass (%) [89]
Carbon	49.590	44.500	47.000
Calcium	-	-	-
Oxygen	39.700	47.300	44.710
Sodium	-	-	-
Chloride	0.001	-	0.001
Potassium	-	-	-
Sulphur	0.060	0.400	0.090
Nitrogen	0.660	1.500	1.300
Water	2.730	-	-
Hydrogen	6.950	6.100	6.000
Ash	3.050	4.000	-

The chemical constitution of orange peel has been studied extensively for its application as a bioadsorbent. As per Marin et al. investigated the roles of three such functional groups ($-NH_2$, -COOH, and -OH) in chromium elimination (2010). The study belonging to them, the residual orange peel bioadsorbent was chemically transformed through methylation, esterification, and acetylation processes to selectively block and hinder specific functional groups [90]. Their findings revealed that the esterification process significantly reduced the adsorption capability, suggesting that the some of active functional groups like carboxylic acid (-COOH) exists or readily available in the adsorbent are crucial for metal ions elimination like chromimum. In contrast, the $-NH_2$ as well as -OH groups were found to have very minor effects. The highest adsorption capability was disclosed by the research scientists was 40.60 mg/g of chromium biosorbed onto pre-processing residual orange peel in one as well as other single or binary mixtures [91]. The elimination percentage and adsorption capability was obtained 4.79 mg per g with 51 % in single phase and for binary system it was increased up to 7.60 mg per g with 79 % for chromium elimination which is prepared by impregnating iron nano-particles with residual orange peel pith [90]. It was reported that using such composite, the capability of adsorption as well as elimination percentage are 5.37 mg per g, 71.0% respectively evaluated against orange peel that is 1.90 mg per and 34% [92]. Table V provides a detailed analysis of the narrated usage of refined orange peel residue or waste for chromium elimination as adsorbent from wastewater or industrial effluents.

Table-V: Chromium elimination using Transformed Orange Peel

Adsorbent	Metal Ions Concentration (mg/L)	Ideal pH	Adsorbent dose (g/L)	Adsorbent Capability (mg/g)	Elimination percentage (%)	References
Pre-treated residual orange peel	10	3.0	10.0	40.56	82	[91]
Transformed orange peel	0-500	4.0	4.0	4.79, 7.60	51, 79	[90]
Orange peel with composites of Iron nano-particles	10-50	1.0	5.0	1.90, 5.37	34, 71	[92]

Transformed Wheat Bran

Wheat bran, a byproduct obtained from agriculture and isolated from the exterior part of wheat seeds during flour milling, is widely recognized for its applications in eliminating heavy metal ions from sewer water/ watsewater as well as effluents generated from industries, particularly for chromium ion elimination. As the most widely cultivated cereal globally, wheat provides an economical, biodegradable, and nutrient-rich resource for such applications. Wheat bran is also viable and cost-effective for use as a biosorbent due to its different functional moieties and 442 m²/g as large surface area, along with a carbon part of 31.80%. According to Ravat et al., The functional moieties present in wheat bran—such as carbonyl (-CO), methoxy ($-OCH_3$), hydroxyl (-OH), and phenolic groups—exhibit strong binding capabilities for heavy metal ions. Whlie Farajzadeh and Monji reported that untransformed wheat bran could eliminate chromium with a topmost adsorption capability of 92.9 mg/g and an elimination efficiency of 88.9%. Advancements in transforming wheat bran have further improved its adsorption efficiency. Ozer et al. (2006) chemically modified wheat bran using sulfuric acid (H_2SO_4), which enhanced its chromium adsorption capacity to 132.9 mg/g at an optimal pH of 1.50. Similarly, Kaya et al., employed 2,3-Dihydroxybutanedioic acid to transform wheat bran. They observed a significant increase in chromium removal efficiency, from 51% without transformation to 90% after transformation. The adsorption capacity improved from 4.50 mg of Cr (VI) to 5.30 mg of Cr (VI) at an ideal pH of 2.2. A comparative analysis summarized in Table VII highlights the efficiency of transformed wheat bran as a cost-effective adsorbent for chromium elimination. The bio-sorption capability of wheat bran and its transformed variants makes it a promising material for environmental remediation efforts.

Table-VI: Chromium Elimination by using transformed Wheat Bran

Adsorbent	Metal Ions Concentration (mg/L)	Ideal pH	Adsorbent dose (g/L)	Adsorbent Capability (mg/g)	Elimination percentage (%)	References
Raw Wheat bran	20	5.0	80.0	93	89.0	[93]
Wheat bran transformed by the use of sulfuric acid	50, 100	1.5	2.0	133	99.9	[94]
Wheat bran transformed by the use of 2,3-Dihydroxybutanedioic acid	52	2.0, 2.2	20	5.28	90.0	[95]

Rice Husk:

Rice husk, a bio-based adsorbent material, is widely recognized for its effectiveness in pollutant removal. As a low-cost and renewable resource, it represents the primary agricultural waste generated during rice processing. The composition of rice husk includes mineral ash (15.1%), lignin (21.4%), cellulose (32.2%), and hemicellulose (21.3%) [96]. Its granular structure, combined with chemical sturdiness and superior mechanical strength, makes it particularly suitable for such applications [97]. Silica can be extracted from residual rice husk using the wet chemical method, demonstrating a strong affinity for chromium [98]. Residual rice husk may be employed both in its raw form and in chemically transformed forms, such as activated carbon produced via ozone treatment. Studies comparing these forms show that chemically transformed rice husk exhibits higher efficiency in chromium (VI) removal [99,100]. Ozone, a stable and powerful oxidizing agent, is commonly employed for activating rice husk. It can also be regenerated, enhancing the material's adsorptive properties. In addition, residual rice husk may be transformed into biochar, a high-carbon solid material obtained through the pyrolysis of rice husk at low temperatures and in the absence of oxygen [101–106]. Scientists has expressed that ozone-treated residual rice husk significantly improves chromium removal compared to raw rice husk. For instance, Sugashini and Begum (2015) achieved 86% chromium elimination by transforming rice husk into activated carbon using ozone treatment [100]. In summary, rice husk—whether in its raw, ozone-transformed, or biochar form—serves as an effective and eco-friendly adsorbent for chromium removal, offering promising potential for wastewater treatment applications

Table-VII describes the indicated the usage of residual rice husk for elimination of heavy metal ions of chromium from wastewater/ sewer water or industrial effluent.

Adsorbent	Metal Ions Concentration (mg/L)	Ideal pH	Adsorbent dose (g/L)	Adsorbent Capability (mg/g)	Elimination percentage (%)	References
Ozone-transformed rice husk	50.0, 100.0	2.0	4.0	8.7-13.1	86.0	[100]
Transformed rice husk	190.0, 850.0	6.8	1-16	-	95.0	[106]

Transformed Sawdust

Sawdust is a waste product or by-product generated from woodworking operations such as sawing, sanding, milling, and routing. It consists of very small wood chips. Sawdust has gained significant importance in the adsorption of wastewater/sewer water pollutants or industrial effluents because of several groups that are functional in its structure, including hydroxyl (-OH) group, carboxyl (-COOH) group, phenolic groups well as amide groups (-$CONH_2$). These groups are highly favorable for adsorbing various types of dyes [107].

Additionally, the adsorption power of sawdust can be enhanced through chemical transformations using acids and bases. Sawdust has been widely employed as an adsorbent for the elimination of heavy metal ions, showing promising results in elimination processes [108].

For example, Politi & Sidiras utilized pine sawdust treated with 0.10–3.60 N H_2SO_4 (sulfuric acid) to remove chromium, achieving a topmost adsorption capability of 20.28 mg/g and an 86% elimination efficiency at an optimal pH of 2 [109]. Similarly, Argun et al. (2007) treated oak sawdust (Quercus coccifera) with hydrochloric acid to enhance its adsorption properties for chromium removal [110].

This acid treatment creates additional active sites while preventing the leaching of tannin compounds, which could otherwise stain treated water. The study reported a topmost elimination efficiency of 84.0% for Cr (VI) and an adsorption capability of 1.70 mg/g at an optimal pH of 3.

Table-VIII highlights the applications of transformed sawdust as an adsorbent for the elimination of metal ions of chromium from wastewater/sewer water and industrial effluents.

Adsorbent	Metal Ions Concentration (mg/L)	Ideal pH	Adsorbent dose (g/L)	Adsorbent Capability (mg/g)	Elimination percentage (%)	References
Sulfuric acid transformed pine sawdust	15-75	2.0	4.0	20.3	-	[109]
Hydrochloric acid transformed oak saw dust (Quercus coccifera)	0.1-100	3.0	60	1.70	84	[110]

Transformed Coconut Waste Material

Coconut waste, or husk, possesses advantageous properties such as configurational stability, porous structure, and high adsorption capacity, making it a suitable adsorbent for wastewater treatment. Coconut waste is commonly obtained from coconut milk processing markets. In India alone, approximately more than 6.5 megatons of coconut are produced annually [111]. The primary constituents of raw coir pith include fats (1.80%), cellulose (38.0%), lignin and resin (25.20%), pentosans (7.50%), ash content (8.70%), and moisture content (11.90%). Among low-cost adsorbents, coconut-based materials like coconut husk, coconut shell fiber, and coir pith have demonstrated excellent adsorption capabilities for removing hazardous pollutants from industrial effluents and wastewater.

The sorption properties of coconut waste stem from the existence of functional groups that are coordinated including hydroxyl (-OH) as well as carboxyl (-CO) groups [112]. Coconut shell and coir pith are particularly effective in removing heavy metals or ions. For example, Namasivayam and co-workers transformed coir pith using cationic surfactant cetyltrimethyl Ammonium Bromide for the elimination of heavy metal ions of chromium. They reported an optimum elimination efficiency exceeding 90.0% at an ideal pH of 2, with the highest adsorption capability recorded at 75.30 mg/g [113].

Similarly, according to Shen et al. achieved a maximum chromium ion removal efficiency of 70% using coconut coir and its derived char [114].

Table-IX summarizes the applications of transformed coconut waste as an effective adsorbent for chromium elimination.

Adsorbent	Metal Ions Concentration (mg/L)	Ideal pH	Adsorbent dose (g/L)	Adsorbent Capability (mg/g)	Elimination percentage (%)	References
Transformed coir pith by the use of cetyltrimethyl Ammonium Bromide	25-95	2.0	50.0	76.30, 1.24	Greater than 90	[113]
Derived char as well as coconut coir	10-450	3.0	1.0	70.40	70	[114]

Activated Carbon:

Activated carbon is an inert carbon matrix with microporous, and heaving increased outer surface area wich is ranging from 650 to 14500 m^2/g, making it ideal for adsorption. It is the mainly the first category of adsorbents physically, encompassing with the extensive range of adsorbents with different types of properties. Due to its unique characteristics, activated carbon exhibits an exceptional ability to capture water-dissolved contaminants through adsorption, a process based on surface interactions between contaminants and the graphitic platelet surfaces of carbon.

Activated carbon is particularly effective in eliminating chromium metal due to its enhanced structure, porosity, and additional innermost surface area for adsorption. Karthikeyan studied the removal of chromium metal ions from wastewater/sewer water by the use of activated carbon which is isolated from sawdust rubber wood, attaining an adsorption capability of 44 mg/g at an optimal pH of 2. This capacity was enhanced in comparison to other types of adsorbents, for example coconut tree sawdust (3.60 mg/g), coconut shell carbon (10.88 mg/g), sugarcane bagasse (13.40 mg/g), and transformed sawdust of Indian rosewood (10 mg/g).

In another study, Kobya (2004) synthesized activated carbon from hazelnut shells, achieving a topmost adsorption capability of 170 mg/g at an ideal pH of 1. This capacity surpassed the adsorption capabilities of other adsorbents, such as wood activated carbon (87.6 mg/g), tyre activated carbon (58.5 mg/g), and coconut shell activated carbon (107.1 mg/g).

Table-X explains with brief summary for the indicated usage of activated carbon for the elimination of chromium meta ions from effluent or wastewater.

Adsorbent	Metal Ions Concentration (mg/L)	Ideal pH	Adsorbent dose (g/L)	Adsorbent Capability (mg/g)	Elimination percentage (%)	References
Syzygium jambolanum nut carbon	20-100	2	5	-	100	[115]
Acrylonitriledivinylbenzene co-polymer	30	2	0.6	101.2	80	[116]
Wood of Tamarind	10-50	6.5	2	-	28	[117]
Wood of Jatropha	30-100	2-10	0.6-2	106.4-140.8	-	[118]
Prawn shell	25-125	-	-	100	98	[119]

Mineral-Based Adsorbents:

Mineral-based adsorbents have attracted significant attention from researchers due to their abundance, ease of retrieval, cost-effectiveness, and strong adsorption capability. Many natural minerals, such as clays, silica, chitosan, and zeolites (including montmorillonite, kaolinite, and bentonite), are known to be effective in the elimination of heavy metal ions. Clay, a type of small particle primarily found on the Earth's surface, is mainly composed of silica, alumina, water, and weathered rocks. Clay as well clay-occupied composite materials have been developed as more adequate adsorbents for the elimination of heavy metal ions from water solutions.

Recent studies often involve the modification and enhancement of clays and chitosan by incorporating other adsorbents to improve their efficiency. For example, a study by Yin et al. [120] utilized a co-condensation method to produce a silica sorbent functionalized with amidoxime groups. Table-XIV presents recent studies that have employed real mineral-based adsorbents for heavy metal ion elimination, using adsorption methods. These studies include information on the targeted metal ions [121,122,123].

Table-XI: Heavy metal adsorption capabilities of different real mineral-based adsorbents

Adsorbent	Target Metal Ions	Ideal pH	Adsorbent Capability (mg/g)	References
Carboxymethyl chitosan–hemicellulose	Cu Cr Hg Ni Cd Mn	6 4 4 4 4 4	362.30 909.10 333.30 42.00 28.20 49.00	[121]
Carboxylate functionalized-chitosan co-polymer	Pb Cu Cd Zn	6 6 6 6	127.91 123.50 108.42 92.27	[122]
Synthetic NASO Zeolite ($Na_6Al_6Si_{10}O_{32}.12H_2O$)	Cd Pb	5 5	649.00 210.00	[123]

Clay mineral adsorbents

The adsorption process involves the attraction and retention of molecules (contaminants) on the surface of the adsorbent (clay). There are various types of clay, each exhibiting unique adsorption properties. Primarily clay based minerals are phyllosilicate minerals which are characterized by layered structural units consisting of one or two tetrahedral silica sheets sandwiched between an octahedral aluminium sheet [124]. Generally, clays possess three distinct types of internal surfaces: edges, external surfaces, and surfaces between silicate layers. Both the external surface and the internal layer are susceptible to modifications during adsorption processes as well as ion exchange. Clay minerals typically develop a small net negative surface charge due to isomorphic substitution. These minerals are widely used as effective adsorbents for removing heavy metal ions from aqueous solutions, as outlined in Table XV, which describes clay minerals, functionalized organic spices, and their applications in the adsorption of various heavy metal ions.

Clay minerals are effective adsorbents due to their properties such as low cost, high surface area, accessibility, and cation exchange capability, among other advantages, which facilitate their use in various applications [125]. In addition to clay minerals, other materials like vermiculites, kaolinites, saponites, halloysites, montmorillonites, and bentonites are also desirable. These materials can be used in their raw form or after processes such as cleansing, purification, reformation, or functionalization [126-132].

Table-XII: Clay based minerals, functionalization organic spices and used for the adsorption of various heavy metal ions

Clay	Organic Spices	Heavy Metal Ions	Effectiveness (mg/g)	References
Magnetite/Kaolin	Ethylenediamine	Pb (II) Cu (II) Cd (II)	86.1 16.5 22.1	[113]
Illite/smectite	3-aminopropyltriethoxysilane	Pb (II)	227.8	[134]
Vermiculite	3-aminopropyltriethoxysilane	Cr (VI)	59.17	[135]
Vermiculite	Ethylamine	Cs	78.17	[136]
Smectite	3-aminopropyltriethoxysilane/Zn	Pb (II)	20	[137]
Montmorillonite	chitosan	Cu (II)	181.5	[138]
Bentonite	3-aminopropyltriethoxysilane 3,2-aminoethylaminopropyltrimethoxysilane	Pb (II)	27.65 29.54	[139]

Silica Gel as an Adsorbent

Silica gel, a partially hydrated material composed of SiO2 units with high porosity, is a typical adsorbent that supports specific interactions. It is considered a good porous material and consists of a three-dimensional polymer formed by silicon dioxide units. Silica gel is particularly effective as an adsorbent for substances like water, phenols, alcohol, amines, and more. Commercial silica gels often contain a mixture of Al2O3 and Fe2O3, which contribute to irreversible sorption and may also have a catalytic effect.

Silica gel is widely studied for water vapor adsorption due to its large surface area and high porosity, making it useful in a variety of adsorption applications. Its unique physical and chemical properties enhance its effectiveness as an adsorbent. Because silica gel is made of silica, it has high thermal stability, which allows it to withstand varying temperatures and pressures in industrial processes. Additionally, it is non-toxic, making it suitable for moisture-adsorbing applications.

Zeolite as an Adsorbent:

Zeolites are natural as well as synthetic hydrated microporous aluminosilicates which are hydrated microporous, which may be characterized by the presence of channels occupied by substitutable cations as well as zeolite water. These materials are not only environmentally friendly but also cost-effective. Natural zeolites are hydrated as well as porus aluminosilicates with pores vary from macropores to mesopores. They possess suitable properties which are ion exchange, adsorption, and dehydration [140,141,142]. Zeolites are primarily composed of aluminosilicate minerals which are hydrated microporous, created from the integrated tetrahedra of silica (SiO4) and alumina (AlO4) moieties [143].

Zeolites are excellent adsorbents, particularly for the elimination of cadmium metal ions from sewer water/wastewater or industrial effluents, due to their superior belongings of ion exchange, large surface area, and hydrophilic nature, making them ideal for separating cadmium metal ions. In many industries, coal is widely used as a fuel, producing fly ash as a co-product, which gives rise to air pollution as well as disposal challenges. However, due to its very reason low cost, fly ash may be utilized for zeolite development through the hydro-thermal method [144]. Javadian successfully transformed fly ash into an aluminosilicate adsorbent which is amorphous, achieving a high adsorption capability of 26.20 mg/g for cadmium metal ions, with an 84% elimination at an ideal pH of 5 [145]. In the same way, Visa also used the hydro-thermal method with sodium hydroxide (NaOH) to convert fly ash to zeolite for the elimination of cadmium metal ions. Their research demonstrated that the product had a larger surface area, prosperous in micropores, and achieved higher than 81% cadmium metal ion elimination at an ideal pH of 7–8. Table-XVI outlines the elimination framework for sequestering cadmium metal ions using zeolite.

Table-XIII: Cadmium metal ions elimination by the use of zeolite.

Adsorbent	Metal Ions Concentration (mg/L)	Ideal pH	Adsorbent dose (g/L)	Adsorbent Capability (mg/g)	Elimination percentage (%)	References
Zeolite	25–100	6.0	25.0		76	[146]
Synthetic zeolite A	100-2000	-	1.0	315.65	-	[147]
Natural zeolite	9-90	5.0	-	9	71	[148]
Oil shale into zeolite	100	7.0	-	95.6	-	[149]
Zeolite from fly ash	1123.1-3370.3	6.5	10.0	57-195	98.6	[150]

Chitosan as an Adsorbent:

Chitin, the second most abundant natural polysaccharide (biopolymer) on Earth, follows cellulose in abundance [151]. It is the primary constituent of the exoskeleton of arthropods and crustacean shells and is also found in the cell walls of fungi [152,153,154]. Chitosan is a polymer which is deacetylated partially, is obtained from chitin by the deacetylation under alkaline conditions, which is separated from shellfish origins. This biopolymer is a low-cost natural adsorbent.

Due to amino as well as hydroxyl (-OH) groups in chitosan's moiety enables chemical modification, which can improve its solubility and electric charge [155]. Chitosan is known for its affordability and efficacy, though it has some drawbacks. These include solubility under acidic conditions, mechanical weakness, and the potential to leach carbohydrate when applied in original form [156,157].

To address some of these limitations, chitosan has been transformed by the use of coating method using ceramic alumina. This coating enhances the affordability of binding points and boosts the mechanical stability of chitosan. The highest adsorption capability recorded for this modified or transformed chitosan was 107.7 mg/g, observed at an ideal pH of 6, with a topmost elimination of 93.80% [158].

In a parallel study, Hydari transformed chitosan by the use of coating it with the help of activated carbon. This modification resulted in an adsorption capability of 52.60 mg/g at an ideal pH of 6, with a 100% elimination rate [159].

Table-XIV shows the data on cadmium metal ion elimination using chitosan from industrial effluent or sewer water/wastewater.

Adsorbent	Metal Ions Concentration (mg/L)	Ideal pH	Adsorbent dose (g/L)	Adsorbent Capability (mg/g)	Elimination percentage (%)	References
Multi-walled carbon nanotubes transformed with chitosan	-	6.0-7.0	-	-	Greater than 90	[160]
Replaced hyoxyl group on chitosan	675	10.0	-	-	95	[161]

2-Oxoglutaric acid transformed magnetic chitosan	100-500	6.0	0.04	201.2	93	[162]
Chitosan composite	100-500	5.6	5.0	92, 122	92	[163]

Outlook and Challenges in Elimination of Heavy Metal Ions from Sewer water/Wastewater

This evaluation highlights the use of bioadsorbents for eliminating chromium and cadmium metal ions from sewer water/wastewater. These adsorbents are low-cost, easily accessible alternatives to commercially available adsorbents. The effectiveness of these adsorbents can be enhanced through modification or impregnation, increasing their capability to eliminate heavy metals from sewer water/wastewater. Achieving optimal adsorption capacity and selectivity requires careful selection of suitable biomass or agricultural waste residues, along with the use of various adsorbents and chemicals to control pH, creating the ideal conditions for the adsorbent to effectively attract and bind with the target ions.

II. Conclusion

This review focuses on emerging potential adsorbents, including agricultural waste, graphene, minerals, and clay-based materials, for the elimination of chromium and cadmium from sewer water/wastewater. The adsorption data aligns with the Langmuir as well as Freundlich models, indicating unique and multidirectional adsorption behaviors. Agricultural waste-based adsorbents are inexpensive, widely available, generate no sludge or emulsion, can be regenerated or recycled, and demonstrate effective technical workability and strong attraction for eliminating heavy metal ions.

Acknowledgement

We are thankful to Dr. Brijesh Pare, Professor and Head of Chemistry Department, Govt. Madhav Science College, Vikram University, Ujjain, Dr. D. Singh Raghuwanshi, Professor, Govt. Madhav Science College, Vikram University, Ujjain and Dr. Veerender Sharma, Department of Textile & Fibre Engineering, Indian Institute of Technology, Hauz Khas, New Delhi for providing their technical support and facilities to carry out research.

Funding Sources

The author(s) received no financial support for the research, authorship, and/or publication of this article.

Conflict of Interest

The authors do not have any conflict of interest.

References:

[1]. MacCarthy, P.; Klusman, R. W.; Cowling, S. W.; Rice, J. A. *Analytical Chemistry,* **1993**, *65 (12)*, 244R-292R.
[2]. Clement, R. E.; Eiceman, G. A.; Koester, C. J. *Analytical Chemistry* **1995**, *67 (12)*, 221R-255R.
[3]. Renge, V. C.; Khedkar, S. V.; Pandey, S. V. *Scientific Reviews and Chemical Communications*, **2012**, *2 (4)*, 580-584.
[4]. Mehdipour, S.; Vatanpour, V.; Kariminia, H. R. *Desalination*, **2015**, *362*, 84-92.
[5]. Shadman, S. M.; Daneshi, M.; Shafiei, F.; Azimimehr, M.; Khorasgani, M. R.; Sadeghian, M.; Motaghi, H.; Mehrgardi, M. A. *In Electrochemical Bio-sensors: Elsevier*, **2019**, 213−251.
[6]. Lakherwal, D. *Int. J. Environ. Res. Dev*., **2014**, *4*, 41−48.
[7]. Tripathi, A.; Ranjan, M. R. *J. Biorem. Biodegrad*., **2015**, *6*, 1-5.
[8]. Thakur, L. S.; Parmar, *M. Int. J.Chem. Phys*., **2013**, *2 (6)*, 6-19.
[9]. Gopalakrishnan, A.; Krishnan, R.; Thangavel, S.; Venugopal, G.; Kim, S. J. *Journal of Industrial and Engineering Chemistry*, **2015**, *30*, 14–19.
[10]. Fu, F.; Wang, Q. *Journal of Environmental Management*, **2011**, *92 (3)*, 407–418.
[11]. Chassary, P.; Vincent, T.; Marcano, J. S.; Macaskie, L. E.; Guibal, E. *Hydrometallurgy*, **2005**, *76*, 131−147.
[12]. Zouboulis, A. I. *Miner. Eng*., **1995**, *8*, 1477−1488.
[13]. Onundi, Y. B.; Mamun, A. A.; Khatib, M. F. A.; Ahmed, Y. M. *Int. J. Sci. Environ. Technol*., **2010**, *7*, 751−758.
[14]. Liu, P.; Borrell, P. F.; Bozic, M.; Kokol, V.; Oksman, K.; Mathew, A. P. *J. Hazard. Mater.*, **2015**, *294*, 177−185.
[15]. Demirbas, E. *Adsorpt. Sci. Technol*., **2003**, *21*, 951.
[16]. Mahmoud, A. M.; Ibrahim, F. A.; Shaban, S.A.; Youssef, N. A. *Egyptian. J. Pet.*, **2015**, *24*, 27.
[17]. Xu, Y.; Chen, J.; Chen, R.; Yu, P.; Guo, S.; Wang, X. *Water Res.,* **2019**, *160*, 148.
[18]. Asere, T. G.; Steven, C. V.; Gupta, S.; Kumar, A. *Appl. Water Sci.*, **2019**, 9, 96 and Laing, G. D. *Sci. Total Environ.*, **2019**, *676*, 706.
[19]. Shobana, R.; Sahayaraj, P. A.; Dharmalingam, V.; Soruba, R. *Int. Res. J. Environment Sci.*, **2014**, *3*, 65.
[20]. Xia, M.; Chen, Z.; Li, Y.; Li, C.; Ahmad, N. M.; Cheema, W. A.; Zhu, S. *RSC Adv.*, **2019**, *9*, 20941.
[21]. Kumar, G. V. S. R. P.; Malla, K. A.; Yerra, B.; Srinivasa Rao, K. *Appl. Water Sci.*, **2019**, *9*, 44.
[22]. Pyrzynska, K. *J. Environ. Chem. Eng*., **2019**, *7*, 102795.
[23]. S. Gupta, S.; Kumar, A. *Appl. Water Sci.*, **2019**, *9*, 96.
[24]. Ahmad, K. U.; Jawed, M. *Desalination*, **2010**, *251*, 137.
[25]. Mve, M. Z.; Makani, T.; Eba, F. *J. Environ. Sci. Technol*., **2016**, *9*, 226.
[26]. Markovic, S.; Stankovic, A.; Lopicic, Z.; Lazarevic, S.; Stojanovic, M.; Uskokovic, D. *J. Environ. Chem. Eng.*, **2015**, *3*, 716–724.
[27]. He, J.; Lu, Y.; Luo, G. *Chem. Eng. J.*, **2014**, *244*, 202–208.
[28]. Reddy, N. A.; Lakshmipathy, R.; Sarada, N. C. *Alex. Eng. J.*, **2014**, *53*, 969–975.

[29]. Akkaya, G.; Guzel, F. *Desalin. Water Treat.*, **2013**, *51*, 7311–7322.
[30]. Alaa El-Din, G.; Amer, A. A.; Malsh, G.; Hussein, M. *Alex. Eng. J.*, **2018**, *57*, 2061–2068.
[31]. Annunciado, T. R.; Sydenstricker, T. H. D.; Amico, S. C. *Mar. Pollut. Bull.*, **2005**, *50*, 1340–1346.
[32]. Ibrahim, T. H.; Gulistan, A. S.; Khamis, M. I.; Ahmed, H.; Aidan, A. *Desalin. Water Treat.*, **2016**, *57*, 6693–6701.
[33]. Boopathy, R.; Karthikeyan, S.; Mandal, A. B.; Sekaran, G. *Environ. Sci. Pollut. Res.*, **2013**, *20*, 533–542.
[34]. Angelova, D.; Uzunov, I.; Uzunova, S.; Gigova, A.; Minchev, L. *Chem. Eng. J.*, **2011**, *172*, 306–311.
[35]. Radetic, M. M.; Jocic, D. M.; Jovancic, P. M.; Petrovic, Z. L.; Thomas, H. F. *Environ. Sci. Technol.*, **2003**, *37*, 1008–1012.
[36]. Choi, H. J.; Yu, S. W. *Environ. Eng. Res.*, **2019**, *24*, 99–106.
[37]. Boleydei, H.; Mirghaffari, N.; Farhadian, O. *Environ. Sci. Pollut. Res.*, **2018**, *25*, 21024–21035.
[38]. Ferrero, F. *J. Hazard. Mater.*, **2007**, *142*, 144–152.
[39]. Cardoso, C. K. M.; Mattedi, S.; Lobato, A. K. D. C. L.; Moreira, I. T. A. *Chemosphere*, **2021**, *279*, 130562.
[40]. Do, N. H.; Tran, V. T.; Tran, Q.; Le, K. A.; Thai, Q. B.; Nguyen, P. T.; Duong, H. M.; Le, P. K. J. *Polym. Environ.*, **2021**, *29*, 1112–1121.
[41]. Dhir, B.; Kumar, R. *Int. J. Environ. Res.*, **2010**, *4*, 427–432.
[42]. Hashem, A.; Abou-Okeil, A.; El-Shafie, A.; El-Sakhawy, M. *Polym.-Plast. Technol. Eng.,* **2006**, *45*, 135–141.
[43]. Hameed, B. H. *J. Hazard. Mater.,* **2009**, *162*, 939–944.
[44]. Altundogan, H. S.; Arslan, N. E.; Tumen, F. *J. Hazard. Mater.,* **2007**, *149*, 432–439.
[45]. Ismail, K.; Ishak, M. A. M.; Ab Ghani, Z.; Abdullah, M. F.; Safian, M. T. U.; Idris, S. S.; Tahiruddin, S.; Yunus, M. F. M.; Hakimi, N. I. N. M. *Renew. Energy*, **2013**, *55*, 357–365.
[46]. Farajzadeh, M.; Monji, A. *Sep. Purif. Technol.*, **2004**, *38*, 197–207.
[47]. Ifelebuegu, A.; Chinonyere, P. *ResearchGate*, **2016**, 61–64.
[48]. Jalali, M.; Aboulghazi, F. *J. Mater. Cycles Waste Manag.*, **2013**, *15*, 548–555.
[49]. Isa, M. H.; Lang, L. S.; Asaari, F. A.; Aziz, H. A.; Ramli, N. A.; Dhas, J. P. A. *Dyes Pigments,* **2007**, *74*, 446–453.
[50]. Iqbal, M.; Saeed, A.; Zafar, S. I. *J. Hazard. Mater.*, **2009**, *164*, 161–171.
[51]. Lv, N.; Wang, X.; Peng, S.; Luo, L.; Zhou, R. *RSC Adv.*, **2018**, *8*, 30257–30264.
[52]. Kamsonlian, S.; Suresh, S.; Majumder, C. B.; Chand, S. *Int. J. Sci. Technol. Manag.,* **2011**, *2*, 1–7.
[53]. Mohan, R.; Chui, E. A.; Biasi, L. A.; Soccol, C. R. *Dover. Braz. Arch. Biol. Technol.*, **2005**, *48*, 37–42.
[54]. Kumar, P. S.; Ramalingam, S.; Sathyaselvabala, V.; Kirupha, S. D.; Murugesan, A.; Sivanesan, S. *Korean J. Chem. Eng.*, **2012**, *29*, 756–768.
[55]. Kenes, K.; Yerdos, O.; Zulkhair, M.; Yerlan, D. *J. Non-Cryst. Solids*, **2012**, *358*, 2964–2969.
[56]. Paulauskiene, T.; Uebe, J.; Karasu, A. U.; Anne, O. *Water Air Soil Pollut.,* **2020**, *231*, 424.
[57]. Mondal, D. K.; Nandi, B. K.; Purkait, M. K. *J. Environ. Chem. Eng.,* **2013**, *1*, 891–898.
[58]. Annunciado, T. R.; Sydenstricker, T. H. D.; Amico, S. C. *Mar. Pollut. Bull.,* **2005**, *50*, 1340–1346.
[59]. Patowary, M.; Pathak, K.; Ananthakrishnan, R. *RSC Adv.*, **2016**, *6*, 73660–73667.
[60]. Nguyen, T. A. H.; Ngo, H. H.; Guo, W. S.; Zhang, J.; Liang, S.; Yue, Q. Y.; Li, Q.; Nguyen, T. V. *Bioresour. Technol.,* **2013**, *148*, 574–585.
[61]. Pehlivan, E.; Altun, T.; Cetin, S.; Iqbal Bhanger, M. *J. Hazard. Mater.,* **2009**, *167*, 1203–1208.
[62]. Wang, J.; Zheng, Y.; Wang, A. *Chem. Eng. J.*, **2012**, *213*, 1–7.
[63]. Singh, S.; Parveen, N.; Gupta, H. *Environ. Technol. Innov.*, **2018**, *12*, 189–195.
[64]. Sidiras, D.; Batzias, F.; Konstantinou, I.; Tsapatsis, M. *Chem. Eng. Res. Des.,* **2014**, *92*, 1781–1791.
[65]. Abid, M.; Niazi, N. K.; Bibi, I.; Farooqi, A.; Ok, Y. S.; Kunhikrishnan, A.; Ali, F.; Ali, S.; Igalavithana, A. D.; Arshad, M. *Int. J. Phytoremediat.,* **2016**, *18*, 442–449.
[66]. Vlaev, L.; Petkov, P.; Dimitrov, A.; Genieva, S. *J. Taiwan Inst. Chem. Eng.,* **2011**, *42*, 957–964.
[67]. Zhu, Y.; Zhang, H.; Zeng, H.; Liang, M.; Lu, R. *Int. J. Environ. Sci. Technol*., **2012**, *9*, 463–472.
[68]. Sadeghi, S.; Dadashian, F.; Eslahi, N. *Int. J. Environ. Sci. Technol*., **2019**, *16*, 1119–1128.
[69]. Zhou, L. T.; Yang, G.; Yang, X. X.; Cao, Z. J.; Zhou, M. H. *Environ. Sci. Pollut. Res.,* **2014**, *21*, 5730–5736.
[70]. Wang, J.; Wang, A. *Fibers Polym.,* **2013**, *14*, 1834–1840.
[71]. Zheng, L.; Zhu, C.; Dang, Z.; Zhang, H.; Yi, X.; Liu, C. *Carbohydr. Polym.,* **2012**, *90*, 1008–1015.
[72]. Bingol, A.; Ucun, H.; Bayhan, Y. K.; Karagunduz, A.; Cakici, A.; Keskinler, B. *Bioresource Technology*, **2004**, *94 (3)*, 245–249.
[73]. Nadeem, M.; Shabbir, M.; Abdullah, M. A.; Shah, S. S.; McKay, G. *Chemical Engineering Journal,* **2009***, 148 (2)*, 365–370.
[74]. Jing, X.; Cao, Y.; Zhang, X.; Wang, D.; Wu, X.; Xu, H. *Desalination,* **2011**, *269 (1)*, 120–127.
[75]. Min, Y. U. E.; Zhang, M.; Bin, L. I. U.; Xing, X. U.; Xiaoming, L. I.; Qinyan, Y. U. E.; Chunyuan, M. A. *Chinese Journal of Chemical Engineering*, **2013,** *21 (11)*, 1260–1268.
[76]. Nadeem, M.; Mahmood, A.; Shahid, S. A.; Shah, S. S.; Khalid, A. M.; McKay, G. *Journal of Hazardous Materials***, 2006**, *138 (3)*, 604–613.
[77]. Rosen, M. J.; Kunjappu, J. T. *John Wiley & Sons*, **2012.**
[78]. Ngah, W. W.; Hanafiah, M. A. K. M. *Bioresource Technology*, **2008**, *99 (10)*, 3935–3948.
[79]. Ullah, I.; Nadeem, R..; Iqbal, M.; Manzoor, Q. *Ecological Engineering*, **2013**, *60*, 99–107.
[80]. Ahmad, W. A.; Ahmad, W. H. W.; Karim, N. A.; Raj, A. S.; Zakaria, Z. A. *International Biodeterioration & Biodegradation*, **2013**, *85*, 571–576.
[81]. Garg, U. K.; Kaur, M. P.; Sud, D.; Garg, V. K. *Desalination*, **2009**, *249 (2)*, 475–479.
[82]. Cronje, K. J.; Chetty, K.; Carsky, M.; Sahu, J. N.; Meikap, B. C. *Desalination*, **2011**, *275 (1)*, 276–284.
[83]. Feng, N.; Guo, X.; Liang, S.; Zhu, Y.; Liu, J. *Journal of Hazardous Materials*, **2011**, *185 (1)*, 49–54.
[84]. Kale, P. N. Citrus. *Handbook of fruit science and technology: Production, composition, storage, and processing,* **1995**, 39-65.
[85]. Mafra, M. R.; Igarashi-Mafra, L.; Zuim, D. R.; Vasques, E. C.; Ferreira, M. A. *Braz. J. Chem. Eng.*, **2013**, *30*, 657–665.
[86]. Bampidis, V. A.; Robinson, P. H. *Anim. Feed Sci. Technol*., **2006**, *128*, 175–217.
[87]. Zapata, B.; Balmaseda, J.; Fregoso-Israel, E.; Torres-Garcia, E. J. *Therm. Anal. Calorim*., **2009**, *98*, 309–315.
[88]. Santos, C. M.; Dweck, J.; Viotto, R. S.; Rosa, A. H.; de Morais, L.C. *Bioresour. Technol*., **2015**, *196*, 469–479.
[89]. Lopez-Velazquez, M. A.; Santes, V.; Balmaseda, J.; Torres-Garcia, E. *J. Anal. Appl. Pyrolysis*, **2013**, *99*, 170–177.
[90]. Marin, A. P.; Ortuno, J. F.; Aguilar, M. I.; Meseguer, V. F.; Saez, J.; Llorens, M. *Biochemical Engineering Journal*, **2010**, *53 (1)*, 2–6.
[91]. Lugo-Lugo, V.; Barrera-Diaz, C.; Urena-Nunez, F.; Bilyeu, B.; Linares-Hernandez, I. *Journal of Environmental Management*, **2012**, *112*, 120–127.
[92]. Lopez-Tellez, G.; Barrera-Diaz, C. E.; Balderas-Hernandez, P.; Roa-Morales, G.; Bilyeu, B. *Chemical Engineering Journal,* **2011**, *173 (2)*, 480–485.
[93]. Farajzadeh, M. A.; Monji, A. B. *Separation and Purification Technology*, **2004**, *38 (3)*, 197–207.

[94]. Ozer, A.; Ozer, D. *Environmental Technology*, **2006**, *25 (6)*, 689–697.

[95]. Kaya, K.; Pehlivan, E.; Schmidt, C.; Bahadir, M. *Food Chemistry*, **2014**, *158*, 112–117.

[96]. Rahman, I. A.; Ismail, J.; Osman, H. *Journal of Materials Chemistry*, **1997**, *7 (8)*, 1505–1509.

[97]. Chuah, T. G.; Jumasiah, A.; Azni, I.; Katayon, S.; Choong, S. T. *Desalination*, **2005**, *175 (3)*, 305–316.

[98]. Adam, F.; Kandasamy, K.; Balakrishnan, S. *Journal of Colloid and Interface Science,* **2006**, *304 (1)*, 137–143.

[99]. Bishnoi, N. R.; Bajaj, M.; Sharma, N.; Gupta, A. *Bioresource Technology*, **2004**, *91 (3)*, 305–307.

[100]. Sugashini, S.; Begum, K. M. M. S. *New Carbon Materials*, **2015**, *30 (3)*, 252–261.

[101]. Lehmann, J. *Nature*, **2007**, *447*, 143–144.

[102]. Woolf, D.; Amonette, J. E.; Street-Perrott, F. A.; Lehmann, J.; Joseph, S. *Nature Communications*, **2010**, *1*, 56.

[103]. Mubarak, N. M.; Kundu, A.; Sahu, J. N.; Abdullah, E. C.; Jayakumar, N. S. *Biomass and Bioenergy*, **2014**, *61*, 265–275.

[104]. Agrafioti, E.; Kalderis, D.; Diamadopoulos, E. *Journal of Environmental Management*, **2014**, *146*, 444–450.

[105]. Ruthiraan, M.; Abdullah, E. C.; Thines, K. R.; Mubarak, N. M. *International Journal of Chemical Engineering*, **2015**, *2*, 18–21.

[106]. Ruthiraan, M.; Mubarak, N. M.; Thines, R. K.; Abdullah, E. C.; Sahu, J. N.; Jayakumar, N. S.; Ganesan, P. *Korean Journal of Chemical Engineering*, **2015**, *32 (3)*, 446–457.

[107]. Sciban, M.; Radetic, B.; Kevresan, Z.; Klasnja, M. *Bioresource Technology*, **2007**, *98*, 402-409.

[108]. Shukla, A.; Zhang, Y. H.; Dubey, P.; Margrave, J. L.; Shukla, S. S. *Journal of Hazardous Materials*, **2002**, *95 (1)*, 137–152.

[109]. Politi, D.; Sidiras, D. *Procedia Engineering,* **2012***, 42*, 1969–1982.

[110]. Argun, M. E.; Dursun, S.; Ozdemir, C.; Karatas, M. *Journal of Hazardous Materials*, **2007**, *141 (1)*, 77–85.

[111]. Chadha, K. L. *Indian Coconut Journal*, **2003**, *36 (4)*, 13–19.

[112]. Tan, W. T.; Ooi, S. T.; Lee, C. K. *Environmental Technology*, **1993**, *14 (3)*, 277–282.

[113]. Namasivayam, C.; Suresh kumar, M. V. *Bioresource Technology*, **2008**, *99 (7)*, 2218–2225.

[114]. Shen, Y. S.; Wang, S. L.; Tzou, Y. M.; Yan, Y. Y.; Kuan, W. H. *Bioresource Technology*, **2012**, *104*, 165–172.

[115]. Muthukumaran, K.; Beulah, S. *Procedia Environmental Sciences*, **2011**, *4*, 266–280.

[116]. Duranog lu, D.; Trochimczuk, A. W.; Beker, U. *Chemical Engineering Journal*, **2010**, *165 (1)*, 56–63.

[117]. Acharya, J.; Sahu, J. N.; Sahoo, B. K.; Mohanty, C. R.; Meikap, B. C. *Chemical Engineering Journal*, **2009**, *150 (1)*, 25-39.

[118]. Gueye, M.; Richardson, Y.; Kafack, F. T.; Blin, J. *Journal of Environmental Chemical Engineering*, **2014**, *2 (1)*, 273–281.

[119]. Arulkumar, M.; Thirumalai, K.; Sathishkumar, P.; Palvannan, T. *Chemical Engineering Journal*, **2012**, *185*, 178–186.

[120]. Yin, X.; Bai, J.; Tian, W.; Li, S.; Wang, J.; Wu, X.; Wang, Y.; Fan, F.; Huang, Q.; Qin, Z. *J. Radioanal. Nucl. Chem.*, **2017**, *313*, 113–121.

[121]. Wu, S. P.; Dai, X. Z.; Kan, J. R.; Shilong, F. D.; Zhu, M. Y. *Chin. Chem. Lett.*, **2017**, *28*, 625–632.

[122]. Dev, V. V.; Baburaj, G.; Antony, S.; Arun, V.; Krishnan, K. A. *J. Clean. Prod.*, **2020**, *255*, 120309.

[123]. Chen, M.; Nong, S.; Zhao, Y.; Riaz, M.S.; Xiao, Y.; Molokeev, M. S.; Huang, F. *Sci. Total Environ.*, **2020**, *726*, 138535.

[124]. Velde, B. *Springer, Berlin*, **1995**, 8–42.

[125]. Ghorbel-Abid, I.; Jrad, A.; Nahdi, K.; Trabelsi-Ayadi, K. *Desalination*, **2009**, *246*, 595–604.

[126]. Bhattacharyya, K. G.; Gupta, S. S. Sep. *Purif. Technol.*, **2006**, *50*, 388-397.

[127]. Uddin, M. K. *Chem. Eng. J.*, **2017**, *308*, 438–462.

[128]. Sen Gupta, S.; Bhattacharyya, K. G. *Phys. Chem. Chem. Phys.*, **2012**, *14*, 6698–6723.

[129]. Brigatti, M. F.; Lugli, C.; Poppi, L.; Venturelli, G. *Clay Miner.*, **1999**, *34*, 637–645.

[130]. Koppelman, M. H.; Emerson, A. B.; Dillard, J. G. *Clays Clay Miner.*, **1980**, *28*, 119–124.

[131]. Barkat, M.; Chegrouche, S.; Mellah, A.; Bensmain, B.; Nibou, D.; Boufatit, M. J. Surf. Eng. Mater. *Adv. Technol.*, **2014**, *04*, 210–226.

[132]. Turan, P.; Dogan, M.; Alkan, M. *J. Hazard. Mater.*, **2007**, *148*, 56–63.

[133]. Zeng, G.; He, Y.; Zhan, Y.; Zhang, L.; Shi, H.; Yu, Z. *Ind. Eng. Chem. Res.*, **2016**, *55*, 1760-1767.

[134]. Li, Z.; Pan, Z.; Wang, Y. *Environ. Sci. Pollut. Res.*, **2020**, *27*, 11683-11696.

[135]. Zhao, R.; Zhou, Z.; Zhao, X.; Jing, G. *Chemosphere*, **2018**, *218*, 458-467.

[136]. Long, H.; Wu, P.; Yang, L.; Huang, Z.; Zhu, N.; Hu, Z. *J. Colloid Interface Sci.*, **2014**, *428*, 295-301.

[137]. Mosai, A. K.; Chimuka, L.; Cukrowska, E. M.; Kotze, I. A.; Tutu, H. *Miner. Eng.*, **2020**, *145*.

[138]. Azzam, E. M. S.; Eshaq, G.; Rabie, A. M.; Bakr, A. A.; Abd-Elaal, A. A.; El Metwally, A. E.; Tawfik, S. M. *Int. J. Biol. Macromol.*, **2016**, *89*, 507-517.

[139]. Guerra, D. J. L.; Mello, I.; Resende, R.; Silva, R. *Water Res. Ind.*, **2013**, *4*, 32-50.

[140]. Akhtar et. al.; Akhtar, F.; Andersson, L.; Ogunwumi, S.; Hedin, N.; Bergstrom, L. *J. Eur. Ceram. Soc.*, **2014**, *34 (7)*, 1643-1666.

[141]. Nabavi et al.; Nabavi, M. S.; Mohammadi, T.; Kazemimoghadam, M. *Ceram. Int.*, **2014**, *40 (4)*, 5889-5896.

[142]. Wang, S.; Peng, Y. *Chem. Eng. J.*, **2010**, *156 (1)*, 11-24.

[143]. Choi, H. J.; Yu, S. W.; Kim, K. H. *Journal of the Taiwan Institute of Chemical Engineers*, **2016**, *63*, 482–489.

[144]. Hui, K. S.; Chao, C. Y. H.; Kot, S. C. *Journal of Hazardous Materials*, **2005**, *127 (1)*, 89–101.

[145]. Javadian, H.; Ghorbani, F.; Tayebi, H. A.; Asl, S. H. *Arabian Journal of Chemistry*, **2015**, *8 (6)*, 837–849.

[146]. Rao, G. P. C.; Satyaveni, S.; Ramesh, A.; Seshaiah, K.; Murthy, K. S. N.; Choudary, N. V. *Journal of environmental management*, **2006**, *81 (3)*, 265-272

[147]. El-Kamash, A. M.; Zaki, A. A.; El Geleel, M. A. *Journal of Hazardous Materials*, **2005**, *127 (1)*, 211–220.

[148]. Hamidpour, M.; Afyuni, M.; Kalbasi, M.; Khoshgoftarmanes, A. H.; Inglezakis, V. J. *Applied Clay Science*, **2010**, *48 (3)*, 342–348.

[149]. Shawabkeh, R.; Al-Harahsheh, A.; Hami, M.; Khlaifat, A. *Fuel*, **2004**, *83 (7)*, 981–985.

[150]. Izidoro, J. D. C.; Fungaro, D. A.; Abbott, J. E.; Wang, S. *Fuel*, **2013**, *103*, 827–834.

[151]. Pakdel P. M.; Peighambardoust, S. J. *Carbohydr. Polym.*, **2018**, *201*, 264–279.

[152]. Sandeep et al.; Sandeep, A.; Sangameshwar, K.; Mukesh, G.; Chandrakant, R.; Avinash, D. *Indo Am. J. Pharm. Res.*, **2013**, *3*, 1564-4574.

[153]. Islam et al.; Islam, M. M.; Masum, S. M.; Rahman, M. M.; Molla, M. A. I.; Shaikh, A.; Roy, S. *Int. J. Basic Appl. Sci.*, **2011**, *11*, 77-80.

[154]. Al Sharabati et al.; Al Sharabati, M.; Abokwiek, R.; Alothman, A.; Tawalbeh, M.; Karaman, C.; Orooji, Y.; Karimi, F. *Environ. Res.*, **2021**, *202*, 111694.

[155]. Samadi, F.Y.; Mohammadi, Z.; Yousefi, M.; Majdejabbari, S. *Int. J. Biol. Macromol.*, **2016**, *82*, 599–606.

[156]. Ren, Y.; Zhang, M.; Zhao, D. *Desalination*, **2008**, *228 (1)*, 135–149.

[157]. Huo, H.; Su, H.; Tan, T. *Chemical Engineering Journal*, **2009**, *150 (1)*, 139–144.

[158]. Wan, M. W.; Petrisor, I. G.; Lai, H. T.; Kim, D.; Yen, T. F. *Carbohydrate Polymers*, **2004**, *55 (3)*, 249–254.

[159]. Hydari, S.; Sharififard, H.; Nabavinia, M.; Reza Parvizi, M. *Chemical Engineering Journal*, **2012**, *193*, 276–282.

[160]. Salam, M. A.; Makki, M. S.; Abdelaal, M. Y. *Journal of Alloys and Compounds*, **2011**, *509 (5)*, 2582–2587.

[161]. Borsagli, F. G. M.; Mansur, A. A.; Chagas, P.; Oliveira, L. C.; Mansur, H. S. *Reactive and Functional Polymers*, **2015**, *97*, 37–47.

[162]. Yang, G.; Tang, L.; Lei, X.; Zeng, G.; Cai, Y.; Wei, X.; Zhou, Y.; Li, S.; Fang, Y.; Zhang, Y. *Applied Surface Science*, **2014**, *292*, 710–716.

[163]. Salah, T. A.; Mohammad, A. M.; Hassan, M. A.; El-Anadouli, B. E. *Journal of the Taiwan Institute of Chemical Engineers*, **2014**, *45(4)*, 1571-1577.