Regular Article

PHYSICAL CHEMISTRY RESEARCH
Published by the
Iranian Chemical Society
www.physchemres.org
info@physchemres.org

Phys. Chem. Res., Vol. 9, No. 2, 211-226, June 2021
DOI: 10.22036/pcr.2021.256683.1852

Application of Agricultural Wastes as a Low-cost Adsorbent for Removal of Heavy Metals and Dyes from Wastewater: A Review Study

A. Farhadi, A. Ameri* and S. Tamjidi
Department of Chemical Engineering, Shiraz Branch, Islamic Azad University, Shiraz, Iran
(Received 20 September 2020, Accepted 22 December 2020)

Water chemical pollution originates from a wide range of toxic derivatives, especially heavy metals and dyes. Its destructive effects on humans and ecosystem have been considered as a serious environmental disaster. Therefore, there is a need to develop technologies to remove toxic pollutants from the environment. Adsorption is one of the most common methods to remove the contaminants from wastewater. Adsorption is an optional method for industrial sewage treatment and a useful instrument for environmental protection. In recent years, numerous studies have been conducted to achieve low-cost, efficient and environmentally friendly adsorbents. Among the low-cost adsorbents, agricultural wastes are the most widely used bio-adsorbents for removing heavy metals and dyes. The advantages of using these compounds are low cost, good efficiency, minimal energy, simple maintenance and high adsorption capacity. This study deals with the risks, effects and resources of heavy metals and dyes in addition to examination of agricultural wastes as low-cost adsorbents. Moreover, equilibrium, kinetic and thermodynamic characteristics of the adsorption process of heavy metal ions were studied.

Keywords: Low-cost adsorbents, Heavy metal, Dye, Agricultural wastes, Waste water

INTRODUCTION

Overpopulation, industrialization and human culture renovation have led to positive and negative effects such as economic development, unfavorable weather, and water and land pollution. Water pollution has received great concern due to the negative effects on living organisms as well as the environment due to large-scale production [1,2]. Heavy metals and dyes are the most important pollutants among the types of pollutants. Heavy metal has been proposed as environmental pollutants in most parts of the world at different concentrations and enters the environment through the discharge of industrial effluents, fuel consumption, discharge of municipal wastewater, consumption of sludge from wastewater treatment as ground fertilizer [3,4]. Releasing heavy metals into industrial sewage is a major concern in the environment [5]. Nowadays, removal of heavy metals from effluents has been legally enforced, since they are non-degradable and may have bio concentration in living tissues. Wastewater containing heavy metals such as chromium, lead, arsenic, copper, iron, manganese, vanadium, nickel, mercury, cobalt, molybdenum, semiotics, *etc*., are among the toxic inorganic pollutants. They might cause environmental problems even in low concentrations and in aquatic environment (surface and groundwater) [6,7]. The amount and number of metals in each wastewater are directly related to the industrial operations. For instance, copper, chromium, zinc and cadmium are widely produced by metal plating. The concentration of heavy metals is much higher than the allowable limit in most wastewater, so they must be removed [8,9]. The presence of these metals in water resources is very harmful for living organisms, leading to skin disorders, nausea, lung cancer, kidney dysfunction, neurological disorders and other complications [10]. In addition to heavy metals, synthetic dyes are applied in various painting processes, industrial printing, paper,

*Corresponding author. E-mail: ameri@iaushiraz.ac.ir

carpet weaving, rubber, sanitary ware and cosmetics. About 56% of the world's total dye production per year is consumed in textile industry as the largest consumer of synthetic dyes [11,12]. The removal of dyes from waste effluent is very environmentally important, because a small amount of dye in water can be toxic and visible [13]. These materials are often resistant to degradation using biological methods and are not destroyed by conventional physical and chemical methods. Dyes can also affect aquatic life, as it prevents sunlight from passing through the water. Dyes can lead to toxicity of the aquatic animals' habitat and serious harm to humans [14,15]. Synthetic dyes have a complex aromatic molecular structure. This makes their structure more stable and makes their biological decomposition more difficult. Dyes may not be fully consumed during textile production and may slightly diffuse into the environment, leading to a high accumulation in the wastewater [16,17]. Dyes inhibit growth of algae, plants and bacteria at various levels, and presence of them does not allow to purify rivers and conventional biological treatment systems [18]. Scientists have proposed various methods for removing heavy metals and dyes from aqueous solutions such as chemical precipitation, filtration, electrochemical refining, ion exchange, chemical oxidation, reduction, reverse osmosis, coagulation and sedimentation [19,20].

Nowadays, these methods are less commonly used due to their high cost and high production of environmental waste, as well as their inefficiency at low concentrations. Adsorption is one of the best and the most efficient methods applied to remove pollutants such as heavy metals and dyes from effluents. It has some useful features such as reversibility, high adsorption capacity, lower cost, cost-effectiveness, and high energy efficiency. Active carbon is one of the most widely used adsorbents due to its active surface and high adsorption capacity in the process of pollutants adsorption from aqueous solutions. However, it is not applied to adsorb metals and dyes in a large scale due to its high cost of production [21,22]. Therefore, the acquisition of low-cost adsorbents has received much attention. Inexpensive adsorbents are usually divided into 5 main categories including (i) agricultural waste, (b) industrial by-products, (iii) sludge, (IV) marine material, (v) soils and minerals [23].

Agricultural waste is mostly applied to remove heavy metals and dyes as a very effective bio adsorbent. The advantages of using these compounds are low cost, high efficiency, minimum energy consumption, simple maintenance and high adsorption capacity [24].

The main purpose of this research is to study the role of agricultural waste as low-cost adsorbents to remove heavy metals and dyes from wastes and effluents. In addition, various models related to synthetic, isothermal, and thermodynamic behaviors are investigated.

HEAVY METALS

The term of heavy metals refer to metal elements with a relatively high density, and degrees of toxicity even at low concentrations [25]. Heavy metals are a common general term for the group of metals with an atomic density of higher than 5 g cm^{-3}. Density is related to the chemical properties of heavy metals. Heavy metals include lead, cadmium, mercury, arsenic, chromium, silver, copper, iron and platinum [26]. Heavy metals are divided into three general categories of transition elements according to the periodic table. Some of them are slightly amphoteric like, rare-earth elements, which are categorized into the lanthanide series (including La itself) and the actinide series (including Ac itself), and some metallic elements of group P. In general, the place of these metals includes groups 3 to 16 in the period 4 onwards in the periodic table. Figure 1 shows the classification of heavy metals based on the periodic table [27].

A trace amount of some heavy metals are essential for metabolism of humans and animals. For instance, titanium is considered as the most biocompatible metal-not harmful or toxic to living tissue-due to its resistance to corrosion from bodily fluids. Zirconium and its salts generally have low systemic toxicity. While zirconium is not toxic, it can cause contact irritation to the skin and eyes. The human body is made of approximately 0.000001 percent zirconium. Vanadium is a metal that naturally occurs in many different minerals and in fossil fuel deposits. The primary industrial use of vanadium is in the strengthening of steel. According to the International Agency for Research on Cancer, vanadium is possibly carcinogenic to humans. There is also a controversy among health experts on whether vanadium is an essential nutrient. The U.S. Environmental Protection

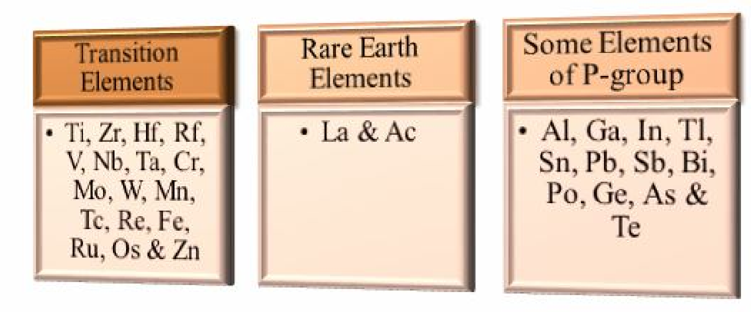

Fig. 1. Classification of heavy metals based on periodic table [27].

Agency's current reference concentration for vanadium indicates that ongoing exposure to vanadium at levels of more than 21 parts per billion per day may lead to negative health effects. Chromium is the 21st most abundant element in the Earth's crust and can be present in different chemical forms in plants, soil and volcanic dust, water, humans and animals. Since chromium is a prevalent natural element, it can be present in air, food and water. The existing standard for total chromium for protection against allergic dermatitis (skin reactions) was set in 1992. The drinking water standard for total chromium is 100 parts per billion. Lead is a common, naturally occurring metal found throughout the environment. Lead seldom occurs naturally in water supplies like rivers and lakes, and lead is rarely present in water coming from a treatment plant. Lead enters drinking water primarily as a result of corrosion or wearing away of materials in the water distribution system and household plumbing that contain lead. The standard concentration of lead in drinking water is less than 15 parts per billion. Manganese is a naturally-occurring metal that is essential to the proper functioning of body. Manganese occurs naturally in both ground and surface water sources, as well as soils that erode into water sources. Adverse health effects may be caused by either inadequate intake or overexposure, however, manganese deficiency is rare. Some epidemiology studies suggest an association between elevated levels of manganese in drinking water with poorer memory, attention and motor function, as well as increased hyperactivity. Molybdenum is a naturally-occurring metal that can be found in small amounts in rocks and soil. It is also present in plants, animals and bacteria. Molybdenum is most commonly used in the production of structural steel, stainless steel, cast iron and other alloys. It is also used in the manufacture of a number of electronic components, pigments, and other specialty applications, and it can be used in metal finishing processes as a replacement for hexavalent chromium. Exposure to molybdenum naturally occurring in food and water at low levels is not known to be harmful. The U.S. Environmental Protection Agency's current health advisory levels (HALs) for molybdenum are 40 parts per billion for life-time exposure, with one-day and 10-day HALs at 80 part per billion. Strontium is an alkaline earth metal that is found naturally in the minerals celestine and strontianite. Strontium shares many physical and chemical properties with calcium and barium and is highly susceptible to chemical changes. Strontium has 16 known isotopes. Strontium, occurring naturally in the earth, has four stable isotopes Sr-84, -86, -87 and -88. Twelve other strontium isotopes are unstable, indicating that they are radioactive. Strontium-90 is the most prevalent radioactive isotope in the environment, although strontium-89 can be found around nuclear reactors. Strontium-85 is used in bone imaging processes by the medical field. The risk posed by strontium depends on the concentration ingested and on the exposure conditions. The U.S. environmental Protection Agency's current reference concentration indicates that ongoing exposure to strontium at levels of more than 4000 parts per billion per day may lead to negative health effects. There is no evidence that drinking water with trace amounts of naturally-occurring strontium is harmful. However, exposure to high levels of naturally-occurring strontium during infancy and childhood can affect bone growth and cause dental changes, and there is some

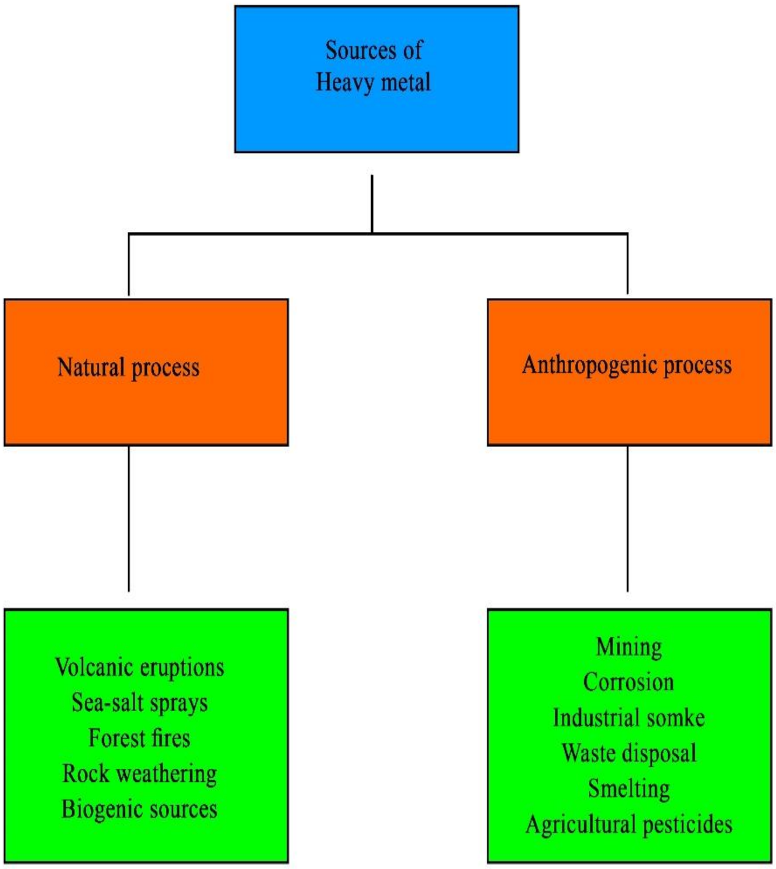

Fig. 2. Heavy metal sources.

evidence that strontium increases bone density in adults. The isotope strontium-90 has been linked to bone cancers and leukemia [28-30].

Illegally removal of unprocessed industrial and domestic wastewater leads to a serious risk to the aquatic ecosystem and reducing the quality of surface and groundwater. They become carcinogenic and even fatal when the concentration of some of these heavy ions exceeds the threshold [31]. These metals cause damage and endanger the health of living organisms when are not metabolized by the body and accumulated in soft tissues. Systems containing these metals can impair cardiovascular function and the function of liver, kidneys, blood, skin, glands, reproduction, immunity, nervousness, urination and digestion [32].

Heavy metal sources can originate from two general natural and human processes [33]. Figure 2 shows a schematic of the sources of heavy metals. Table 1 shows the sources, effects and standard values of some heavy metals on humans and drinking water [33-36].

DYES

Dye is a colorful natural or synthetic material that is used for painting, printing on fabrics, paper, leather and other materials. Dyes typically use an aqueous solution. They are able to adhere to compatible surfaces through physical adsorption or mechanical retention through covalent bonds with salt or metals by creating a solution. Annual production of commercial dyes applied in various industries is estimated as more than seven cases. An average of 100 tons dye per year are discharged as waste in the water. Dyes are a dangerous class of organic pollutants in

Table 1. Sources, Effects and Standard Values of some Heavy Metals on Humans and Drinking Water [33-36]

Heavy metal	Maximum contaminant levels	Sources	Effects
Silver	0.1	Mining Industrial scrap	Toxicity to the skin and the tissues of other organs, respiratory problems, inflammation of the lungs and throat, stomach pain
Arsenic	0.01	Arsenic mining and smelting coal combustion industrial production with arsenic as raw materials	Impact on essential cellular processes such as phosphorylation and ATP synthesis
Barium	2	Mining Electrolysis	Heart arrhythmia, respiratory failure, gastrointestinal disorder, muscle contraction, and hypertension
Cadmium	0.005	Electroplating Nnonferrous metallurgy	Carcinogenic, mutagenic, endocrine disorders, lung injury, bone fragility, calcium imbalance in biological systems
Total Chrome	0.1	Tanneries Pulp and rubber manufacturing applications	Hair loss, allergic dermatitis
Copper	1	Copper mining and smelting Metal Processing Machinery manufacturing Steel production	Renal-cerebral dysfunction; high concentrations lead to liver cirrhosis and chronic anemia and gastrointestinal inflammation
Inorganic mercury	0.002	Fossil fule Mining Pulp Paper industries	Autoimmune diseases, depression, sleepiness, fatigue, hair loss, insomnia, memory loss, restlessness, impaired vision, tremor, bad temper, brain damage, renal and pulmonary failure
Nickel	0.2 (WHO)	Nickel Ore mining and smelting Production and processing process of alloy steel Coal, oil combustion emissions of dust Electroplating, nickel plating, and production process	Allergic skin diseases such as itching, lung, nose, sinuses and throat cancers in the case of persistent inhalation, the immunotoxin, neurotoxic, genotoxic, effect on fertility, hair loss

Table 1. Continued

Lead	0.015	Road transport Wastewater from lead battery industry Sewage from lead chemical plant Electronic waste	High exposure to children can impair growth, decrease intelligence, short-term memory loss, learning disabilities and coordination, cardiovascular risk
Zinc	5	Mining and metallurgy Electroplating Instrumentation factory Paper mills	Dizziness, fatigue and so on

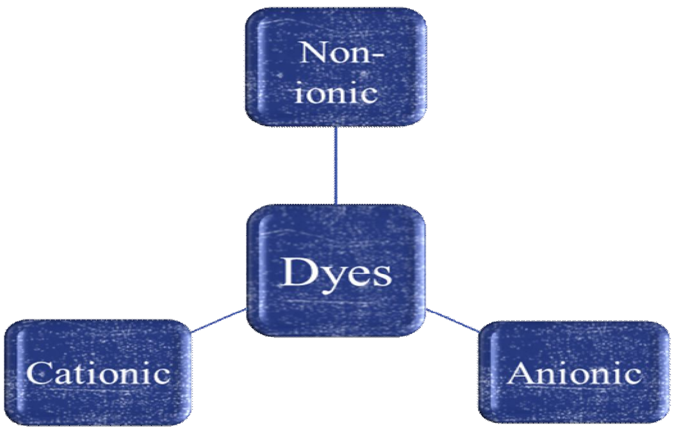

Fig. 3. Types of dyes.

the environment that are released directly and indirectly into water resources. Therefore dyes removal from wastewater or drinking water is a major concern of the environment [37,38]. Knowledge of the sources of such pollutants contribute to their removal. These dyes enter the environment through natural and human sources. The amount of entering these dyes and pollutants to the environment is more than the produced amount by natural processes. Major sources of pollution in the environment include mines, domestic effluents and effluents of smelting and extracting metals, discharging chemical products, toxins, insecticides, herbicides, industrial discharges, radioactive effluents, and petroleum hydrocarbons [39], pigments of dyeing and weaving industries, plastics, Papermaking and printing industries, cosmetics. In addition, there will be some problems in the treatment process, due to the synthetic origin and the presence of complex molecules in the structure of dyes [40]. Dyes can be classified based on chemical structure, load, color, and applications. Figure 3 generally shows the classification of dyes. They can be classified into three categories; cationic, anionic, and non-ionic [41]. Cationic dyes include all basic dyes such as azo, xanthan, Triphenylmethane, *etc*. These dyes have a positive charge while dissolving in the aqueous solution. The most common cationic dyes are methylene blue, Malachite green, crystal violet, the original red 29, the blue base 159, the yellow base 28, and so on. These dyes are used to make ink and painting paper, nylon, and polyester. Anionic dyes can also be divided into three categories, direct dyes, acid dyes, and reactive dyes. These dyes obtain a negative charge in the aqueous solution [42]. The most common anionic dyes are methyl orange, Congo red, direct red 23, reactive black 5, and so on. Each dye has its own application depending on the structure and the ability of adhesion. These dyes are applied to transfer dye to wool, silk, leather, and paper [43]. In addition, non-ionic dyes include disperse dyes, which are mainly used to produce colored plastics, polyester, polyamide, *etc*. Common non-ionic colors are Direct Green 97. Dispersion of dyes can result in allergies. These dyes are highly toxic at the time of contact with colored materials [44]. The presence of dyes, even in very small amounts, severely affects the liver, kidneys, brain and human reproductive system, and lead to skin irritation, respiratory disorders, and even cancer [38].

ADSORPTION PROCESS

Adsorption is currently considered as an impressive and cost-effective method to treat wastewater. The process of adsorption leads to flexibility in design and utilization, and in many cases, high-quality effluents. Moreover, adsorption is reversible, and suitable adsorbents can be reconstituted and recycled [45]. This method is used as a single operation in chemical engineering processes to remove effluent contaminants [46]. It is a mass transfer process which involves the accumulation of materials at a two-phase interface, such as a liquid-liquid, gas-liquid, gas-solid or liquid-solid interfaces. Adsorption is performed either physically or chemically. Physical adsorption is a reversible phenomenon, and the gravitational forces between solid molecules and the adsorbate are weak Van der Waals forces and is introduced as an exothermic phenomenon; *i.e.*, its enthalpy value is negative.

However, the gravitational forces between solid molecules and the adsorbate are strong chemical bond in chemical adsorption and absorb energy many times more than physical adsorption. Therefore, this phenomenon is irreversible and requires a large amount of energy which leads to positive enthalpy value and endothermic phenomenon [47, 48].

AGRICULTURAL WASTE AS A LOW-COST ADSORBENT

Agricultural waste is a low cost, abundant and environmentally friendly resource that is used as a very effective adsorbent. The most common sources to remove dye and heavy metals are coconut shells, orange peel, pomegranate peel, banana peel, squash coal, tea waste, pistachio peel, rice hulls ash, coffee powder, pomelo peel, garlic peel and peat bagasse. The main components of agricultural waste include hemicelluloses, lignin, lipids, proteins, simple sugars, water, hydrocarbons and starches which contain various types of functional groups. These functional groups lead to increasement of active sites and better adsorption of pollutants [23]. Various studies have been conducted on the adsorption of heavy metals and dyes from effluents so far.

In following, the resultant efficiency and optimal conditions for agricultural waste, as an adsorbent, to remove a variety of dyes and heavy metals are discussed. In most of the studies performed, the removal of pollutants has been efficiently carried out, confirming the effectiveness of agricultural waste to remove pollutants from the environment. Tables 2 and 3 illustrate the maximum adsorption capacity, along with the optimal adsorption conditions for the removal of heavy metals and dyes using agricultural waste.

Li *et al.* (2008) used orange peel to remove Cd(II), Ni(II), Zn(II) and Co(II). The removal efficiency values of Cd(II), Ni(II), Zn(II) and Co(II) under optimal conditions of pH = 6, adsorbent dose of 0.025 g l^{-1}, and the initial concentration of metal ions 0.001 mg l^{-1}, were 93.72, 80.11, 87.23 and 81.06, respectively. In addition, the results showed that the adsorption process followed the Langmuir and Freundlich adsorption isotherm models and Pseudo first-order kinetic model [49]. Feng and Guo (2012) applied

Table 2. Capacity and Optimal Conditions of Various Agricultural Wastes in the Removal of Heavy Metals from Water and Wastewater

Bio-adsorbent	Pollutant	pH	Conc. (mg l^{-1})	Dose (g l^{-1})	Removal efficiency (%)	q_{max} (mg g^{-1})	Ref.
Orange peel	Cd(II)	6	0.001	0.025	93.72	-	[49]
Orange peel	Ni(II)	6	0.001	0.025	80.11	-	[49]
Orange peel	Zn(II)	6	0.001	0.025	87.23	-	[49]
Orange peel	Co(II)	6	0.001	0.025	81.06	-	[49]
Orange peel	Cu(II)	5.5	50	0.01	93.7	70.73	[50]
Orange peel	Pb(II)	5.5	50	0.01	99.4	209.8	[50]
Orange peel	Zn(II)	5.5	50	0.01	86.6	56.18	[50]
Pomegranate peel	Ni(II)	6	50	10	-	50	[51]
Pomegranate peel	Cu(II)	5.8	20	0.25	-	55	[52]
Pomegranate peel	Pb(II)	5.6	50	0.25	-	64	[52]
Banana peel	cd(II)	8	10	0.1	97	35.52	[53]
Tea waste	Cu(II	5.5	100	1.5	64	48	[54]
Tea waste	Pb(II)	5.5	200	1.5	92	65	[54]

orange peel to remove Cu(II), Pb(II) and Zn(II). The optimum conditions in their experiments were pH = 5.5, adsorbent dose of 0.01 g l^{-1} and the initial metal ions concentration of 50 mg l^{-1}. The removal efficiency values of Cu(II), Pb(II) and Zn(II) obtained were 93.7, 99.4 and 86.6, respectively [50]. Bhatnagar and Minocha (2010) have used pomegranate peel to remove Ni(II) under optimal conditions, pH = 6, 10 g l^{-1} adsorbent dose and 50 mg l^{-1} initial concentration of metal ions. The highest adsorption capacity was 50 mg g^{-1}. Moreover, the results revealed that the adsorption process followed the Langmuir adsorption isotherm model and the Pseudo second-order kinetic model. The values obtained from the thermodynamic parameters showed the spontaneous and endothermic adsorption process along with irregularity increases [51].

In another study, El-Ashtoukhy *et al.* (2010) removed Cu(II) and pb(II) using pomegranate peel. The pH applied in their tests were pH = 5.8 for Cu(II) and pH = 5.6 for pb(II). The adsorbent dose of 0.25 g l^{-1} and the initial concentration of 20 mg l^{-1} for copper ion and 50 mg l^{-1} for lead ion led to adsorption capacities of 55 and 64, respectively. The Freundlich adsorption isotherm model and the Pseudo second-order kinetic model were matched with experimental data for Cu(II), as well as the Langmuir and the Pseudo second-order models for pb(II) ions [52]. Cd(II) was removed from the industrial wastewater using banana peel by Memon *et al.* (2008). Their results indicated that the maximum adsorption capacity was 35.53 mg g^{-1} with pH = 8, adsorbent dose of 0.1 g l^{-1} and initial concentration of metal ion 10 mg l^{-1}. Moreover, the results showed that the adsorption process followed the Langmuir adsorption isotherm model and the Pseudo second-order kinetic model. The values of Gibbs energy demonstrated that the process of adsorption was spontaneous and endothermic [53].

Table 3. Capacity and Optimal Conditions of Different Agricultural Wastes in Removing Dyes from Water and Wastewater

Bio-adsorbent	Pollutant	pH	Conc. (mg l^{-1})	Dose (g l^{-1})	Removal efficiency (%)	q_{max} (mg g^{-1})	Ref.
Pistachio peels	Methylene blue	8	100	0.15	99	602	[55]
Rice hulls ash	Methylene blue	6.8	50	3	95	690	[56]
Rice hulls ash	Indigo carmine	6.5	50	10	96	65.9	[57]
Coffee powder	Rhodamine B	2	15	0.05	-	5.255	[58]
Coffee powder	Rhodamine 6G	2	15	0.05	-	17.369	[58]
Pomelo peel	Reactive blue 114	2	100	20	85	16	[59]
Garlic peel	Direct red 12B	2	50	0.3	99	37.96	[60]
Pomegranate peel	Direct blue 106	2	20	2.5	72	42.59	[61]
Pomegranate peel	Congo red	7	30	20	98	55	[62]
Surfactant-modified coconut coir pith	Direct red 12B	5	50	20	90	76.3	[63]
Surfactant-modified coconut coir pith	Rhodamine B	10	10	20	90	14.9	[63]
Coal fly ash	Rhodamine B	3	100	20	98	2.86	[64]

Amarasinghe and Williams (2007) investigated the potential of tea waste to remove Cu(II) and pb(II) from aqueous solutions. They reported the removal efficiency of Cu(II), and pb(II) by tea waste as 64 and 92, respectively. The experiment conditions were pH = 5.5, the adsorbent dose of 1.5 g l^{-1} and the initial concentrations of 100 and 200 mg l^{-1} for copper and lead ions, respectively. The Langmuir and Freundlich adsorption isotherms were appropriate for Cu(II) and pb(II), respectively, although, the Pseudo second-order kinetic model had been reported for both metal ions [54].

Vucurovic *et al.* (2011) applied maize stem parenchymatous ground tissue to remove two cationic and anionic dyes from aqueous solutions. The experiments were performed at the pH range 2-6 and initial concentration 20-50 mg l^{-1}. The maximum capacities for removal of cationic and anionic dyes were 160.84 mg g^{-1} at pH = 6 and 167.01 mg g^{-1} at pH = 2, respectively [55]. Chandrasekhar and Pramada (2006) utilized rice hulls ash to remove methylene blue from waste stream. They used the pH value 6.8, the adsorbent dose 3 g l^{-1}, and the initial concentration of metal ions 50 mg l^{-1} in their experiments. These conditions caused a maximum adsorption capacity of 690 mg g^{-1}. The results of isotherm models demonstrated that the adsorption process fitted both the Langmuir and Freundlich models. Also, the Pseudo second-order kinetic model was better fitted with experimental data [56]. Lakshami *et al.* (2009) adsorbed Indigo Carmine dye onto the rice husk ash under optimum conditions of pH = 5.4 and adsorbent dose of 10 g l^{-1} after 8 h. The thermodynamic analysis and measurement of entropy, enthalpy and

Gibbs free energy changes showed that adsorption process was endothermic and spontaneous in this study [57].

Shen and Gondal (2017) used coffee powder to remove Rhodamine B and Rhodamine 6G. The maximum adsorption capacities for Rhodamine B and Rhodamine 6G were 5.255 and 17.369 mg gl^{-1}, respectively. The operating conditions of experiments were pH = 2, adsorbent dose = 0.05 g l^{-1} and the initial concentration of dyes = 15 mg l^{-1}. The Langmuir and Freundlich adsorption isotherms and the Pseudo first- and second-order kinetic models were the proposed models for Rh B and Rh 6G, respectively [58]. Argun *et al.* (2014) removed Reactive Blue 114 (RB114) dye using pomelo peel waste. The maximum capacity of the dye was 16 mg g^{-1} at pH value of 2 and temperature of 303 K. The range of initial dye concentration was 1-200 mg l^{-1} [59]. Asfaram *et al.* (2014) investigated the performance of garlic peel to remove direct red 12B from solution. The desirable and fantastic removal efficiency of 99% was obtained within 25 min for the adsorbent dose of 4 g l^{-1} and 50 g l^{-1} for dye concentration. The Langmuir adsorption isotherm and the Pseudo second-order kinetic model and endothermic adsorption process were other results in this study [60].

Amin (2009) used pomegranate peel charcoal to remove direct blue 106 from aqueous solution. The removal efficiency of 72% was measured under optimal conditions pH = 2, the adsorbent dose of 2.5 g l^{-1} and the dye initial concentration of 20 g l^{-1}. In addition, the results showed that the adsorption process followed the Freundlich adsorption isotherm model and the Pseudo second-order kinetic model [61]. Ghaedi *et al.* (2012) applied activated carbon prepared from Myrtus communis and pomegranate peel to remove Congo red. The maximum capacities for dye adsorption measured were 19.231 and 10 mg g^{-1} for pomegranate and Myrtus communis, respectively. Increasing pH caused higher adsorption performance. Pomegranate peel followed the Langmuir adsorption isotherm, however, Myrtus communis fitted well with Freundlich isotherm [62]. In another research, Sureshkumar and Namasivayam (2009) used surfactant-modified coconut coir pith to directly remove the red 12B and Rhodamine B dyes. They could remove these two dyes by 76.3 and 14.9 mg g^{-1}, respectively with pH value of 5, adsorbent dose of 20 g l^{-1} and initial concentration of dyes 20 mg l^{-1} [63].

Chang *et al.* (2009) evaluated the adsorption of Rhodamine B using fly ash. The removal efficiency of Rhodamine B by 80 g l^{-1} fly ash was only 54%. Combination of Fenton oxidation by fly ash adsorption increased the removal efficiency to 98% [64].

Tables 2 and 3 show the capacity and optimum conditions of various agricultural wastes in the removal of heavy metals and dyes, respectively, from water and wastewater.

ADSORPTION ISOTHERMS AND KINETICS

The adsorption isotherms provide necessary information such as adsorption mechanisms, the affinity of the sorbent, surface properties as well as internal bonds using the obtained various parameters. Therefore, adsorption isotherm curves describe the relationship between the quantity of adsorbed metal and the residual heavy metal ions in the solution [65]. In most cases, equilibrium-state behavior of an adsorbent is studied based on isothermal models such as Langmuir and Freundlich models [66].

The prediction rate of the adsorption-desorption process is one of the most important factors to select suitable adsorbent. The kinetics study of the process reveals the adsorption capacity with time when the adsorbate adsorbs on the surface of the adsorbent. The most popular kinetic models are the pseudo-first-order and pseudo-second-order kinetic models [40,67].

Tables 4 and 5 present a summary of the studies performed on the application of kinetic and isothermal models for the removal of heavy metals and dyes using agricultural wastes.

The surface of the agricultural wastes contains polar functional groups like phenols, ketones, acids and aldehydes. These functional groups are involved in the chemical bonding between metal ions and polar sites on the adsorbent surface. Thus, adsorption reaction is the rate-limiting step in most of adsorption processes of heavy metals and dyes by agricultural wastes. The mass of metal ions on the surface of adsorbent and the amount of metal ions adsorbed are two main parameters affecting the rate of adsorption. Thus, it is concluded that most of the adsorptions processed by agricultural wastes follow the pseudo-second-order kinetic model [68].

Table 4. Isothermal and Kinetic Models Used in Various Studies for Removal of Heavy Metals

Bio-adsorbent	Pollutant	Fitted isotherm model	Fitted kinetics model	Ref.
Orange peel	Cd(II), Ni(II), Zn(II), Co(II)	Langmuir, Freundlich	Pseudo-First order	[49]
Orange peel	Cu(II), Pb(II), Zn(II)	Langmuir	-	[50]
Pomegranate peel	Ni(II)	Langmuir	Pseudo-Second order	[51]
Pomegranate peel	Cu(II)	Freundlich	Pseudo-Second order	[52]
Pomegranate peel	Pb(II)	Langmuir	Pseudo-Second order	[52]
Banana peel	Cd(II)	Langmuir	Pseudo-Second order	[53]
Tea waste	Cu(II), Pb(II)	Langmuir, Freundlich	Pseudo-Second order	[54]

Table 5. Isothermal and Kinetic Models Used in Various Studies for Removal Dyes

Bio-adsorbent	Pollutant	Fitted isotherm model	Fitted kinetics model	Ref.
Pistachio peels	Methylene blue	Langmuir	Pseudo-Second order	[55]
Rice hulls ash	Methylene blue	Langmuir, Freundlich	Pseudo-Second order	[56]
Rice hulls ash	Indigo Carmine	Freundlich	Pseudo-Second order	[57]
coffee powder	Rhodamine B	Langmuir	Pseudo-First order	[58]
coffee powder	Rhodamine 6G	Freundlich	Pseudo-Second order	[58]
Pomelo peel	Reactive Blue 114	Langmuir	Pseudo-Second order	[59]
Garlic peel	Direct Red 12B	Langmuir	Pseudo-Second order	[60]
Pomegranate peel	Direct blue 106	Freundlich	Pseudo-Second order	[61]
Pomegranate peel	Congo red	Langmuir	Pseudo-Second order	[62]
Surfactant-modified coconut coir pith	Direct red 12B	Langmuir	Pseudo-Second order	[63]
Surfactant-modified coconut coir pith	Rhodamine B	Langmuir	Pseudo-Second order	[63]
Coal fly ash	Rhodamine B	Langmuir	-	[64]

THERMODYNAMIC STUDIES

Thermodynamic parameters are highly significant in describing the adsorption process and achievement of equilibrium state. The thermodynamic parameters include enthalpy variations ($\Delta H°$), entropy variations ($\Delta S°$), and Gibbs free energy variations ($\Delta G°$). The value of $\Delta G°$ can be calculated from Eq. (1),

Table 6. Thermodynamic Parameters Used in Various Studies for Removal Heavy Metal and Dyes

Bio-adsorbent	Pollutant	ΔG° (kJ mol^{-1})				ΔH° (kJ mol^{-1})	ΔS° (J mol^{-1} K^{-1})	Ref.
		298.15K	308.15K	318.15K	328.15K			
Pomegranate peel	Ni(II)	-34.4	-	-	-	8.6	144.2	[51]
Banana peel	Cd(II)	-	-7.4	-	-	40.56	-110	[53]
Pistachio peels	Methylene blue	-2.13	-1.23	-0.93	-0.33	17.25	600	[55]
Rice hulls ash	Iindigo carmine	-23.66	-24.86	-25.85	-26.90	7.77	107.41	[57]
Coffee powder	Rhodamine B	-	-	2.420	4.80	52.18	170.49	[58]
Coffee powder	Rhodamine 6G	-	-	-3.31	-0.654	52.24	190.28	[58]
Garlic peel	Direct Red 12B	-95.39	-111.2	-130.16	-160.91	-54.45	213.69	[60]
Surfactant-modified coconut coir pith	Direct red 12B	-29.16	-31.05	-32.45	-33.94	21.85	167.85	[63]
Surfactant-modified coconut coir pith	Rhodamine B	-28.84	-30.30	-31.46	-32.91	14.62	142.75	[63]

$$\Delta G^{\circ} = -RT \ln K_{th} \quad (1)$$

where R is the universal gas constant (8.314 J mol^{-1} K^{-1}), T is the absolute temperature (K), and K_{th} is the equilibrium constant, as determined from Eq. (2),

$$Kth = \frac{q_e}{C_e} \quad (2)$$

where q_e is the adsorbed amount of heavy metal on the adsorbent surface in an equilibrium state (mg g^{-1}) and C_e is the residual amount of ion in the solution at equilibrium [69]. According to the van't Hoff model and Eq. (3), the values of ΔH° and ΔS° can be obtained as the slope and intercept of the plot of lnK_{th} against 1/T, respectively.

$$\ln K_{th} = \frac{-\Delta G^{\circ}}{RT} = \frac{-\Delta H^{\circ}}{RT} + \frac{\Delta S^{0}}{R} \quad (3)$$

A positive value of ΔH° indicates the endothermic nature of the adsorption process and the formation of strong bonds between the metallic ion and the adsorbent. On the other hand, a negative value of ΔH° characterizes the exothermic nature of the adsorption of the metallic ion on the adsorbent. A positive value of ΔS° indicates an increase in irregularity across the solid-solution interface during the adsorption process, making slight structural changes to both the adsorbent and the adsorbate, while a negative value of ΔS° signifies a decrease in irregularity upon the adsorption [70]. Tables 6 provides a summary of thermodynamic studies performed on the removal of heavy metals and dyes using agricultural wastes.

CONCLUSIONS

This review study suggests that using low-cost adsorbents is very cost-effective compared to conventional adsorbents in adsorption processes. Among the low-cost adsorbents, the agricultural waste is the most widely used bio-adsorbent for removing heavy metals and dyes. The advantages of using these compounds are low cost, good efficiency, minimal energy consumption, simple maintenance, and high adsorption capacity. In general, the removal of heavy metals and dyes by agricultural waste, due to the adsorption process, has a favorable adsorption efficiency and capacity in comparison with other more expensive adsorbents. The performance of different adsorbents depends on the chemical nature of the material and the physical/chemical conditions of examination such as the solution pH, the initial concentration of the dye, and the adsorbate dose; accordingly, the parameters of the optimal values reported in prior studies were discussed. Based on the study results pertaining to isothermal, kinetic and thermodynamic features of the adsorption process, the agricultural wastes often follow Langmuir and Freundlich adsorption isotherm model and the Pseudo second-order kinetic models. In addition, the values obtained from the thermodynamic parameters indicate that the adsorption process is usually appropriate, spontaneous, and either exothermic or endothermic.

REFERENCES

[1] Ahmadi, A.; Foroutan, R.; Esmaeili, H.; Tamjidi, S., The role of bentonite clay and bentonite clay@ MnFe2O4 composite and their physico-chemical properties on the removal of Cr(III) and Cr(VI) from aqueous media. *Environ. Sci. Pollut. Res.* **2020**, *27*, .14057-14044DOI: 10.1007/s11356-020-07756-x.

[2] Vickers, N. J., Animal communication: when i'm calling you, will you answer too? *Curr. Biol.* **2017**, *27*, R713-R715. DOI: 10.1016/j.cub.2017.05.064.

[3] Kanagaraj, J.; Senthilvelan, T.; Panda, R. C.; Aravindhan, R.; Mandal, A. B., Biosorption of trivalent chromium from wastewater: an approach towards Green chemistry. *Chem. Eng. Technol.* **2014**, *37*, 1741-1750. DOI: 10.1002/ceat.201200716.

[4] Crini, G., Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment. *Prog. Polym. Sci.* **2005**, *30*, 38-70. DOI: 10.1016/j.progpolymsci.2004.11.002.

[5] Singh, R.; Gautam, N.; Mishra, A.; Gupta, R., Heavy metals and living systems: An overview. *Indian J. Pharmacol.* **2011**, *43*, 253 -246, DOI: 10.4103/0253-7613.81505.

[6] Ong, S. -A.; Toorisaka, E.; Hirata, M.; Hano, T., Comparative study on kinetic adsorption of Cu(II), Cd(II) and Ni(II) ions from aqueous solutions using activated sludge and dried sludge. *Appl. Water Sci.* **2013**, *3*, 325-321. DOI: 10.1007/s13201-013-0084-3.

[7] Liu, C.; Bai, R., Recent advances in chitosan and its derivatives as adsorbents for removal of pollutants from water and wastewater. *Curr. Opin. Chem. Eng.* **2014**, *4*, 62-70. DOI: 10.1016/j.coche.201.4.01.004.

[8] Elzahabi, M.; Yong, R. N., pH influence on sorption characteristics of heavy metal in the vadose zone. *Eng. Geol.* **2001**, *60*, 61-68. DOI: 10.1016/S0013-7952(00)00089-2.

[9] Wu, Y.; Pang, H.; Liu, Y.; Wang, X.; Yu, S.; Fu, D.; Chen, J.; Wang, X., Environmental remediation of heavy metal ions by novel-nanomaterials: a review. *Environ. Pollut.* **2019**, *246*, 608-620. DOI: 10.1016/ j.envpol.2018.12.076.

[10] Sud, D.; Mahajan, G.; Kaur, M. P., Agricultural waste material as potential adsorbent for sequestering heavy metal ions from aqueous solutions-A review. *Bioresour. Technol.* **2008**, *99*, 6017-6027. DOI: 10.1016/j.biortech.2007.11.064.

[11] Min, J. H.; Woo, M. -K.; Yoon, H. Y.; Jang, J. W.; Wu, J. H.; Lim, C. -S.; Kim, Y. K., Isolation of DNA using magnetic nanoparticles coated with dimercaptosuccinic acid. *Anal. Biochem.* **2014**, *447*, 114-118. DOI: 10.1016/j.ab.2013.11.018.

[12] Subramaniam, R.; Ponnusamy, S. K., Novel adsorbent from agricultural waste (cashew NUT shell) for methylene blue dye removal: optimization by response surface methodology. *Water Resour. Ind.* **2015**, *11*, 64-70. DOI: 10.1016/j.wri.2015.07.002.

[13] Rangabhashiyam, S.; Anu, N.; Selvaraju, N., Sequestration of dye from textile industry wastewater using agricultural waste products as adsorbents. *J. Environ. Chem. Eng.* **2013**, *1*, 629-641. DOI: 10.1016/ j.jece.2013.07.014.

[14] Chiou, M. -S.; Ho, P. -Y.; Li, H. -Y., Adsorption of anionic dyes in acid solutions using chemically cross-linked chitosan beads. *Dyes Pigm.* **2004**, *60*, 69 .84-DOI: 10.1016/S0143-7208(03)00140-2.

[15] Kadirvelu, K.; Kavipriya, M.; Karthika, C.; Radhika,

M.; Vennilamani, N.; Pattabhi, S., Utilization of various agricultural wastes for activated carbon preparation and application for the removal of dyes and metal ions from aqueous solutions. *Bioresour. Technol.* **2003**, *87*, 129-132. DOI: 10.1016/S0960-8524(02)00201-8.

[16] Dinçer, A. R.; Güneş, Y.; Karakaya, N.; Güneş, E., Comparison of activated carbon and bottom ash for removal of reactive dye from aqueous solution. *Bioresour. Technol.* **2007**, *98*, 834-839. DOI: 10.1016/j.biortech.2006.03.009.

[17] He, F.; Hu, W.; Li, Y., Biodegradation mechanisms and kinetics of azo dye 4BS by a microbial consortium. *Chemosphere* **2004**, *57*, 293-301. DOI: 10.1016/j.chemosphere.2004.06.036.

[18] Adegoke, K. A.; Bello, O. S., Dye sequestration using agricultural wastes as adsorbents. *Water Resour. Ind.* **2015**, *12*, 8-24. DOI: 10.1016/j.wri.2015.09.002.

[19] Esmaeili, H.; Tamjidi, S.; Abed, M., Removal of Cu(II), Co(II) and Pb(II) from synthetic and real wastewater using calcified Solamen Vaillanti snail shell. *Desalin. Water Treat.* **2020**, *174*, 324-335. DOI: 10.5004/dwt.2020.24880.

[20] Duman, O.; Ayranci, E., Attachment of benzo-crown ethers onto activated carbon cloth to enhance the removal of chromium, cobalt and nickel ions from aqueous solutions by adsorption. *J. Hazard. Mater.* **2010**, *176*, 231-238. DOI: 10.1016/j.jhazmat.2009.11.018.

[21] Demirbas, A., Heavy metal adsorption onto agro-based waste materials: a review. *J. Hazard. Mater.* **2008**, *157*, 220-229. DOI: 10.1016/j.jhazmat.2008.01.024.

[22] Tao, H. -C.; Zhang, H. -R.; Li, J. -B.; Ding, W. -Y., Biomass based activated carbon obtained from sludge and sugarcane bagasse for removing lead ion from wastewater. *Bioresour. Technol.* **2015**, *192*, 611-617. DOI: 10.1016/j.biortech.2015.06.006.

[23] Elliott, C.; Colby, T.; Iticks, H., Activated carbon obliterans alter aspiration of activated charcoal. *Chest* **1989**, *96*, 672-674. DOI: 10.1016/j.susmat.2016.06.002.

[24] Agarwal, M.; Singh, K., Heavy metal removal from wastewater using various adsorbents: A review. *J. Water Reuse Desalin.* **2017**, *7*, 387-419. DOI: 10.2166/wrd.2016.104.

[25] He, J.; Lu, Y.; Luo, G., Ca(II) imprinted chitosan microspheres: an effective and green adsorbent for the removal of Cu(II), Cd(II) and Pb(II) from aqueous solutions. *Chem. Eng. J.* **2014**, *244*, 202-208. DOI: 10.1016/j.cej.2014.01.096.

[26] Duruibe, J. O.; Ogwuegbu, M. O. C.; Egwurugwu, J. N., Heavy metal pollution and human biotoxic effects. *Int. J. Phys. Sci.* **2007**, *2*, 112-118. DOI: 10.5897/IJPS.9000289.

[27] Appenroth, K. -J., Definition of heavy Metals and their Role in Biological Systems. In Soil Heavy Metals, Springer: Berlin, Germany, **2010**, pp. 19-29.

[28] Jamshaid, M.; Khan, A. A.; Ahmed, K.; Saleem, M., Heavy metal in drinking water its effect on human health and its treatment techniques-a review. *Int. J. Biosci.* **2018**, *12*, 223-240. DOI: 10.12692/ijb/12.4.223-240.

[29] Gautam, R. K.; Sharma, S. K.; Mahiya, S.; Chattopadhyaya, M. C., Contamination of Heavy Metals in Aquatic Media: Transport, Toxicity and Technologies for Remediation. In Heavy Metals In Water: Presence, Removal and Safety, Royal Society of Chemistry: London, **2014**.

[30] Mara, D.; Horan, N. J., Handbook of Water and Wastewater Microbiology, Elsevier, **2003**.

[31] Wadhawan, S.; Jain, A.; Nayyar, J.; Mehta, S. K., Role of nanomaterials as adsorbents in heavy metal ion removal from waste water: A review. *J. Water Process Eng.* 2020, *33*, 101038. DOI: 10.1016/j.jwpe..2019.101038

[32] [32] AbiD, B. A.; BrbootI, M. M.; Al-ShuwaikI, N. M., Removal of heavy metals using chemicals precipitation. *Eng. Technol. J.* **2011**, *29*, 595-612. Masindi, V.; Muedi, K. L., Environmental contamination by heavy metals. *Heavy Metals* **2018**, 10, 132-115 DOI: 10.5772/intechopen.76082.

[33] Tamjidi, S.; Esmaeili, H.; Moghadas, B. K., Application of magnetic adsorbents for removal of heavy metals from wastewater: a review study. *Mater. Res. Express* **2019**, *6*, 102004. DOI: 10.1088/2053-159/1ab3ffb.

[34] Jan, A. T.; Azam, M.; Siddiqui, K.; Ali, A.; Choi, I.; Haq, Q. M., Heavy metals and human health: mechanistic insight into toxicity and counter defense system of antioxidants. *Int. J. Mol. Sci.* **2015**, *16*, 29592-29630. DOI: 10.3390/ijms161226183.

[35] Tchounwou, P. B.; Yedjou, C. G.; Patlolla, A. K.; Sutton, D. J.; Luch, A., Molecular, clinical and environmental toxicology. *Mol. Clin. Environ. Toxicol.* **2012**, *3*, 133-164. DOI: 10.1007/978-3-7643-8340-4_6.

[36] Shikuku, V. O.; Achieng, G. O.; Kowenje, C. O., Removal of Dyes From Wastewater by Adsorption Onto Low-Cost Adsorbents. In Impact of Textile Dyes on Public Health and the Environment, IGI Global: Pennsylvania, United States, **2020**, pp. 239-257.

[37] Tara, N ;.Siddiqui, S. I.; Rathi, G.; Chaudhry, S. A.; Asiri, A. M., Nano-engineered adsorbent for the removal of dyes from water: A review. *Curr. Anal. Chem.* **2020**, *16*, 14-40. DOI: 10.2174/ 1573411015666190117124344.

[38] Forgacs, E.; Cserhati, T.; Oros, G., Removal of synthetic dyes from wastewaters: a review. *Environ. Int.* **2004**, *30*, 953-971. DOI: 10.1016/ j.envint.2004.02.001.

[39] Reddad, Z.; Gerente, C.; Andres, Y.; Le Cloirec, P., Adsorption of several metal ions onto a low-cost biosorbent: kinetic and equilibrium studies. *Environ. Sci. Technol.* **2002**, *36*, 2067-2073. DOI: 10.1021/ es0102989.

[40] Saxena, R.; Saxena, M.; Lochab, A., Recent progress in nanomaterials for adsorptive removal of organic contaminants from wastewater. *Chem. Select* **2020**, *5* , 353-335. DOI: 10.1002/slct.201903542.

[41] Yagub, M. T.; Sen, T. K.; Afroze, S.; Ang, H. M., Dye and its removal from aqueous solution by adsorption: A review. *Adv. Colloid Interface Sci.* **2014**, *209*, 172-184. DOI: 10.1016/j.cis.2014.04.002.

[42] Ngulube, T.; Gumbo, J. R.; Masindi, V.; Maity, A., An update on synthetic dyes adsorption onto clay based minerals: A state-of-art review. *J. Environ. Manage.* **2017**, *191*, 35-57. DOI: 10.1016/ j.jenvman.2016.12.031.

[43] Tan, K. B.; Vakili, M.; Horri, B. A.; Poh, P. E.; Abdullah, A. Z.; Salamatinia, B., Adsorption of dyes by nanomaterials: recent developments and adsorption mechanisms. *Sep. Purif. Technol.* **2015**, *150*, 229-242. DOI: 10.1016/j.seppur.2015.07.009.

[44] Kandisa, R. V.; Saibaba, K. V. N.; Shaik, K. B ;. Gopinath, R., Dye removal by adsorption: a review. *J. Biorem. Biodegrad.* **2016**, *7*, 371. DOI: 10.4172/2155-6199.1000371.

[45] Crini, G.; Lichtfouse, E.; Wilson, L. D.; Morin-Crini, N., Adsorption-oriented Processes Using Conventional and Non-conventional Adsorbents for Wastewater Treatment. In Green Adsorbents for Pollutant Removal, Springer: Berlin, Germany, **2018**; pp. 23-71.

[46] Sadegh, H.; Ali, G. A. M.; Gupta, V. K.; Makhlouf, A. S. H.; Shahryari-ghoshekandi, R.; Nadagouda, M. N.; Sillanpää, M.; Megiel, E., The role of nanomaterials as effective adsorbents and their applications in wastewater treatment. *J. Nanostruct. Chem.* **2017**, *7*, 1-14. DOI: 10.1007/s40097-017-0219-4.

[47] Cooney, D. O., Adsorption Design for Wastewater Treatment, CRC Press, 1998.

[48] Li, X.; Tang, Y.; Cao, X.; Lu, D.; Luo, F.; Shao, W., Preparation and evaluation of orange peel cellulose adsorbents for effective removal of cadmium, zinc, cobalt and nickel. *Colloids Surf., A* **2008**, *317*, 512-521. DOI: 10.1016/j.colsurfa.20.07.11.031

[49] Feng, N. -C.; Guo, X. -Y., Characterization of adsorptive capacity and mechanisms on adsorption of copper, lead and zinc by modified orange peel. *Trans. Nonferrous Met. Soc. China* **2012**, *22*, 1224-1231. DOI: 10.1016/S1003-6326(11)61309-5.

[50] Bhatnagar, A.; Minocha, A. K., Biosorption optimization of nickel removal from water using Punica granatum peel waste. *Colloids Surf., B* **2010**, *76*, 544-548. DOI: 10.1016/j.colsurfb.2009.12.016.

[51] El-Ashtoukhy, E. S.; Amin, N. K.; Abdelwahab, O ,. Removal of lead(II) and copper(II) from aqueous solution using pomegranate peel as a new adsorbent. *Desalination* **2008**, *223*, 162-173. DOI: 10.1016/ j.desal.2007.01.206.

[52] Memon, J. R.; Memon, S. Q.; Bhanger, M. I.; Memon, G. Z.; El-Turki, A.; Allen, G. C., Characterization of

banana peel by scanning electron microscopy and FT-IR spectroscopy and its use for cadmium removal. *Colloids Surf., B* **2008**, *66*, 260-265. DOI: 10.1016/ j.colsurfb.2008.07.001.

[53] Amarasinghe, B.; Williams, R. A., Tea waste as a low cost adsorbent for the removal of Cu and Pb from wastewater. *Chem. Eng. J.* **2007**, *132*, 299-309. DOI: 10.1016/j.cej.2007.01.016.

[54] Vučurović, V. M.; Razmovski, R. N.; Miljić, U. D.; Puškaš, V. S., Removal of cationic and anionic azo dyes from aqueous solutions by adsorption on maize stem tissue. *J. Taiwan Inst. Chem. Eng.* **2014**, *45*, 1700-1708. DOI: 10.1016/j.jtice.2013.12.020.

[55] Chandrasekhar, S.; Pramada, P. N., Rice husk ash as an adsorbent for methylene blue-effect of ashing temperature. *Adsorption* **2006**, *12*, 27. DOI: 10.1007/ s10450-006-0136-1.

[56] Lakshmi, U. R.; Srivastava, V. C.; Mall, I. D.; Lataye, D. H., Rice husk ash as an effective adsorbent: Evaluation of adsorptive characteristics for Indigo Carmine dye. *J. Environ. Manage.* **2009**, *90*, 710-720. DOI: 10.1016/j.jenvman.2008.01.002.

[57] Shen, K.; Gondal, M. A., Removal of hazardous Rhodamine dye from water by adsorption onto exhausted coffee ground. *J. Saudi Chem. Soc.* **2017**, *21*, S120-S127. DOI: 10.1016/j.jscs.20.13.11.005

[58] Argun, M. E.; Güclü, D.; Karatas, M., Adsorption of Reactive Blue 114 dye by using a new adsorbent: Pomelo peel. *J. Ind. Eng. Chem.* **2014**, *20*, 1079-1084. DOI: 10.1016/j.jiec.2013.06.045.

[59] Asfaram, A.; Fathi, M. R.; Khodadoust, S.; Naraki, M., Removal of direct red 12B by garlic peel as a cheap adsorbent: kinetics, thermodynamic and equilibrium isotherms study of removal. *Spectrochim. Acta, Part A* **2014**, *127*, 415-421. DOI: 10.1016/ j.saa.2014.02.092.

[60] Amin, N. K., Removal of direct blue-106 dye from aqueous solution using new activated carbons developed from pomegranate peel: adsorption equilibrium and kinetics. *J. Hazard. Mater.* **2009**, *165*, 52-62. DOI: 10.1016/j.jhazmat.2008.09.067.

[61] Ghaedi, M.; Tavallali, H.; Sharifi, M ;.Kokhdan, S. N.; Asghari, A., Preparation of low cost activated carbon from Myrtus communis and pomegranate and their efficient application for removal of Congo red from aqueous solution. *Spectrochim. Acta, Part A* **2012**, *86*, 107-114. DOI: 10.1016/j.saa.20.11.10.012.

[62] Sureshkumar, M. V.; Namasivayam, C., Adsorption behavior of Direct Red 12B and Rhodamine B from water onto surfactant-modified coconut coir pith. *Colloids Surf., A* **2008**, *317*, 277-283. DOI: 10.1016/ j.colsurfa.2007.10.026.

[63] Chang, S. -H.; Wang, K. -S.; Li, H. -C.; Wey, M. -Y.; Chou, J. -D., Enhancement of Rhodamine B removal by low-cost fly ash sorption with Fenton pre-oxidation. *J. Hazard. Mater.* **2009**, *172*, 1131-1136. DOI: 10.1016/j.jhazmat.2009.07.106.

[64] Krishnani, K. K.; Meng, X.; Christodoulatos, C.; Boddu, V. M., Biosorption mechanism of nine different heavy metals onto biomatrix from rice husk. *J. Hazard. Mater.* **2008**, *153*, 1222-1234. DOI: 10.1016/j.jhazmat.2007.09.113.

[65] Abshirini, Y.; Foroutan, R.; Esmaeili, H., Cr(VI) removal from aqueous solution using activated carbon prepared from Ziziphus spina-christi leaf. *Mater. Res. Express* **2019**, *6*, 045607. DOI: 10.1088/2053-1591/11fb45.

[66] Sharafzad, A.; Tamjidi, S.; Esmaeili, H., Calcined lotus leaf as a low-cost and highly efficient biosorbent for removal of methyl violet dye from aqueous media. *Int. J. Environ. Anal. Chem.* **2020**, 1-24. DOI: 10.1080/03067319.2020.1711894.

[67] Martins, R. J. E.; Vilar, V. J. P.; Boaventura, R. A. R., Kinetic modelling of cadmium and lead removal by aquatic mosses. *Braz. J. Chem. Eng.* **2014**, *31*, 229-242. DOI: 10.1590/S0104-66322014000100021

[68] Romero-Gonzalez, J.; Peralta-Videa, J. R.; Rodriguez, E.; Delgado, M.; Gardea-Torresdey, J. L., Potential of Agave lechuguilla biomass for Cr(III) removal from aqueous solutions: Thermodynamic studies. *Bioresour. Technol.* **2006**, *97*, 178-182. DOI: 10.1016/j.biortech.2005.01.037.

[69] Liu, Z.; Lu, Y.; Li, X.; Chen, H.; Hu, F., Adsorption of phosphate from wastewater by a ZnO-ZnAl hydrotalcite. *Int. J. Environ. Anal. Chem.* **2019**, *99*, 1415-1433. DOI: 10.1080/03067319.2019.1622696.