BAJOPAS Volume 16 Number 2, December, 2023

http://dx.doi.org/10.4314/bajopas.v16i2.9

Bayero Journal of Pure and Applied Sciences, 16(2): 63 - 77
Received: 03/05/2023
Accepted: 14/10/2023
ISSN 2006 – 6996

ACTIVATED CARBON AND NANOCOMPOSITE ADSORBENTS USED FOR THE REMOVAL OF DYES AND HEAVY METALS FROM AQUEOUS SOLUTION USING ADSORPTION TECHNIQUE - A REVIEW

Abdullahi, M. R.* and Sulaiman, M.S.
Department of Pure and Industrial Chemistry, Bayero University Kano, Nigeria
Corresponding author: mrabdullahi86@gmail.com

ABSTRACT
Excessive discharged of dyes and heavy metals as a result of developments in the industrial activities has resulted to an increased in environmental pollution and caused serious negative effects to human and other living organisms. Activated carbon derived from agricultural residues and nanocomposites has been widely used as less expensive adsorbents mainly for the removal of various pollutants from aqueous solution and the use adsorption technique has been the most effective, less cost and promising method for the removal of wide range of pollutants. This review focuses on the use of various adsorbents derived from activated carbons and nanocomposites that has been used for the removal of toxic pollutants from aqueous solution. However, adsorption isotherms, kinetics and thermodynamics of different adsorption systems are also highlighted.
Keywords: Dyes, heavy metals, activated carbon, nanocomposites

INTRODUCTION

Activated carbon

Activated carbon refers to an amorphous or crystalline carbonaceous material with a high degree of porosity and large internal surface area (Saleem *et al.*, 2019). Activated carbon can be produced from wide range of agricultural waste such as wood, sawdust, nut shells, rice husk and so on. Other sources of activated carbon precursors includes non-renewable materials such petroleum residues, anthracite, coal, peat and lignite (Ahmedna *et al.*, 2000). Activated carbon has been widely used as adsorbent mainly for the removal of pollutants from industrial wastewater (Kebede and Gashaw, 2017).

Activated carbons are generally classified based on their particle sizes into powder and granular activated carbon (Babel andKurniawan, 2004). Powder activated carbons (PAC) has a particle size range between 0.015 to 0.025 mm and are mostly used in liquid-phase adsorption in domestic and industrial wastewater treatment while granular activated carbon (GAC) has a particle size range between 0.6 mm to 4 mm and are mostly applied in both liquid and gas phases. (Zhang *et al.*, 2008; Foo and Hameed, 2011).

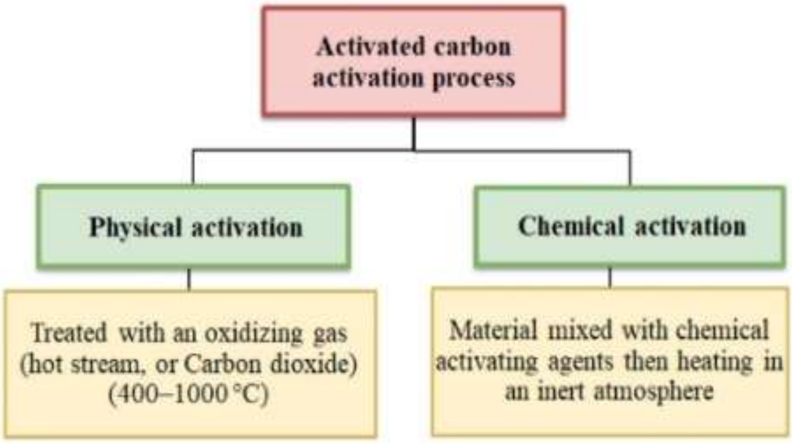
(a) Powder (b) Granular

Figure 1: Types of activated carbon (a) powder (b) granular (Fahim *et al.*, 2022)

Activated carbon preparation

Generally, activated carbon preparation involves the following steps namely, activation and carbonisation.However, the most commonly used activation methods comprise of physical and chemical methods (Scheme 1). Physical activation is a two-step process that involves carbonisation (pyrolysis) of the starting material in an inert atmosphere at a high temperature between 800 –1100 °C followed by activation of the carbonised material by using steam, carbon dioxide or air mixtures (Bouchelta *et al.,*2008). In this method, the raw material is carbonised first by using steam or carbon dioxide followed by activation.

The purpose of activation is to further develop porosity and create structures that will leads to the formation of fine solid cavities in activated carbon. In chemical method, the precursors (raw materials) are impregnated by an activating agent followed by heating process at a given time and temperatures ranging from 400 – 900 °C depending on the type of the precursor (Yahya *et al*., 2015; Dehghani *et al*. 2020).
Phosphoric acid (H_3PO_4), zinc chloride ($ZnCl_2$), sodium hydroxide (NaOH) and potassium hydroxide (KOH) are the most commonly used activating agents. $ZnCl_2$ or H_3PO_4 are mostly used for lignocellulosic materials, but $ZnCl_2$ is more effective in producing activated carbon with good surface area and good micropores while H_3PO_4 is more effective in producing activated carbon with mesoporous structure and larger pore volumes. However, H_3PO_4 is more environmentally friendly as compared to $ZnCl_2$ (Asadullah*et al*., 2007). Activated carbon produced by using $ZnCl_2$ cannot be used in food and pharmaceutical industries (Al-Qodah and Shawabkah, 2009). But, activation with H_3PO_4 gives better carbon yield with less harmful properties (Romero-Anaya *et al*., 2012).However, it has been reported that activated carbon produced using potassium hydroxide usually has better performance and surface area in comparison to sodium hydroxide, but sodium hydroxide is cheaper and less harmful compared to potassium hydroxide (Huang *et al*. 2014; Byamba-Ochir*et al*. 2016).



Scheme 1: physical and chemical activation methods (Fahim *et al*., 2022)

Carbonisation is a thermal decomposition process that involves the removal of volatile matter content and other non-carbon species such as hydrogen, nitrogen and oxygen in the form of liquid and gases, leaving behind a rigid skeleton of carbon in the formof aromatic sheets and strips (Yakout and El-deen, 2016).

Nanocomposite

Composites are simply defined as multiphase materials that are produced from combination of two or more materials with different physical or chemical properties which when combined together, they produce a new material with different properties from the individual components (Abdullahi *et al*., 2014). Nanocomposites are composite materials in which at least one of the phases has dimensions in nano size range between 1-100 nm. Nanocomposite materials are environmentally friendly and biodegradable materials of the 21st century with an annual growth rate of 25% because of their multifunctional properties as well as uniqueness and combination of properties which are not found in conventional composites (Camargo *et al*., 2009). Nanocomposites have received much attention in the treatment of various pollutants from wastewater and are also used for the degradation of dyes because of their small sizes and larger internal surface areas (Srivastava *et al*., 2016; Farooq *et al.,* 2017). The most commonly used methods for nanocomposites preparation comprises chemical methods such as colloidal, suspension in solvents, sol gel process, in-situ intercalative polymerization, melt intercalation and so on (Kazlagic *et al*., 2019).

Dyes

These are coloured materials which are capable of imparting colour onto fabric by using physical or chemical binding. They are basically natural or synthetic organic compounds that can bind themselves to the surfaces or fabrics in order to provide brightness and lasting colour.

They are widely applied in various industries like leather, textile, paper, rubber, cosmetics, plastic, pharmaceuticals, food industries and so on (Chincholi *et al*., 2014; Seow and Lim, 2016). Dyes are toxic materials that could lead to liver and kidney dysfunction, respiratory problems and increased risk of cancer attack in human (Igwegbe *et al*., 2020). The proportion of dyes discharged into the environment by different industries is presented in Figure 2.

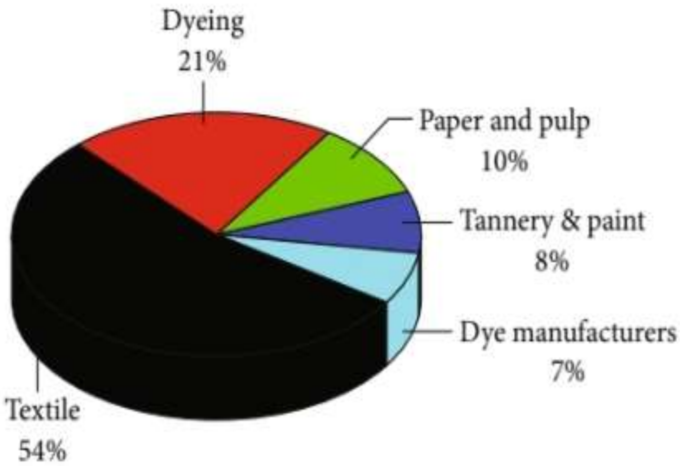


Figure 2: proportion of dyes discharged into the environment by different industries (Sharma *et al.,* 2022)

Heavy metals

Heavy metals are metallic elements with relatively high density greater than 4 g/cm^3. Some heavy metals like chromium and lead are toxic or poisonous substances even at low concentration. Heavy metals are non-degraded material that occurs naturally in the earth crust which persist in the environment and enters into the body of living organisms through food, water and air leading to serious threats to human and other organisms (Adebayo *et al*., 2015). Natural activities such as like volcanic eruption, forest fire, weathering of rocks and anthropogenic activities like mining, power plant waste, industrial and agricultural activities are the major sources of heavy metal leading to environmental pollution (Sankhla *et al*., 2021). Example of heavy metals include chromium (Cr), cadmium (Cd), lead (Pb), arsenic (As), zinc (Zn), mercury (Hg) and so on (Duruibe*et al*., 2007). Heavy metals like Zn, Cu, Mn, Ni and Co are considered macronutrients which are required for plant growth whereas metals like Cr, Pb, Cd and Hg are toxic and have no any biological function (Canli and Atli, 2003). The various sources of heavy metals are presented in Figure 3.

Figure 3: Sources of heavy metals

Adsorption

Adsorption is a process in which molecules of gases, liquids or metal ions are accumulated or deposited at the solid surface. In order words, adsorption is separation technique method that is used to separate substances from liquid or gas phase. The substance that is deposited at the solid surface is called "Adsorbate"while the solid surface on which the deposition takes place is called "Adsorbent" (Harun *et al*., 2020). In terms of mode of operations, batch and column adsorption are utilized.

Batch adsorption is an independent process and most commonly used adsorption method for removal of pollutants from aqueous solution. In batch mode method, the effects of operating parameters like pH, adsorbate concentration, adsorbent dosage, time and temperature are studied. After attaining the equilibrium, the adsorbent is removed from water usually by filtration (Patel, 2021). The process is simple, easy and can adsorb pollutant at very low concentration, but its major drawback is that is not suitable for industrial application (Patel, 2019).

Column adsorption method also referred to as fixed bed or continuous adsorption method and is widely used for the removal of large quantity of pollutants from wastewater. In this method, solution of adsorbate is continuously passed through column at certain flow rate having adsorbate continuously contacted with adsorbent surface. The great advantage of this method is that it can be used to adsorbed higher amount of adsorbate and can be used for industrial purpose (Yelebe *et al*., 2013). However, the method is very expensive as it requires large amount of adsorbent and optimization of various factors (Patel, 2021).

Factors affecting adsorption process

Adsorption performance is influenced by a number of factors some of which includes initial concentration of the adsorbate, contact time, pH, adsorbent dosage and temperature. These factors are briefly discussed as follows:

Initial concentration: This plays a vital role in adsorption process. At higher initial concentration, there is availability of ions in the solution thereby surrounding the binding sites of the adsorbent and eventually get adsorbed leading to an increase in the adsorption capacities (Mhemeed, 2018).

Contact time: Determining the optimum time of contact in adsorption process gives an idea of the required time needed by the adsorbent to adsorb the maximum amount of the adsorbate in the adsorption system. It has been reported that the adsorption capacities for most adsorbent increases with increase in contact time (Elsayed *et al*., 2020).

pH of the solution:This is the most important factor affecting adsorption process and the adsorption capacity of adsorbent is strongly dependent upon the pH of the solution. The pH affects the degree of specification of ions and the ionization of surface functional groups. Proper selection of pH in adsorption system is very vital in determining the maximum adsorption capacity (Elsayed *et al*., 2020).

Adsorbent dosage:This is another important factor that influences adsorption process. Determining the required amount of adsorbent dosage can predict the cost of adsorbent that would be used in adsorption procees. Generally, increase in dosage results in aggregation or overlapping of the adsorption sites which subsequently reduces the available surface area of the adsorbent and lower the adsorption capacity (Hameed and Foo, 2010).

Temperature: Influence of temperature on adsorption capacity depends on the type of adsorbents and it can predict whether the adsorption is endothermic or exothermic in nature. Increase in temperature results in pores enlargement and enhances solubility of the adsorbates and promotes molecular attraction between the absorbate and adsorbents (Hameed and Foo, 2010).

Adsorbent derived from activated carbon for the removal of dyes

Elsayed *et al*. (2016) reported a study on adsorption of tartrazine azo-dye from aqueous solution on activated carbon produced from apricot stones by chemical activation with phosphoric acid using batch and fixed bed adsorption methods. The finding of the study revealed that the BET surface area and total pore volume of activated carbon were found to be 774 m^2/g and 1.26 cm^3/g, respectively. Batch adsorption studies showed that there was increase in adsorption capacity from 22.6 to 76 mg/g with an increase in the initial dye concentrations from 25 to 100 mg/L whereas fixed bed studies showeda decrease in maximum adsorption capacity from 2.53 mg/g to 1.88 mg/g with an increase in flow rate from 2.7 to 5.7 mL/min.

Sebata *et al.* (2013) investigated the adsorption efficiency of adsorbent produced from bambara groundnut hulls for the removal of atrazine from aqueous solution. The adsorption of atrazine was found to be pH and time dependent in which the optimum adsorption was reached at pH 7.0 and contact time of 120 min respectively.

The effect of adsorbent dosage showed that the removal efficiency increases with increase in adsorbent dosage and the maximum removal was achieved using 0.9 g of the adsorbent, but increase in temperature have resulted to decrease in removal efficiency. The adsorption isotherm and the kinetic study were found to follow Freundlich adsorption isotherm and pseudo first-order models respectively. Desorption study also showed that 45-70 % of the adsorbent was recovered.

Gupta *et al.* (2017) used an adsorbent derived from belpatra bark for the removal of red RB dye from aqueous solution. Batch adsorption studies showed that the maximum removal capacity obtained was 94.0% at 20 mg/L of dye concentration, adsorbent dosage of 0.5 g, pH 3, contact time range of 40-45 minutes and temperature of 320 K. The adsorption isotherm studies were best described by Langmuir adsorption isotherm model.

In another study conducted by (Sathya *et al.* 2020), adsorbent derived from *Murrayakoenigii*stem biochar was used for removal of crystal violet dye from textile effluent. Batch adsorption studies was conducted and the maximum dye adsorption capacity obtained was 50 mg/g. Langmuir and Freundlich isotherms were modeled and the experimental data showed better fitting to Langmuir adsorption isotherm model with high correlation coefficient, R^2 value of 0.939 compared to Freundlich adsorption model with R^2 value of 0.870. Kebede and Gashaw(2017) utilized activated carbon obtained from tannery waste for the removal of azo metal complex dyes from aqueous solution. The BET surface area of the adsorbent was found to be 535.02 m^2/g and the maximum removal efficiency obtained from batch adsorption experiments at concentration of 40-160 mg/L, pH 6-9, contact time of 120 minutes and adsorbent dosage of 2 g were 97 and 93% for mordant black 11 dye and red azo dye respectively. The adsorption kinetic study was found to follow pseudo second-order model. Activated carbon derived from palm oil shell has been used for the removal of methylene blue dye from aqueous solution. The surface area and total pore volume of adsorbent was found to be 596.20 m^2/g and 0.34 cm^3/g respectively. Batch and column adsorption methods were used to study the adsorption and it was found from batch study that the maximum adsorption capacity of 243.90 mg/g was obtained at 30°C, pH 6.5 and initial concentration of 50–500 mg/L while column study revealed that the maximum bed capacity of 40.86 mg/g was obtained at 100 mg/L of initial dye concentration, bed height of 6 cm and 20 mL/min flow rate. The kinetic and isotherm of adsorption process showed better fittings to pseudo second-order and Langmuir isotherm model respectively (Tan *et al.,* 2008).

Agricultural waste obtained from *Raphiahookerie* fruit epicarp was used as less expensive adsorbent with very rough surface, wider pores with exterior opening, low BET surface area (0.0351 m^2/g), moisture content (0.60 %) and ash content (4.17 %).

The adsorptive performance was investigated on removal of Rhodamine B dye and it was found that the adsorption capacities increased from 43.5 mg/g to 312 mg/g as the concentration increased from 50 to 400 mg/L. The maximun monolayer adsorption capacity was found to be 666.67 mg/g. The study further revealed that the adsorption system followed pseudo second-order kinetic model (Inyinbor *et al*., 2016).

Khasri *et al*. (2021) evaluate the adsorption performance of adsorbents derived from melunak and rubber wood sawdust using chemical activation with potassium hydroxide respectively. Batch adsorption studies on removal of remazol brilliant violet 5R dye from aqueous solutionwas conducted and the finding of the studies revealed that as the concentration increased from 25 to 300 mg/L, there was corresponding increase in dye removal from 19.61 to 151.50 mg/g onto melanuk activated carbon and from 19.20 to 150.02 mg/g onto rubber wood saw dust activated carbon. The values of correlation coefficients from kinetic studies on both adsorbents were found to be 0.999 and 0.995 which indicated that the adsorption system obeyed the pseudo second-order model.

Alhujaily *et al*. (2020) utilized mush room waste with a well developed porous surface as adsorbent for rapid removal of anionic dyes such as Direct Red 5B, Direct Black 22, Direct Black 71, and Reactive Black 5 from aqueous solution. The study revealed that the maximum adsorption capacities for Direct Red 5B, Direct Black 22, Direct Black 71, and Reactive Black 5 were found to be 18 mg/g, 15.46 mg /g, 20.19 mg/g and 14.62 mg/g respectively. Four different adsorption isotherm models namely Langmuir, Redlich–Peterson, Freundlich and Dubinin–Radushkevich isotherm models were used to explain the adsorption process. However, the experimental data for all the adsorption systems followed the Langmuir and Redlich–Peterson isotherm models. Thermodynamic study indicated that the adsorption processes were endothermic and spontaneous in nature.

Park *et al*. (2020) reported adsorption study using inexpensive adsorbent obtained from palm kernel shells for removal of crystal violet dye from wastewater. Adsorption isotherm studies revealed that Langmuir and Freundlich isotherm models showed good fitness with relatively high with R^2 values of 0.954 and 0.924 respectively. The values of Langmuir (Q_m) and Freundlich (K_F) maximum adsorption capacities were determined to be 24.45 mg/g and 2.07 mg/g respectively. Kinetic study indicated that pseudo second-order model showed better fitting and the values of various parameters from thermodynamic studies such as change Gibbs free energy of adsorption ΔG, change in enthalpy of adsorption ΔH and change in entropy of adsorption, ΔS indicated a feasible and endothermic process with an increase in disorder or randomness at interfaces between dye molecules and solid adsorbent surface.

Abdus-salam and Buhari (2014) used mango seeds as adsorbent for effective removal of alizarin and fluorescein dyes aqueous solution. The adsorbent was found to have a large surface area of 819.80 m^2/g, iodine number of 762 mg/g and low ash content value of 2.23%. The maximum percentage removals at equilibrium concentration of 30 mg/L for the uptake of alizarin and fluorescein dye were 90.44% and 91.32%, respectively. Langmuir isotherm model described the adsorption systems for both alizarin and fluorescein dyes.

Adsorbent derived from activated carbon for the removal of heavy metals

Abdullahi and Alkali, (2023) reported a study on adsorption of Cr(VI) ions from aqueous solution using activated carbon derived from bambara nut shells was investigated in aqueous solution using batch adsorption technique. The maximum removal of Cr (VI) ions was 68.00 mg/g at pH 2, adsorbent dosage 0.01 g and contact time of 60 minute.

The Equilibrium data of adsorption revealed that the adsorption of Cr(VI) ions onto activated carbon showed better fitting to Langmuir isotherm in comparison to Freundlich, Temkin and Dubinin-Radaushkevich isotherm models. The value of Langmuir monolayer coverage was 55.56 mg/g. However, the kinetics of adsorption was best described by pseudo second-order model with highest correlation coefficient, R^2 value of 0.984.

Thermodynamics parameters of adsorption revealed negative value of Gibb's free energy (ΔG) indicating a feasible and spontaneous adsorption process whereas the positive value of change in enthalpy (ΔH) indicates that the adsorption process was endothermic in nature while the positive value of change in entropy (ΔS) revealed that there is an increase in randomness at solid-solution interface during adsorption process.

In a separate study reported by Yunusa and Ibrahim, (2022), low-cost activated carbon obtained from desert date seed shell by chemical activation with H_3PO_4 has been utilized for the removal of hexavalent chromium from aqueous solution. Batch experiments were conducted to investigate the influence of operating variables such as pH, contact time, adsorbent dosage, initial concentration and temperature. The amount of Cr(VI) adsorbed (99.01 mg/g) was observed at a pH value of 2.

Georgieva *et al*. (2015) worked on activated carbon obtained from black rice husk for the removal of hexavalent Cr(VI) from aqueous solution and it was observed that the adsorption system depends on solution pH whereby the highest removal efficiency (99.50 %) was achieved at pH 2 and beyond this pH, no further increase in removal efficiency was noticed. Other optimum conditions for adsorption were established at initial concentration of 50 mg/L, contact time of 60 minutes and adsorbent dosage of 15 g/L. Kinetic study showed that pseudo second order favoured the adsorption process.

Mekonnen *et al*. (2015) reported study on adsorption of Cr(VI) onto some selected local adsorbent obtained from avocado kernel seeds, sawdust and papaya peels. The effects of various parameters were investigated. The maximum adsorption performance was achieved pH 1.0 and contact time, 160 min, sawdust adsorbent was found to have the highest removal efficiency of 98.18 %, avocado kernel seed, 96.35 % and papaya peel with 94.58 %.

The study further revealed that increase in temperature as well as adsorbent mass resulted in increase in the removal efficiency of Cr(VI) but, increase in initial concentration resulted to decrease in removal efficiency. The kinetics study and adsorption isotherms were found to follow pseudo second- order kinetics and Freundlich isotherm model respectively. However, thermodynamic study revealed feasible and exothermic adsorption process.

Kushwaha and Upadhyay (2015) investigated study on removal of chromium using an adsorbent derived from neem sawdust. The finding of the study showed that the maximum removal (84 %) was attained at pH 2.

Momcilovic *et al.* (2011) used pine cone based activated carbon as adsorbent for the removal of Pb(II) ions from an aqueous solution. Batch adsorption at optimum concentration of 100 mg/L, adsorbent dosage 2 mg/L, contact time 60 minutes and pH greater than 6 was evaluated and the maximum adsorption capacity was found to be 27.53 mg/g. Pseudo second order kinetic and Langmuir isotherm model described the adsorption process respectively.

Dada *et al*. (2012) investigated various isotherm models on adsorption of Zn(II) onto rice husk adsorbent modified with phosphoric acid. Amongst the isotherm models studied, it was reported that Langmuir model had better fitting with highest value of correlation coefficients, R^2 value of 0.9919 and the value of Langmuir maximum monolayer coverage was 101.01 mg/g and the value for separation factor R_L was determined to be 0.133 indicating favourable adsorption. Moreover, the value for the adsorption intensity (1/n = 0.89) obtained using Freundlich model also confirmed a favourable adsorption process. The value of heat of adsorption determined by Temkin was 25.34 J/mol. Similarly, Dubinin Radaushkevich model revealed that the value of mean energy was 0.7 kJ/mole and this indicated physical adsorption process.

Adsorption of Cu(II) ion from aqueous solution using *Uncariagambir* adsorbent has been reported and adsorption process was influenced by pH, adsorbent dosage, and temperature. It was found that the maximum removal efficiency of 83.78 % was achieved when using 0.3 g of adsorbent at 180 min, pH 5.0 and concentration 10 mg/L. However, the thermodynamic studies suggested that adsorption process is spontaneous and endothermic in nature. Langmuir adsorption isotherm model and pseudo second kinetic model were found to explain the process of adsorption (Tong *et al.,* 2011).

In another study, adsorbent derived from Baobab fruit shell biomass was used for adsorption of Pb(II)and Cu(II)ions from aqueous solution. It was observed that the adsorption of metal ions onto biomass adsorbent increased with increase in adsorbent dosage whereby the percentage removal for Pb(II)uptake was found to be 68% at optimum pH 5.5, adsorbent dose of 0.7 g, metal ion concentration of 10 mg/L and contact time of 120 minute and the maximum percentage removal for Cu(II)was 67.8 % at optimal pH 6, adsorbent dose of 0.9 g, metal ion concentration of 20 mg/L and contact time of 120 minutes. The findings of the studies indicated that the adsorption isotherm for removal of Pb(II) and Cu(II) followed Temkin adsorption isotherm model with the highest R^2 values of 0.9977 and 0.9967 respectively (Chigondo *et al.,* 2013).

Duraisamy *et al.* (2015) have used bamboo activated carbon to remove Pb(II) ions from an aqueous solution. The adsorbent was found to be highly effective and it has the surface area of 807 m^2/g and pore volume of 0.65 cm^3/g, the uptake of Pb(II) was found to increased from 32.93 % to 97.33 % with the increase in adsorbent dose from 4 g/L to 40 g/L. Increase in contact time and pH of the solution resulted in higher removal. About 96.07 % removal was achieved within 30 minute at an optimal pH 5.0.

Kinetic data and equilibrium isotherm model was fitted to pseudo second order model and Freundlich isotherm model respectively. Thermodynamic studies showed the adsorption process to be spontaneous and endothermic in nature.

Table 1: Adsorbent derived from activated carbon for the removal of dyes and heavy metals

Adsorbent	Adsorbate	Adsorption capacity (mg/g)	Reference
Rubber seed shell	Methylene blue	769.23	Hanafiah *et al.*, 2021
water hyacinth	Crystal violet dye	322.58	Kulkarni *et al.*, 2017
waste modified with polyethylenimine	Congo red dye	77.52	Wong *et al.*, 2020
Banana peel	Malachite green	243.90	Saechiam and Sripongpun, 2019
Rice husk	Malachite green	6.50	Muinde *et al.,* 2017
Spent mushroom waste	Reactive Black 5	14.62	Alhujaily *et al.*, 2020
poplar leaf	Methylene blue	135.40	Han *et al.*, 2012
Palm Kernel Shell	Cr(VI)	125.00	Mehr*et al.*, 2019
Almond shell	Cr(VI)	165.70	Rai*et al.*, 2019
Rice husk ash	Mn(II)	18.84	Adekola*et al.*, 2016
Baobab fruit shell	Zn(II)	29.20	Adekola and Abdus-Salam, 2018
Peganumharmala-L	Ni(II)	68.02	Ghasemi*et al.,* 2014
Sugarcane bagasse	Zn(II)	23.70	Krishnan *et al.*, 2016
Deniellaoliveri	Pb(II)	0.72	Adebayo *et al.*, 2016
Modified wasp cast	Methylene Blue	60.89	Nwosu and Salami, 2013

Nanocomposite adsorbents for the removal of dyes

Alorabi *et al.* (2020) produced a highly effective adsorbent derived from Fe_3O_4-CuO-activated carbon nanocomposite for the removal of bromophenol blue dye from aqueous solution. The size of nanocomposites were determined to be less than 100 nm and its surface morphology showed homogeneous distribution of CuO and Fe_3O_4 nanoparticles over the surface of activated carbon. It was found that the highest removal efficiency obtained was 97% within 120 minutes at optimal concentration of 20 mg/L, pH 9 and adsorbent dosage of 0.06 g/L.

From thermodynamics study, the negative value of ΔG (- 22.09 kJ/mol) and positive value of ΔH (8.87 kJ/mol) revealed spontaneous and exothermic adsorption process respectively. The experimental and calculated q_e values were in good agreement with each other. The value of correlation coefficient, R^2 for pseudo second-order was close to unity (0.995) which also confirmed that pseudo second-order kinetic model described the adsorption process.

Chen *et al.* (2019) worked on adsorbent derived from Fe_3O_4/CeO_2 nanocomposite for the removal of Acid Black 210 from aqueous solution. Batch adsorption studies showed that when the initial dye concentration varied from 20 mg/L to 80 mg/L at pH range of 3-7 and contact hours of 120 minutes, the highest dye adsorption capacity was found to be 90.50 mg/g.The adsorption kinetics was best described by pseudo second-order with R^2 value of 0.9999 and the q_e values calculated (19.46 mg/g) and that of experimental (19.43 mg/g) were quite too close to each other. The adsorption isotherm fitted Langmuir model. The values of separation factor R_L (0.05) was found to be less than 1 which also suggests a favourable adsorption process.

Kamaraj*et al.* (2020) investigated a study on adsorbent derived from ZnO/Activated carbon nanocomposites for the removal of methylene blue dye from real tannery effluents. BET surface area and pore volume of nanocomposites were 890.9 m^2/g and 0.47 cm^3/g respectively. The findings of the study revealed that the maximum percentage removal was 92 % at pH 10, initial concentration of 50 mg/L, contact time of 150 min and 50 mg of dosage.

Hossain *et al.* (2021) evaluated the adsorption performance of a graphene oxide ammonium/ferric sulfate nanocomposites for the removal of anionic dye, basic black 7 (BB7) and cationic dye, acid black 210 (AB210) from real tannery wastewater. Batch adsorption was first carried out and the optimized conditions obtained were applied on the real tannery effluent. It was found that the maximum percentage removal for both dyes was 100 % at contact time of 2 min. However, the optimum values of pH were 7 and 4, adsorbent dosage of 0.129 g/L and 1.19 g/L and for AB210 and BB7 respectively. Ai and Jiang (2012) applied a cylindrical graphene carbon nanotube for the removal of methylene blue dye.

The study showed that the adsorption process was pH-dependent and the maximum adsorption capacity was found to be 81.97 mg/g. Equilibrium adsorption isotherm study fitted best to Langmuir isotherm with R^2 value of 0.9665. Deng *et al.* (2013) investigated study on removal of Cd(II), methylene blue (MB) and orange G (OG) dyes from aqueous solution using graphene oxide nanocomposites adsorbent. The findings of their study showed that increase in pH of the solution resulted to higher removal efficiencies for Cd(II) and MB, but decrease in removal efficiency was observed in OG with increase in pH value. The adsorption capacities were also found to increase sharply with time and the time required attain equilibrium was 165 min, 405 min and 405 min for Cd(II), MB and OG, respectively. Adsorption kinetic data and isotherm studies for the uptake of both Cd(II) and dyes onto graphene oxide nanocomposites followed the pseudo second-order kinetic model Langmuir adsorption models. Biocompatible composites obtained from Sodium Alginate/titaniananoparticle have been used for removal of Direct Red 80 (DR80) and Acid Green 25 (AG25) from aqueous solution. Batch adsorption study was carried out and the adsorption capacities were found to increase with increase in initial dye concentration. The quantity of dye adsorbed increases as the adsorbent dosage varied from 0.15–1.0 g for 20 minutes. However, it has been observed that the maximum adsorption capacities for both dyes were reached at pH 2. (Mahmoodi *et al.*, 2011).

In another study, Wang *et al.* (2011) reported adsorption performance of graphene based nanocomposites adsorbent for removal of organic dye, fuchsine. The composites were in nanometer size with particles size of 20 nm and the maximum percentage removal efficiency was found to be 99.4% at adsorbent dosage of 0.4 g/L and pH 5.5. Kinetic and isotherm studies fitted to pseudo second-order and Langmuir isotherm model respectively.

Nanocomposite adsorbents for the removal of heavy metals

Obayomi*et al.* (2020) reported adsorption study using cobalt ferrite almond supported nanocomposites ($CoFe_2O_4$/Ac) for removal of Cr(VI) and Pb(II) ions from tannery effluents. The study showed that the maximum removal percentage of Cr(VI) and Pb(II) ions was found to be 98.2 % and 96.4 % respectively at pH 5, adsorbent dosage, 0.8 g and contact time of 80 mins.

El-sherif *et al.* (2017) investigated the CeO_2-TiO_2-Fe_2O_3 mixed nanoparticles adsorbent prepared using co-precipitation method for the rapid removal of uranium ions from industrial wastewater. The adsorption isotherms data for the uptake of uranium ions was best explained using Freundlich and Hasely adsorption isotherm models. Adsorption process was also found to be pH dependent, and the maximum adsorption capacity was achieved at pH 6. The kinetics of adsorption study followed pseudo-second order model.

Magnetic biocomposite based on peanut husk, Fe_3O_4/peanut with BET surface area of 5.46 m^2/g was used for adsorption of Cr(VI) ions in aqueous phase. A batch adsorption study was carried out and it was found that the maximum adsorption at optimum pH 3 and initial concentration of 50 mg/L was 3.75 mg/g. Adsorption isotherm study revealed that Langmuir adsorption isotherm fitted the adsorption data with corresponding Langmuir maximum adsorption capacity of 58.4 mg/g. However, the adsorption kinetic study followed pseudo second-order model with R^2 value of 0.955 (Han *et al.*, 2022).

Adegoke *et al.* (2020) studied adsorptive removal of Cr(VI) ions from aqueous solution using synthetic goethite, activated carbon and their corresponding composite. The maximum adsorption capacities were reached at pH of 3 and adsorbent dosage of 0.02 g with corresponding adsorption capacities of 45.59 mg/g, 46.01 mg/g and 32.96 mg/g for goethite, activated carbon and composites respectively. Adsorption isotherm studies revealed that the adsorption process followed Langmuir adsorption isotherm model with activated carbon being the most fitted in comparison to goethite and composite. Desorption studies using 1M HNO_3 showed that 94.66%, 91.81%, 36.33 % can be desorbed for goethite, activated carbon and the composites respectively.

Zhou *et al.* (2019) utilized hydroxyapatite/carbon composite for rapid removal of Pb(II) ions from aqueous solution. The composite produced was mesoporous in nature with an average diameter of 12.24 m^2/g. BET surface area and total pore volume were determined to be 60.42 m^2/g and 0.18 cm^3/g respectively. Batch adsorption studies showed that the adsorbent had a very good adsorption capacity of 416.67 mg/g.

Jain *et al.* (2018) produced iron oxide/activated carbon nanocomposites for the removal of Cr(VI), Cu(II) and Cd(II) ions. It was reported that the maximum percentage removal was reached at pH 2 for Cr(VI) and pH 6 for both Cu(II) and Cd(II). Adsorption isotherm studies reveal that Langmuir isotherm model gave higher R^2 values corresponding to 0.9994, 0.9998 and 0.9750 for Cr(VI), Cu(II) and Cd(II) respectively.

Thermodynamic studies showed that the adsorption processes was endothermic in nature.

Table 2: Adsorbent derived from nanocomposites for the removal of dyes and heavy metals

Adsorbent	Adsorbate	Adsorption capacity (mg/g)	Reference
$MnFe_2O_4$/GO	Neural red dye	90.00	Alsaiari *et al.,* 2021
Fe_3O_4/activated carbonnanocomposites	Methyl orange	215.00	Sun *et al.*, 2018
graphene/magnetite nanocomposite	Methylene blue	43.82	Ai *et al.*, 2011
chitosan-palygorskite nanocomposites	Pb(II)	58.50	Rusmin*et al.*, 2022
Fe_3O_4/bentonite nanocomposites	Cu(II)	19.6	Yan *et al.*, 2016)
Fe_3O_4/CeO_2 nanocomposites	Acid black 210 dye	90.50	Chen *et al.*, 2019
Chitosan/nZVI nanocomposites	Rhodamine B dye	458.81	Dada *et al.,* 2018
Magnetite-baobab composite	Zn(II)	38.25	Abdus-Salamand Adekola, 2018
Goethite composite	Cr(VI)	6.35	Adegoke *et al.*, 2020
Chitosan-bentonite	Cu(II)	20.9	Fulatan*et al.*, 2011
Chitosan/clay	Ni(II)	32.36	Tirtom*et al.*, 2012

CONCLUSION

The use of adsorbents derived from activated carbon and nanocomposites have gained much interest over the years in the treatment of various pollutants from aqueous solution because of their unique properties in terms of large internal surface area and good porous structures. Batch adsorption technique has been the most effective method that could be used for the treatments of dyes and heavy metals from industrial wastewater. The applicability different type of adsorbents and the influence of various factors on adsorption performances are highlighted in this review.

REFERENCES

Abdullahi, D., Okezie, Q. and Mohammed, A. B. (2014). Preparation and Properties of date seed/Natural Rubber Composites. *International Journal of Emerging Technology and Advanced Engineering,* 4 (9), 152-156.

Abdullahi, M.R. and Alkali, M. I. (2023).Removal of Chromium (VI) from Aqueous Solution Using Activated Carbon Derived from Modified Bambara Nut Shells (*Vignasubterranea (L.) verdc.). Journal of Applied Science and Environmental Management,* 27(3), 421-431*.*

Abdus-salam, N. and Adekola, S. K. (2018). Adsorption studies of Zn (II) on magnetite, baobab (Adansoniadigitata) and magnetiote-baobab composite. *Applied water science*, 8 (8), 1-11.

Abdus-salam, N. and Buhari, M. (2014). Adsorption of Alizarin and Fluorescein Dyes on adsorbent prepared from Mango Seed. *Pacific Journal of Science and Technology*, 15(1), 232-244.

Adebayo, G. B., Adegoke, H. I.andSidiq, F. (2016). Adsorption of Pb(ll) by Modified and Activated carbon Prepared from *DeniellaOliveri*Stem Bark. *Journal of Chemical Society of Nigeria, 41(1) 19-26.*

Adebayo, G. B., Adegoke, H.I., Jamiu, W., Balogun, B.B. and Jimoh, A.A. (2015). Adsorption of Mn (II) and Co (II) ions from aqueous solution using Maize cob activated carbon: Kinetics and Thermodynamics Studies. *Journal of Applied Science and Environmental Management*, 19 (4), 737-748.

Adegoke, H.I., Adebayo, G.B. and Fauzeeyat, S. (2020). Adsorption of Cr (VI) ions onto goethite, activated carbon and their composite: kinetic and thermodynamic studies. *Applied Water Science*, 10 (9), 1-18.

Adekola, F.A., Adegoke, H.I. and Ajikanle, R.A. (2016).Kinetic and equilibrium studies of Pb (II) and Cd (II) adsorption on African wild mango (*Irvingiagabonensis*) shell. *Bulletin of Chemical Society of Ethiopia,* 30 (2), 185-198.

Ahmedna, M., Marshall, W.E. and Rao, R. M. (2000).Production of granular activated carbons from select agricultural by-products and evaluation of their physical, chemical and adsorption properties.*Bioresource Technology*, 71, 113–123.

Ai, L., and Jiang, J. (2012). Removal of methylene blue from aqueous solution with self-assembled cylindrical graphene-carbon nanotube hybrid. *Chemical Engineering Journal*, *192*, 156–163.

Ai, L., Zhang, C., and Chen, Z. (2011). Removal of methylene blue from aqueous solution by a solvothermal-synthesized graphene/magnetite composite. *Journal of Hazardous Materials*, *192* (3), 1515–1524.

Alhujaily, A., Yu, H., Zhang, X. and Ma, F. (2020). Adsorptive removal of anionic dyes from aqueous solution using spent mushroom waste. *Applied water science*, 10 (7), 1-12.

Alorabi, A. Q., Hassan, M.S. and Azizi, M. (2020).Fe_3O_4-CuO-activated carbon composite as an efficient adsorbent for bromophenol blue dye removal from aqueous solutions.*Arabian Journal of Chemistry*, 13, 8080–8091.

Al-Qodah, Z. and Shawabkah, R. (2009). Production and characterization of granular activated carbon from activated sludge. *Brazilian Journal of Chemical Engineering,* 26 (1), 127–136.

Alsaiari, N.S., Katubi, K.M. M, Alzahrani, F. M., Siddeeg, S.M. and Tahoon, M.A. (2021).Synthesis of Manganese Ferrite/Graphene Oxide Magnetic Nanocomposite for Pollutants Removal from water.*Processes* 9, 589.

Asadullah, M., Rahman, M.A., Motin, M.A and Sultan, M. B. (2007).Adsorption studies on activated carbon derived from steam activation of jute stick char. *Journal of Surface Science and Technology*, 23 (2), 73–80.

Babel, S., Kurniawan, T.A. (2004). Cr (VI) removal from synthetic wastewater using coconut shell charcoal and commercial activated carbon modified with oxidizing agents and/or chitosan. *Chemosphere*, 54(7), 951-967.

Bouchelta C, Medjram M. S, Bertrand, O., Bellat, J. P (2008). Preparation and characterization of activated carbon from date stones by physical activation with steam.*Journal of Analytical and Applied Pyrolysis,* 82, 70-77.

Byamba-Ochir N, Shim W. G, Balathanigaimani, M. and Moon, H. (2016). Highly porous activated carbons prepared from carbon rich Mongolian anthracite by direct NaOH activation. *Applied Surface Science*, 379, 331–337.

Camargo, P.H.C., Satyanarayana, K.G. and Wypych, *F. (2009).*Nanocomposites: Synthesis, Structure, Properties and New Application Opportunities. *Materials Research,* 12 (1), 1-39.

Canli, M. and Atli, G. (2003).The relationships between heavy metal (Cd, Cr, Cu, Fe, Pb and Zn) levels and the size of six Mediterranean fish species.*Environmental Pollution,* 12(1), 129-136.

Chen, D., Gao, S., Zhang, W., An, Z. and. Kong, S. (2019). Adsorption of anionic dye onto magnetic Fe_3O_4/CeO_2 nanocomposite: Equilibrium, kinetics, and thermodynamics*. Adsorption Science and Technology,* 0 (0), 1-20.

Chigondo, F., Nyamunda, B. C., Sithole, S. C., and Gwatidzo, L. (2013). Removal of lead (II) and copper (II) ions from aqueous solution by baobab (Adononsia digitata) fruit shells biomass. *Journal of Applied Chemistry*, *5* (1), 43–50.

Chincholi, M., Sagwekar, P., Nagaria, C., Kulkarni, S., and Dhokpande, S. (2014). Removal of dye by adsorption on various adsorbents: A review. *International Journal of Science Engineering and Technology Research*, 3, 835-840.

Dada, A. O., Inyinbor, A.A., Adekola, F.A., Odebunmi, E.O., Bello, O.S. and Ayo- Akere, S. (2018). Kinetics and isotherm modeling of adsorption of Rhodamine B dye onto chitosan supported zerovalent iron nanocomposites (C-nZVI). *International Journal of civil engineering and technology*, 9 (11), 1591 – 1605.

Dada, A.O., Olalekan, A.P., Olatunya, A.M. and Dada, O. (2012).Langmuir, Freundlich, Temkin and Dubinin–Radushkevich Isotherms Studies of Equilibrium Sorption of Zn^{2+} Unto Phosphoric Acid Modified Rice Husk.*IOSR Journal of Applied Chemistry, 3(1), 38-45.*

Dehghani, M.H., Heidarinejad, Z., Heidari, M., Javedan, G., Ali, I. and Sillanpaa, M. (2020). Methods for preparation and activation of activated carbon: a review. *Environmental Chemistry Letters,* 18 (2), 393-415.

Deng, J. H., Zhang, X. R., Zeng, G. M., Gong, J. L., Niu, Q. Y. and Liang, J. (2013). Simultaneous removal of Cd (II) and ionic dyes from aqueous solution using magnetic graphene oxide nanocomposite as an adsorbent. *Chemical Engineering Journal,* 226,189–200.

Duraisamy, R., Khan, M. A., Alemayehu, A., and Berekete, A. K. (2015). Removal of Lead ion from aqueous solution by Bamboo activated Carbon.*International Journal of Water Research, 5*(4), 33–46.

Duruibe, J.O., Ogwuegbu, M. O.C. and Egwurugwu, J. N. (2007).Heavy metal pollution and human biotoxic effects. *International Journal of Physical Sciences*, 2 (5), 112-118.

Elsayed, A., Osman, D., Attia, S., Ahmed, H.,Shoukry, E., Mostafa, Y., Taman, A. (2020). A Study Pollutants from Wastewater by Low Cost Biosorbent. *Egyptian Journal of Chemistry,* 63(4), 1429-1442

Elsayed, M. A., Albroomi, H. I., Baraka, A. and Abdelmaged, M.A. (2016). Batch and fixed-bed adsorption of tetrazine ado dye onto activated carbon prepared from apricot stones. *Applied water science,* 7(4), 2063-2074.

El-sherif, R. M., Lasheen, T. A. and Jebril, E. A. (2017). Nanoparticles for rapid removal of uranium ions from industrial waste solutions. *Journal of Molecular Liquids*, 241, 260–269.

Fahim, I. S., Husien, S., El-taweel, R. M., Salim, A.I., Said , L.A. and Radwan, A.G. (2022). Review of activated carbon adsorbent material for textile dyes removal: Preparation, and modeling.*Current Research in Green and Sustainable Chemistry* 5, 100325

Farooq, S. Saeed, A., Sharif, M., Hussaina, J., Mabood, F. and Iftekhar, M. (2017).Process optimization studies of crystal violet dye adsorption onto novel, mixed metal $NiO.5CoO.5Fe_2O_4$ferrospinelnanoparticles using factorial design.*Journal of Water Process Engineering* 16, 132–141.

Foo, K.Y., Hameed, B.H.(2011). Microwave assisted preparation of activated carbon from pomelo skin for the removal of anionic and cationic dyes. *Chemical Engineering Journal*, 173 (2), 385-390.

Fulatan, C. M., Kan, C.C., Dalida, M.L., Hsien, K. J., Pascua, C. and Wan, M.W. (2011). Comparative and Competitive adsorption of copper, lead and nickel using chitosan immobilized on bentonite. *Carbohydr.Polym*. 83(2), 528-536.

Georgieva, V.G, Tavlieva, M.P., Genieva, S.D. and Vlaev, L. T. (2015).Adsorption kinetics of Cr (VI) ions from aqueous solutions onto black rice husk ash.*Journal of Molecular Liquids,* 208, 219–226.

Ghasemi, M., Ghasemi, N., Zahedi, G., Alwi, S. R. W., Goodarzi, M. and Javadian, H. (2014). Kinetic and equilibrium study of Ni (II) sorption from aqueous solutions onto Peganumharmala-L, *International Journal of Environmental Science and Technology*, 11, 1835–1844.

Gupta, V., Agarwal, A., Singh, M.K. and Singh, N.B. (2017). Removal of Red RB Dye from Aqueous Solution by Belpatra Bark Charcoal (BBC) Adsorbent.*Journal of Materials and Environmental Sciences*, 8(10), 3654-3665.

Hameed, B.H. and Foo, K Y. (2010).An overview of dye removal via activated carbon adsorption process.*Desalination and Water Treatment,* 19, 255-274.

Han, R., Li, Q., Dovi, E., Aryee, A.A., Li, Z. and Qu, L. (2022). Magnetic biocomposite based on peanut husk for adsorption of hexavalent chromium, congo red and phosphate from solution:Characterization, kinetics, equilibrium and antibacterial studies. *Chemosphere*, 287, 132030

Han, X., Niu, X. and Ma, X. (2012). Adsorption characteristics of methylene blue on poplar leaf in batch mode: Equilibrium, kinetics and thermodynamics. *Korean Journal of Chemical Eng*ineering, 29(4), 494-502.

Hanifiah, M. M., Nizam, N. M., Mahmoudi, E., Halim, A. A. and Mohammad, A. (2021).The removal of anionic and cationic dyes from an aqueous solution using biomas based activated carbon. *Scientific Reports*, 10(1), 1-13.

Harun, Z., Sazali, N. Sazali, N. (2020).A review on batch and column adsorption of various adsorbents towards the removal of heavy metal.*Journal of Advanced Research in Fluid Mechanics and Thermal Sciences* 67(2), 66-88.

Hossain, M.I., Soliman, M.M., El-Naggar, M.E., Sultan, M.D., Kechi, A., Abdelsalam, N.R., Abu-saied, M.A. and Chowdhury, M. (2021). Synthesis and characterization of graphene oxide-ammonium ferric sulfate composite for the removal of dyes from tannery wastewater. *Journal of Materials Research and Technology*, 12, 1715-1727.

Huang.F.C., Lee, C. K. and Han, Y. L. (2014) Preparation of activated carbon using micro-nano carbon spheres through chemical activation. *Journal of Taiwan*

Institute of Chemical Engineers, 45(5), 2805–2812.

Igwegbe, C.A. Onukwuli, O.D., Onyechi, K.K. and Ahmadi, S. (2020). Equilibrium and kinetic analysis of vat yellow 4 uptake from aqueous environment by modified rubber seed shells: Non linear modeling. *Journal of Materials and Environmental Sciences*, 11(9), 1424-1444

Inyinbor, A.A., Adekola, F.A. and Olatunji, G.A. (2016). Kinetics, isotherms and thermodynamic modeling of liquid phase adsorption of Rhodamine B dye onto Raphiahookerie fruit epicarp. *Water Resources and Industry* 15, 14–27.

Jain, M., Yadav, M., Kohout,T., Lahtinen, M., Garg, V. K. and Sillanpaa, M. (2018). Development of iron oxide/activated carbon nanoparticle composite for the removal of Cr(VI), Cu(II) and Cd(II) ions from aqueous solution. *Water Resources and Industry* 20, 54–74.

Kamaraj, M., Srinivasan, N.R., Aseefa, G., Adugna, A.T. and Kebede, M. (2020). Facile development of sunlit ZnOnanoparticles-activated carbon hybrid from pernicious weed as an operative nano adsorbent for removal of methylene blue and chromium from aqueous solution: Extended application in tannery industrial waste water. *Environmental Technology and Innovation*, 17, 100540.

Kazlagic, A., Hajlovac, M., Badnjevic, A., and Miklicanin, E.O. (2019). Nanocomposites: A brief review. *Health and Technology*, 10 (1), 51 – 59.

Kebede, F. and Gashaw, A. (2017). Removal of Chromium and Azo Metal-Complex Dyes Using Activated Carbon synthesized from Tannery Wastes. *The Open Access Journal of Science and Technology,* 5, 1–30.

Khasri, A., Jamir, M.R.M., Ahmad, A. A. and Ahmad M.A. (2021). Adsorption of Remazol brilliant violet 5R dye from aqueous solution onto melunak and rubber wood sawdust based activated carbon: interaction mechanism, isotherm, kinetics and thermodynamic properties. *Desalination and Water Treatment*. 216, 401-411.

Krishnan, K. A., Sreejalekshmi, K., Vimexen, V., & Dev, V. V. (2016).Evaluation of adsorption properties of sulphurised activated carbon for the effective and economically viable removal of Zn (II) from aqueous solutions.*Ecotoxicology and Environmental Safety*, 124, 418–425.

Kulkarni, M. R., Revanth, T., Acharya, A. and Bhat, P. (2017).Removal of Crystal Violet dye from aqueous solution using water hyacinth:Equilibrium, kinetics and thermodynamics study.*Resource-Efficient Technologies,*3, 71–77.

Kushwaha, P. and Upadhyay, K. (2015). Adsorption of pollution load from tannery effluent by using Neem Sawdust as an adsorbent. *International Journal of Chemical Studies* 3(1), 1–3.

Mahmoodi, N.M., Hayati, B., Arami, M. Bahrami, H. (2011).Preparation, characterization and dye adsorption properties of biocompatible composite (alginate/titaniananoparticle).*Desalination ,* 275(1-3), 93–101.

Mehr, M.R., Fekri, M.H., Omidali, F., Eftekhari, N., Akbari-adergani, B. (2019).Removal of Chromium (VI) from Wastewater by Palm Kernel Shell-Based on a Green Method.*Journal of Chemical Health Risks,* 9(1):75-86.

Mekonnen, E., Yitbarek, M. and Soreta, T. R. (2015). Kinetic and Thermodynamic Studies of the Adsorption of Cr(VI) onto Some Selected Local Adsorbents. *South African Chemical Institute,* 68, 45–52.

Mhemeed, A. M. (2018). A General Overview on the Adsorption.*Indian Journal of Natural Sciences.*9 (51), 16127-16131.

Momcilovic, M., Purenovic, M., Bojic, A., Zarubica, A. and Randelovic, M. (2011). Removal of lead(II) ions from aqueous solutions by adsorption onto pine cone activated carbon. *Desalination* 276,53–59.

Muinde, V. M., Onyari, J. M., Wamalwa, B., Wabomba, J. and Nthumbi, R. M. (2017). Adsorption of Malachite Green from Aqueous Solutions onto Rice Husks: Kinetic and Equilibrium Studies. *Journal of Environmental Protection*, 8:215-230.

Nwosu, F.O. and Salami, A.O. (2013).Equilibrium, Kinetics and Thermodynamic Studies of Adsorption of Methylene Blue using Raw and Modified Wasp Cast. *Nigerian Journal of Science, 47, 51-61.*

Obayomi, K.S., Yahya, M.D., Abdulkadir, M.B., Iyaka, Y.A. and Olugbenga, A.G. (2020). Characterization of cobalt ferrite-supported activated carbon for removal of chromium and lead ions from tannery wastewater via adsorption equilibrium. *Water Science and Engineering,* 13, (3), 202-213.

Park, S-J., Moon, J-K., Lee, C-G., Quansah, J. O. and Kyi, P.P. (2020).The Removal of Crystal Violet from Textile Wastewater Using Palm Kernel Shell-Derived Biochar.*Applied sciences*, 10 (7), 2251-2264.

Patel, H. (2019). Fixed-bed column adsorption study: a comprehensive review. *Applied Water Science*, 9 (3), 1 – 17.

Patel, H. (2021). Comparison of batch and fixed bed column adsorption: a critical review. *International Journal of Environmental Science and Technology*, 1 – 18.

Rai, M.K., Giri, B.S., Nath Y., Bajaj, H., Soni, R.P., Singh, R.S. and Rai., B.N. (2018). Adsorption of Hexavalent Chromium from Aqueous Solution by Activated Carbon Prepared from Almond Shell: Kinetics, Equilibrium and Thermodynamics Study. Journal of Water Supply: Research and Technology, 67(8), 724-737.

Romero-Anaya, A. J, Lillo-Rodenas, M.A, Lecea, C.S.M. and Linares-Solano, A. (2012). Hydrothermal and conventional H_3PO_4 activation of two natural bio-fibers. *Carbon*, 50, 3158–69.

Rusmin, R., Sarkar, B., Mukhopadhyay, R., Tsuzuki, T., Liu, Y. and Naidu, R. (2022).Facile one pot preparation of magnetic chitosan-palygorskite nanocomposite for efficient removal of lead from water.*Journal of Colloid and Interface Science*, 608 (1), 575-587.

Saechiam, S. and Sripongpun, G. (2019).Adsorption of Malachite Green from synthetic Wastewater using Banana Peel Adsorbents.Songklanakarin.*Journal of Science and Technology* 41(4):21-29.

Saleem, J., Bin Shahid, U., Hijab, M., Mackey, H. and McKay, G. (2019).Production and applications of activated carbons as adsorbents from olive stones*. Biomass Conversion and Biorefinery,* 9, 775–802.

Sankhla, M S., Kumar, R., Jadhav, S. Sonone, S.S. (2021). Water Contamination by Heavy Metals and their Toxic Effect on Aquaculture and Human Health through Food Chain.*Letters in Applied Nanobioscience*, 10, 2, 2148 - 2166

Sathya, K., Saniya, A., Nagarajan, K., Yogesh, M., Jayalakshmi, H., Praveena, P. and Bharathi, S. (2020). Modelling of the removal of crystal violet dye from textile effluent using *Murrayakoenigii*stem biochar.*Desalination and Water Treatment,* 356–365.

Sebata, E., Moyo, M., Guyo, U., Ngano, N. P., Nyamunda, B. C., Chigondo, F., Shumba, M. (2013). Adsorptive Removal of Atrazine from Aqueous Solution Using Bambara Groundnut Hulls (*Vigna Subterranean*). *International Journal of Engineering Research and Technology*, *2*(5), 312–321.

Seow, T.W. and Lim, C. K. (2016).Removal of Dye by Adsorption: A Review. *International Journal of Applied Engineering Research*, 11(4), 2675-2679.

Sharma, G., Sharma,S., Kumar, A., Lai, C.W., Naushad, M., Iqbal, **S. J.** andStadler, F.J. (2022). Activated Carbon as Superadsorbent and Sustainable Material for Diverse Applications. Adsorption Science & Technology,1-22.

Srivastava, V.C., Singh, S., Mandal, T. K., Mall, I.D. and Lo, S.L. (2016).Synthesis and application of green mixed-metal oxide nanocomposite materials from solid waste for dye degradation*. Journal of Environmental Management* 181, 146-156.

Sun, A-C., Juang, R-S., Yei, Y-C., Liao, C-S., Lin, K-S., Lu, H-C.and Wang, S-F. (2018). Synthesis of magnetic Fe_3O_4 /activated carbon nanocomposites with high surface area as recoverable adsorbents, *Journal of the Taiwan Institute of Chemical Engineers*.1-10.

Tan, I. A. W., Ahmad, A. L., and Hameed, B. H. (2008). Adsorption of basic dye using activated carbon prepared from oil palm shell : batch and fixed bed studies*. Desalination*, *225*, 13–28.

Tirtom, V.N., Dincer, A., Becerik, S., Aydemir, T. and Celik, A. (2012). Comparative adsorption of Ni(II) and Cd(II) ions on epichlorohydrincrosslinkedchitosan-clay composite beads in aqueous solution. *Chemical Engineering Journal,* 197,379-386.

Tong, K. S., Kassim, M. J., and Azraa, A. (2011). Adsorption of copper ion from its aqueous solution by a novel biosorbent Uncaria gambir : Equilibrium , kinetics , and thermodynamic studies. *Chemical Engineering Journal*, 170(1), 145–153.

Wang, C., Feng, C., Gao, Y., Ma, X., Wu, Q., and Wang, Z. (2011). Preparation of a graphene-based magnetic nanocomposite for the removal of an organic dye from aqueous solution. *Chemical Engineering Journal*, *173* (1), 92–97.

Wong, S., AbdGhafar, N. Ngadi, N., Razmi, F. A. Inuwa, I.M., Mat, R. and Amin, N. A. S. (2020). Effective removal of anionic textile dye using adsorbent synthesized from coffee waste. S*cientific Reports,* 10 (1), 1-13.

Yahya, M. A., Al-Qodah, Z. and Ngah, C. Z. (2015). Agricultural bio-waste materials as potential sustainable precursors used for activated carbon production: a review. *Renewable and Sustainable Energy Reviews,* 46, 218–235.

Yakout, S.M. and El-deen, G.S. (2016).Characterization of activated carbon prepared by phosphoric acid activation of olive stone.*Arabian Journal of Chemistry*, 9 (2), 51155 – 51162.

Yan, L., Li, S., Yu, H., Shan, R., Du, B., and Liu, T. (2016). Facile solvothermal synthesis of Fe_3O_4/bentonite for efficient removal of heavy metals from aqueous solution. *Powder Technology*, *301*, 632–640.

Yelebe, Z. R., B. Z. Yelebe, and R. J. Samuel (2013).Design of fixed bed column for the removal of metal contaminants from industrial wastewater.*Journal of Engineering and Applied Sciences,* 5(2), 68-77.

Yunusa, U. and Ibrahim, M. B. (2020).Equilibrium and Thermodynamic Studies on Adsorption of Hexavalent Chromium from Aqueous Solution onto Low Cost Activated Carbon.*International Journal of Engineering and Manufacturing,* 2, 52-70.

Zhang, N., Lin, L.S., Gang, D. (2008). Adsorptive removal of selenite from water using iron-coated GAC adsorbents.*Water Researc*h. 42 (14), 3809-3816.

Zhou, S., Long, Y., Jiang, J., Hu, J., Hu, X. and .Yang, Q. (2019). Removal of Pb (II) from aqueous solution by hydroxyapatite/carbon composite: Preparation and adsorption behavior. *Colloids and Surfaces* A 577, 471–479.