The role of nanoadsorbents and nanocomposite adsorbents in the removal of heavy metals from wastewater: A review and prospect

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ABSTRACT: Significant attention has been given to nanotechnology as an emerging approach in water/wastewater treatment for heavy metals removal. Numerous research works on synthesizing, fabrication and upgrading nanoparticles have reported as an efficient adsorbent in removal of wide range of heavy metals from wastewater. This review intends to provide researchers with understanding and knowledge regarding the efficient nanoadsorbents, their adsorption mechanism towards selected heavy metals and fundamental principles of nanoadsorbent materials synthesis. In addition, further attention on the modification of nanoadsorbent and development of nanocomposites are highlighted in this paper as value added products to increase the adsorption capacity and enhance the heavy metals removal. Possible challenges and direction on utilization of nanocomposites for heavy metal removal in real wastewater effluent are discussed in view of their removal capability and cost efficiency. Future research works on developing a cost-effective way of nanocomposite production and toxicity testing of nanomaterials in wastewater applications are recommended. Further studies on the efficiency of the nanoadsorbents in pilot or industrial scale are highly needed to test the practicality of the nanoadsorbents for selected heavy metals removal from real wastewater.

Keywords: Nanomaterials; adsorption mechanism; adsorption capacity; wastewater treatment.

INTRODUCTION

Water is an important element that is consumed by human and all living things having a key role in our survival. The growing world population, depleting water resources and climate change causing prolonged droughts, floods and other consequences have rendered clean water a competitive resource worldwide (UN-Water 2020). Therefore, it is necessary to have a sustainable and reliable treatment technologies to ensure the clean water supply continuously either to domestic or industrial usage. Production of wastewater is increased proportionally with the increasing global population; hence it is vital to remove all pollutants from wastewater in providing adequate water quality for human and environmental needs (Boretti & Rosa, 2019; Teklehaimanot et al., 2015). A broad range of contaminants exist in wastewater such as heavy metals, organic and inorganic compounds that have been released from industrial effluent will give harmful effects towards human and ecosystem (Dubey et al., 2016; Hasbullah et al., 2018). Thus, removal of unsafe

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pollutants from wastewater especially heavy metal ions is significant.

Over the years, the main cause for the release of heavy metals into environment is due to rapid industrialization. Heavy metal is any dense metallic chemical element or metalloid with hazardous properties, and it is naturally occurring element that can be found throughout the earth's crust. Water with heavy metals contamination is one of the major problems that increased dramatically which led to the environmental and health concerns worldwide (Ali et al., 2020; Masindi & Muedi, 2018; Mehdinia et al., 2020). The main sources of heavy metals are wastewater effluents of modern chemical industries such as metal plating facilities, battery manufacturing, fertilizer, mining, paper and pesticides, metallurgical, mining, fossil fuel, tannery and plastic production (Ali et al., 2020; Ihsanullah et al., 2016).

Heavy metals such as arsenic, lead, copper, cadmium, chromium, silver and other hazardous metallic pollutants need to be removed from wastewater effluent in turn to make water safe and consumable to the living things. The major means of heavy metals entering the body is through drinking water. Though our body needs some heavy metals, excessive exposure of heavy metals will lead human to serious health problems such as gastrointestinal tract, cardiac, vascular and central nervous system as well as affect mental health (Krause et al., 2015; Pramanik et al., 2016). Other possible symptoms because of heavy metals toxicity are depression, sleep disorder, aggressive behavior, mood swings and memory loss (Masindi & Muedi, 2018; Tchounwou et al., 2012). The permissible concentrations limits for each selected heavy metal and their toxicities effect on human are summarized in Table 1 below.

Table 1. Standard limit of selected heavy metals in drinking water (WHO, 2017)

Heavy metals contaminant	EPA maximum contamination level (mg/L)	WHO guideline value (mg/L)	Effects on human health
Lead	0.015	0.01	Damage the fetal brain, diseases of the kidneys, circulatory system, and nervous system
Chromium	0.1	0.05	Headache, diarrhea, nausea, vomiting, carcinogenic
Cadmium	0.005	0.003	Kidney damage, renal disorder, human carcinogen
Copper	1.3	2	Liver damage, Wilson disease, insomnia
Arsenic	0.01	0.01	Skin manifestations, visceral cancers, vascular disease
Mercury	0.002	0.006	Rheumatoid arthritis, and diseases of the kidneys, circulatory system, and nervous system
Nickel	-	0.07	Dermatitis, nausea, chronic asthma, coughing, human carcinogen
Zinc	5	3	Depression, lethargy, neurological signs and increased thirst

The common conventional methods that had been utilized to remove heavy metals from wastewater effluents are chemical precipitation, solvent extraction, ion exchange, electrochemical removal, and coagulation. However, these methods have limitations such as inconvenient, large space needed, incomplete removal, high energy consumption, low efficiency, generation of toxic sludge, and expensive disposal (Burakov et al., 2018; Siddiqui & Chaudhry, 2017.) Therefore, adsorption approach is selected as the best alternative to remove heavy metals from wastewater. It has been proved that adsorption is the most preferred method for purification, due to effectiveness, convenient stability, utility, low-cost, ease of operation and high performance (González et al., 2017; İnce & Kaplan İnce, 2017). Adsorption is defined as mass transfer

process by which a substance (adsorbate) is transferred from the liquid phase to the surface of solid (adsorbent) and bounded by physical and/or chemical interactions(Khulbe & Matsuura, 2018). Conventional adsorbents including carbon and natural sources showed the capability to remove heavy metals from wastewater with high removal of rate up to 99%. The most widely used carbon source is activated carbon while natural source adsorbents are from dead or living biomass such as algae, fungi and some higher plants (Farooq et al., 2010; Karnib et al., 2014; Mqehe-Nedzivhe et al., 2018; Saleem et al., 2019). Other wastewater treatment for heavy metals removal was also investigated using microbial fuel cell where the pollutants are removed by the application of electricity in the presence of microbes as a biocatalyst (Das et al., 2019). However, lack of specificity, poor recyclability, high energy consumption, electric current instability, high material cost, low adsorption efficiencies and capacities hindered their application in concentrated solutions (Baruah et al., 2019; Thekkudan et al., 2017). Hence, various cost-effective, techno-economical and universal adsorbents especially nanoadsorbents have been developed in many water and wastewater applications especially for heavy metals removal from wastewater (Ali et al., 2020; Thekkudan et al., 2017).

From many previous findings, nanomaterials have been produced as a novel high efficiency adsorbent for heavy metal removal from wastewater (Hua et al., 2012; Ray & Shipley, 2015; Wang, 2012; Yang et al., 2019). The development of well-designed nanoadsorbents from metal oxides and carbon sources have been utilized in broad industrial applications including bioprocess, environmental remediation and their unique characteristics such as high reactivity, biocompatibility, high surface to volume ratio, reversibility, metal binding capability and comparatively low cost as well as high degree of functionalization make them as potential high efficient

adsorbents for wastewater treatment and water purification applications (Mohd et al., 2017; Dave & Chopda, 2014; Qu et al., 2013). Pacheco et al., (2006) also reported the capability of nanoadsorbents that can adsorb the contaminants in terms of molecular size, hydrophobicity and speciation behaviour. Besides that, nanoadsorbents are also enable the manufacturing processes to consume raw materials efficiently without releasing any toxic by-products (Burakov et al., 2018). Utilization of different types of adsorbents including conventional and nanostructured materials in removing heavy metals from wastewater has been well reviewed by different authors (Baruah et al., 2019; Burakov et al., 2018; İnce and Kaplan İnce, 2017). Xu's group and Yang's group contributed significantly to the understanding of nanomaterials and their application (Xu et al., 2018; Yang et al., 2019). These groups systematically reviewed the wide range of nanoadsorbents for heavy metals removal and their preparation, but few information was elaborated on the knowledge of the adsorption mechanism which is the interaction between nanoadsorbents and heavy metals that has been influenced by parametric effects on adsorption process (Xu et al., 2018; Yang et al., 2019; Hasbullah et al., 2019). On the basis of utilization of nanoadsorbents for heavy metals removal in wastewater treatment, this review aims at presenting an overview on the existing nanoadsorbents and their adsorption mechanism that can be exploited for the synthesis of advanced nanoadsorbents. The scope of this review will be elucidated on the basic principle of adsorption process including adsorption mechanism, isotherm and kinetic models to provide guidance in the designing of ideal nanoadsorbents system. Then, categories of current nanoadsorbents, advanced nanocomposite development are also discussed and compared based on their advantages and limitations. Finally, possible

recommendations for future researches and applications of the nanoadsorbents are suggested.

Mechanism of metal ions adsorption by nanoadsorbent

Adsorption process involves physical and chemical interaction between an adsorbent and an adsorbate which depends on the reacting environment (Cheng et al., 2012; Hasbullah et al., 2018). Physical interactions involve a weak van der Waals forces between the adsorbate and adsorbent with a reversible process. The interactions will form monolayer or multilayer adsorption and not very specific. Meanwhile, in chemical mode of adsorption, ionic or covalent bond occurs and makes the process highly specific. The irreversible chemical interaction will form monolayer adsorption (Hasbullah et al., 2019). There are several types of adsorption mechanisms that explain the adherence of metal ions adsorbates such as surface adsorption, precipitation, electrostatic interaction and ion exchange as illustrated in Fig. 1.
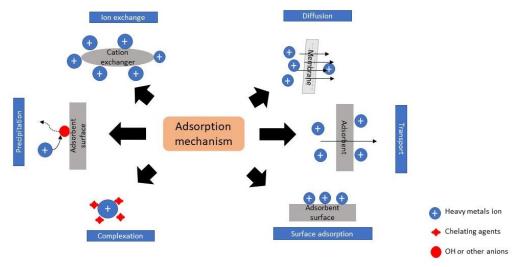

Fig. 1. Various adsorption mechanisms of metal ion adsorbate on nanoadsorbent

The mechanism of heavy metals adsorption can also be explained in detail by studying the adsorption isotherms, kinetics and thermodynamics. Apparently, the adsorption mechanisms on nanoadsorbents depend on the chemical nature and properties of the material. Besides that, various parametric effects such as solution pH, initial metal concentration, adsorbent's dosage, contact time and temperature influenced the nature of adsorption phenomenon as well (Batool et al., 2018; Wang et al., 2020). The details of each type of adsorption mechanism are explained here.

Adsorption isotherm

Adsorption isotherms are used to quantify the quantity of adsorbate that an adsorbent can adsorb at equilibrium conditions and constant temperature. This adsorption equilibrium relationship known as an isotherm, allows the adsorption capacity of the adsorbent to be calculated at any given liquid-phase adsorbate concentration. The equilibrium sorption phase is achieved when the concentration of the adsorbate remains unchanged due to zero net transfer of pollutant that is adsorbed and desorbed from the surface of the adsorbent. This equilibrium phenomenon is vital for adsorption mechanism pathways optimization, surface properties indication and adsorbents capacities as they can describe the relationship of contaminants with the adsorbents (El-Khaiary, 2008; Kyzas & Matis, 2015). The equilibrium solid-phase

adsorbate concentration can be calculated from an experimental data that varies the adsorbent dose and/or the initial adsorbate concentration (Kyzas & Matis, 2015). From here, the relationship with the equilibrium liquid-phase concentration can also be established. The equilibrium capacity is calculated using a mass balance expression as Equation 1:

$$q_e = \frac{V}{M}(C_o - C_e) \qquad (1)$$

where q_e is capacity of adsorption at equilibrium (mg/g), C_o is initial concentration of adsorbate (mg/L), C_e is equilibrium concentration of adsorbate (mg/L), V is volume of aqueous solution

added to bottle (L), and M is mass of adsorbent (g). There are four regular isotherm models that have been utilized which are the Langmuir, Brauener-Emmett-Teller (BET), Freundlich, and Redlich-Peterson isotherms. These isotherm models are important to determine the most correlation between adsorbate and adsorbent as well as will provide the basis for the design of ideal adsorption system (Auwal & Hossen, 2018; Chen, 2015; Kyzas & Matis, 2015). Summary of each of the models and their parameters are listed in Table 2. Determination of the best fit isotherm model is obtained using the correlation of linear regression (R^2) to evaluate the data according to their equation.

Table 2. Isotherm Models

Model	Equation	Parameters and Constants
Langmuir	$q_e = \frac{QK_LC_e}{1+K_LC_e}$	Q: maximum value of metal ion adsorption per unit weight of adsorbent (mg/g) K_L: Langmuir constant (L/mg) C_e: equilibrium concentration of adsorbate (mg/L)
Freundlich	$q_e = K_F C_e^{1/n}$	K_F: Freundlich parameters related to the sorption capacity (mg/g) n: intensity of the sorbent C_e: equilibrium concentration of adsorbate (mg/L)
Redlich-Peterson	$q_e = \frac{AC_e}{1+BC_e^{\beta}}$	A and B: isotherm constants of Redlich–Peterson (L/mg) β: exponential term which lies between 0 and 1 C_e: equilibrium concentration of adsorbate (mg/L)
Bruener-Emmett-Teller	$q_e = \frac{q_s C_{BET} C_e}{C_s - C_e 1 + (C_{BET}-1)\left(\frac{C_e}{C_s}\right)}$	C_{BET}: BET adsorption isotherm (mg/L) C_s: adsorbate monolayer saturation concentration (mg/L) C_e: equilibrium concentration of adsorbate (mg/L) q_s: theoretical isotherm saturation capacity (mg/g) q_e: equilibrium adsorption capacity (mg/g)

The Langmuir isotherm model indicates that the adsorption of heavy metals occurs by monolayer adsorption on a homogeneous surface where the adsorption sites have equal affinities toward the adsorbate (Azizian et al., 2018; Chen, 2015). Fig. 2 illustrates the monolayer adsorption mechanism of heavy metals ion on the surface of nanoadsorbent. The important characteristics of the Langmuir isotherm can be expressed by a dimensionless constant known as equilibrium parameter R_L as defined in Equation 2 below where this parameter

indicates the shape of isotherm (Weber & Chakkrovarti, 1974; Kajitvichyanukul & Ananpattarachai, 2013).

$$R_L = \frac{1}{1+K_LC_o} \qquad (2)$$

The value of R_L is calculated and the type of isotherm can be defined as favourable when $0 < R_L < 1$, linear when $R_L = 1$, unfavourable when $R_L > 1$ and irreversible when $R_L = 0$.
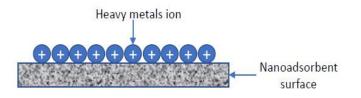
Fig. 2. Monolayer adsorption mechanism of Langmuir model adapted from Milewska-Duda et al., (2000)

Meanwhile, the Freundlich isotherm model describes that the uptake of metal ions occurs on a heterogeneous surface without uniform distribution of adsorption heat on the surface (Al-Ghouti et al., 2019). From the equation of Freundlich above, K_F and n parameters can be obtained by linearized Equation 3 below:

$$\log q_e = \left(\frac{1}{n}\right)\log C_e + \log K_F \qquad (3)$$

where $1/n$ is the intensity of adsorption or heterogeneity factor from slope value while K_F is the adsorption capacity obtained from *y*-intercept of the plotted graph. The $1/n$-value indicates the degree of non-linearity between the concentration of solution and adsorption and often describes in the range of $0 < 1/n < 1$. The higher the $1/n$ value, more favorable is the adsorption and when the $1/n = 1$, it signifies that the relative adsorption (adsorption partition) of the chemical was the same across the whole range tested, which is unusual (Alimohammadi et al., 2017; Kyzas et al., 2014; Singh, 2016). The visual of the Freundlich isotherm is represents in Fig. 3.
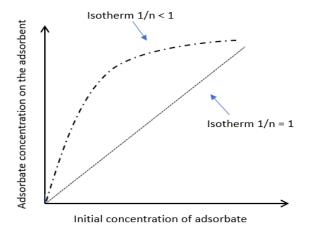

Fig. 3. Visual representation of Freundlich isotherm model adapted from Singh (2016)

The Redlich-Peterson model denotes that the adsorption equilibrium over a broad range of adsorbate concentration. This model is an empirical isotherm with three parameters that integrates elements from both the Langmuir and Freundlich isotherms models and can be applied either in homogeneous or heterogeneous surface (Ayawei et al., 2017; Kumara et al., 2014). The linear form of the Redlich-Peterson isotherm can be expressed as in Equation 4 as follows:

$$\ln\frac{C_e}{q_e} = \beta \ln C_e - \ln A \qquad (4)$$

The determination of Redlich-Peterson constants is obtained by plotting a graph of C_e/q_e versus C_e where β is slope and A is y-intercept. The β value modifies the curve of the graph, when the β value increases, the curvature increases. The calculated value indicates that when $\beta = 1$ the curve is same as Langmuir models and the value of β is usually less than 1 for Redlich-

Peterson isotherm equation (Wu et al., 2010).

Another isotherm model of adsorption process is Bruener-Emmett-Teller (BET) isotherm model which represents the multilayer adsorption of the adsorbate to the surface of adsorbent. From BET isotherm model, the surface area and the porosity of the materials can be determined

(Kecili & Hussain, 2018). Many researchers have utilized BET method to analyze the surface area of various carbon-based adsorbents such as activated carbon and carbon nanotubes (Kacan, 2016; Kumar & Jena, 2016; Maryam et al., 2013). The illustration of multilayer adsorption of heavy metals ions on nanoadsorbent is displayed in Fig. 4.
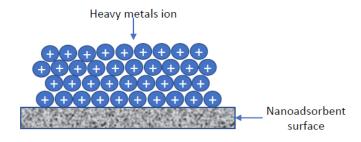

Fig. 4. Multilayer adsorption mechanism by BET isotherm model adapted from Lyubchik et al., (2011)

Adsorption kinetics

Adsorption kinetics is the adsorption uptake measurement with respect to time at a constant pressure or concentration. It is employed to quantify the diffusion of adsorbate in the adsorbent or membrane pores (Saha & Grappe, 2017). The rate of retention or release of a solute from an aqueous solution to solid-phase interface can be described by adsorption kinetics at certain experimental condition such as adsorbent dosage, flow rate, temperature and pH (William Kajjumba et al., 2018). Mathematical modelling of adsorption kinetics describes the adsorption

mechanism and rate controlling steps including external mass transport, chemical reaction kinetics and diffusion models (Torrik et al., 2019). Four models of adsorption kinetics (pseudo-first order, pseudo-second order, Elovich and intraparticle diffusion) are the most cited in many published works related to the adsorption models of heavy metals because they can fit the obtained data (Mercado-Borrayo et al., 2014; Xu et al., 2018). The linear form equation and parameters description of the adsorption kinetics models are given in Table 3.

Table 3. Adsorption Kinetic Models

Model	Equation Basic and Linear Form	Parameters and Constants
Lagergren, pseudo-first order model	$\dfrac{dq}{dt} = k_1(q_e - q)$ $q_t = q_e\left(1 - e^{-k_1 t}\right)$	q_e: Equilibrium adsorption capacity (mg/g) q: Time adsorption capacity (mg/g) k_1: First-order rate coefficient (l/min)
Ho, pseudo-second order model	$\dfrac{dq}{dt} = k_2(q_e - q)^2$ $\dfrac{t}{q} = \dfrac{t}{q_e} + \dfrac{1}{k_2 q_e^2}$	q_e: Equilibrium adsorption capacity (mg/g) q: Time adsorption capacity (mg/g) k_2: Second-order rate coefficient (g/mg min)
Elovich equation	$\dfrac{dq}{dt} = \alpha\exp(-\beta q_t)$ $q_t = \beta\ln(\alpha\beta) + \ln(t)$	q_t: Time adsorption capacity (mg/g) α: Initial adsorption rate (mg/g min) β: Desorption constant (g/mg)
Intra-particle diffusion	$q_t = k_i t^{1/2} + C$	q_t: Time adsorption capacity (mg/g) k_i: rate constants (mg/g.min$^{1/2}$) C: constant that approximates the thickness of the boundary layer (mg/g)

The kinetics model can explain the adsorption mechanism in detail. The Lagergren, pseudo-first order kinetic model is used based on the adsorptive capacity. The rate constant of k_1 is the time scale for the process to achieve equilibrium. It is stated to decrease when increasing the initial concentration which is indicates that a longer time is needed if the initial concentration is higher (Tan & Hameed, 2017). Some reports have found that k_1 is independent of initial concentration which is expected to be affected by other experimental conditions of temperature and pH (Tan & Hameed, 2017; Yousef et al., 2011). The first order rate constant, k_1 and adsorption capacity, q_e can be determined from the slope and intercept of linear graph of (q_e-q_t) versus t, respectively. The pseudo-second order model assumes that the adsorption rate is controlled by electron sharing and transfer between adsorbate and adsorbent through chemical adsorption where the rate of adsorption of solute is proportional to the available sites on the adsorbent (Xu et al., 2018). By plotting the linear graph, values of second order rate coefficient, k_2 and equilibrium adsorption capacity (q_e) can be calculated from the intercept and slope from the graph of t/q_t versus t, respectively.

The Elovich model helps to envisage the mass/surface diffusion as well as activation/deactivation energy of a system which includes the chemical reactions (Kajjumba et al., 2018). The model assumes that the adsorption rate of solute decreases exponentially as the amount of adsorbed solute increases. The graph of q_t vs t will aid to determine the nature of adsorption on the heterogeneous surface of the adsorbent. For the intraparticle model, the rate limiting step during adsorption is examined and it is divided by three steps: i) liquid film diffusion to the adsorbent surface, ii) pore liquid diffusion and iii) adsorption and desorption of the adsorbate (Xu et al., 2018; Kajjumba et al., 2018; Yildiz, 2018). The schematic diagram of the three consecutive steps for physical mechanism of heavy metal ions adsorption on the surface of nanoadsorbent is illustrated in Fig. 5.
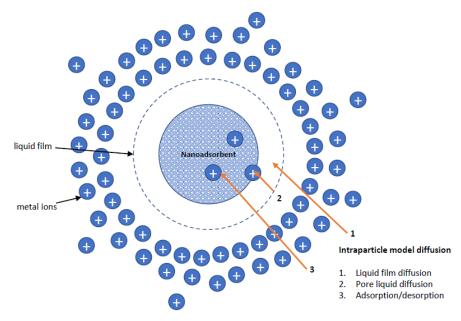

Fig. 5. Schematic diagram of adsorption mechanism for intraparticle kinetics model adapted from Yildiz (2018)

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Thermodynamics

The adsorption thermodynamics can be divided into three parameters which are adsorption Gibbs' free energy, enthalpy change and entropy change. Thermodynamic studies are investigated to identify the effects of temperature on the adsorption process. Three thermodynamics state can be determined by each equation as stated in Table 4.

Table 4. Thermodynamics state and mathematical equations

Thermodynamics parameter	Equation
Gibbs's free energy ($\Delta G°$)	$\Delta G° = -RT \ln K_o$
Enthalpy change ($\Delta H°$)	$\Delta G° = \Delta H° - T\Delta S°$
Entropy change($\Delta S°$)	$\ln K_o = \Delta S° / R - \Delta H° / RT$

Thermodynamic calculations basic principle is based on the adsorption isotherm, which gives the amount of the metals adsorbed in the porous adsorbent structure as a function of the amount at equilibrium in the solutions (Lyubchik et al., 2011). Furthermore, thermodynamic studies provide information on various adsorbent structural characteristics and their effects on metal ions adsorption. The negative value of $\Delta G°$ indicates the spontaneous adsorption process while positive value of $\Delta G°$ shows the adsorption is not spontaneous. In contrast, $\Delta H°$ value gives information either the adsorption process is endothermic or exothermic where positive value of $\Delta H°$ is an endothermic adsorption process (Kecili & Hussin 2018). The correlation of equilibrium, kinetics and thermodynamics data using theoretical or empirical equations can be used for the analysis and prediction of adsorption data. All these mathematical models including linear and non-linear equations are applicable in describing experimental data of adsorption isotherms.

Synthesis of nanoadsorbent

There are two fundamental approaches to synthesis nanoadsorbents which are top-down and bottom-up approach to obtain nanomaterials of desired sizes, shapes, and functionalities(El-sayed, 2020; Singh et al., 2018). Top-down approach is the conventional method where the process starts from larger particle (macroscopic) and the size reduction to nano-scale is done by externally- controlled source of energy applied such as erosion, sputtering, reactive milling, high energy ball milling and mechanical alloying (Singh et al., 2018; Soni et al., 2018). However, the main problem faced by top-down method is associated with the crystallographic and the surface structure destruction that might be occurred during particle size reduction (El-sayed, 2020). Therefore, bottom-up approach is such a modern and new technique to synthesize nanoadsorbent materials. The bottom-up approach applies physical and chemical processes that operate at the nanoscale to integrate main components into bigger structures. The bottom-up approach includes molecular self-assembly, sol-gel, supercritical fluid, chemical and physical vapor deposition where these methods produce nanomaterials with less surface defects, less contamination, homogeneous chemical composition and narrow particle size distribution (El-sayed, 2020; Khaled-Habiba et al., 2014). Despite the difficulty to scale-up production, this bottom-up approach is the preferred technology because it can produce nanoadsorbent materials with specific properties fitted to the remediation required (El-sayed, 2020). Fig. 6 below shows the route of synthesis for both top-down and bottom-up approaches in carbon-based nanomaterials synthesis.
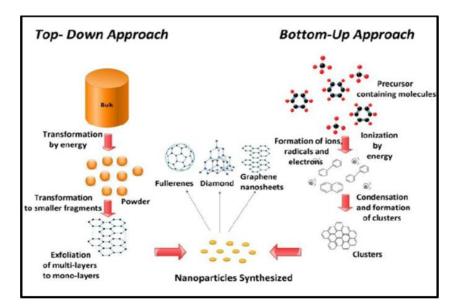
Fig. 6. Bottom-up and the top-down approaches in synthesis of carbon-based nanomaterials (Habiba et al., 2014)

Type of nanoadsorbent in wastewater treatment

There are many types of nanoadsorbent that have been utilized in water/wastewater treatment and the most commonly used nanomaterials are classified into three categories depending on their morphology, size and chemical properties which are; 1) carbon-based nanoadsorbents; 2) metal oxide- based nanoadsorbents and 3) polymer based nanoadsorbents. The details and examples on each type of nanoadsorbents are explained below.

Carbon-based nanoadsorbents

Carbon based nanoadsorbents including carbon nanotube (CNT), multiwalled carbon nanotube (MWCNT) and graphene have been widely utilized in many adsorption processes for wastewater treatment. Due to their unique characteristics of high specific surface areas, large pore volumes, nontoxicity, noncorrosive and existences of oxygen-containing surface, these nanoadsorbents exhibit high removal efficiency of contaminants (i. e heavy metals) from wastewater.

CNT is one dimensional material under carbon-based nanoadsorbent class. Various types of CNTs have been utilized extensively in removal of heavy metals including mercury, lead, copper, nickel, chromium, cadmium and arsenic from aqueous solutions through adsorption process (Li et al., 2005; Rodríguez & Leiva, 2019; Šolic et al., 2020). These heavy metals are considered the most hazardous due to bioaccumulative, non-biodegradable and can extremely be harmful to plants, animals and human. The hollow and multilayered structure of CNT owing to its high surface area characteristic can contribute to the high adsorption efficiency (Baruah et al., 2019). Surface modification of CNTs using strong oxidizing agents such as sulphuric acid and potassium permanganate leads to the introduction of hydroxyl and carboxyl functional groups. Functionalized CNTs have been reported to increase the binding capacity of heavy metal ions through electrostatic bonding and create the active sites on CNTs for heavy metals adsorption (Fu & Wang, 2011; Mallakpour & Khadem, 2018).

Previous findings compared the efficiency of functionalized MWCNT for heavy metals adsorption at different pH values where the percentage removal and

sorption capacity increased when the value of pH was increased indicating adsorption process is strongly dependent on pH (Elsehly et al., 2016; Rodríguez & Leiva, 2019; Šolic et al., 2020). The adsorption mechanism of functionalized MWCNT was mainly of ionic interaction where the interactions between metal ions and carboxyl and hydroxyl groups has occurred (Elsehly et al., 2016; Šoli´c et al., 2020). On the other hand, Robati (2013) investigated the adsorption studies of lead ions removal by MWCNT and MWCNT-COOH and the result exhibited the adsorption system fitted well with pseudo-second order kinetic indicating that the expression characteristics of reaction mechanism at variable concentrations were excellent in the removal of lead from aqueous solution (Robati, 2013). Other findings on adsorption mechanism for copper removal from MWCNT also showed the ion exchange mechanism between copper ions and MWCNT with high copper removal effectiveness of 93% (Gupta et al., 2017). Recent research conducted by Bankole et al., (2019) reported that functionalized CNT was better in adsorption capacity of several heavy metals compared to purified CNT and the data obtained agreed well with Temkin model adsorption isotherm indicating good interaction between sorbate and sorbent, which is an evidence of an ion-exchange mechanism during the adsorption. Therefore, it can be concluded that both pure CNTs and functionalized CNTs are promising nanoadsorbents in heavy metals removal but functionalized CNTs possesses better adsorption capacity.

Another carbon based nanoadsorbent that is widely utilized in wastewater treatment is graphene. Graphene is a unique two-dimensional structure consisting of a single atomic layer of sp^2 hybridized carbon atoms and densely packed in a honeycomb crystal lattice. Graphene is the strongest, yet lightest material known. It has excellent characteristics in terms of mechanical, electronic and thermal properties. Theoretically, graphene has a large specific surface area of 2620 m^2/g, the value of Young's modulus is 1 TPa with 130 GPa of intrinsic strength. Due to hydrophobic nature and water repellant of graphene, it is not suitable to be utilized in water applications (Yoon et al., 2016). Hence, synthesizing of graphene oxide (GO) would be the best alternative to overcome this issue due to addition of oxygenous functional groups which contribute to the hydrophilicity properties of that nanoparticle (Nair et al., 2012; Yu et al., 2020). Graphene oxide (GO) is the oxidized form of graphene which is prepared by chemical oxidation of graphite resulting in extended graphene sheets decorated with epoxy and hydroxyl functional groups in the basal planes and carboxylic acid groups at the edges (Dreyer et al., 2010). GO is highly utilized in adsorption process due to existence of abundant oxygen functionalized groups, easy for large-scale production and high surface area (Alam et al., 2018; Mohan et al., 2017). Previous findings reported that graphene and graphene-based nanomaterials are promising nanoadsorbents and become the forefront research in water/wastewater treatment process due to strong mechanical stability, hydrophilicity, high negative charge density, ease of fabrication, industry scale production and the ability in heavy metal ion adsorption from wastewater (Jayakaran et al., 2019; Kyzas et al., 2014; Mkhoyan et al., 2009; Mohan et al., 2017; Peng et al., 2017; Yu et al., 2020).

Previous findings by Madadrang et al., (2012) reported on the comparison of nanoadsorbents from GO, GO-EDTA and reduced GO-EDTA for lead removal. Accordingly, they found that GO-EDTA displayed enhanced adsorption capacity. The experimental data showed that adsorption mechanism fitted well with Langmuir isotherm model which involved two ion exchange of adsorption processes;

i) interaction of lead ions onto the surface of GO to form the complex and ii) complex formation of EDTA with lead and -COOH group for complete removal of lead (Kumar et al., 2019; Madadrang et al., 2012). Previous study by Sitko et al., (2013) investigated the adsorptive properties of GO towards divalent metal ions such as copper, zinc, cadmium and lead. In this work, the maximum adsorption capacities of copper, zinc, cadmium and lead on GO at pH 5 were 294, 345, 530, 1119 mg g^{-1}, respectively while the adsorption isotherms and kinetic studies were fitted well with Langmuir isotherm and pseudo second order kinetic models, respectively for all divalent metal ions (Sitko et al., 2013). The mechanism of adsorption between GO and divalent metal ions is illustrated in Fig. 7.
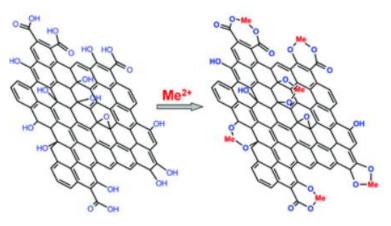

Fig. 7. Schematic diagram of adsorption process of divalent metal ions on GO (Sitko et al., 2013)

The study of Mohan *et al*. (2017) synthesized graphene oxide-MgO nanohybrid for removal of lead ions from aqueous solution. From the results, lead adsorption by graphene oxide -MgO mechanisms are controlled by external mass transfer and intraparticle diffusion, the Langmuir model also suggested the monolayer adsorption has occurred. Meanwhile, White et al., (2018) sorted out carboxylated graphene oxide for large adsorption of copper on the surface of graphene oxide-COOH compared to the graphene oxide and both GO and GO-COOH were fitted well with the Langmuir isotherm. The optimization of adsorption conditions of lead removal by GO also reported to be at pH 7 with initial concentration of 100 mg/L, 10 minutes of contact time and fitted with Langmuir isotherm model (Nik-Abdul-Ghani et al., 2019). Graphene oxide-chitosan nanofibers revealed that adsorption kinetics and equilibrium data for lead were described by double-exponential kinetics and Redlich–Peterson isotherm models and this nanofiber showed high reusability with up to fifth cycle of regeneration (Hadi Najafabadi et al., 2015).

The modification on GO by synthesizing the magnetic GO (MGO) by Ain et al., (2020) for heavy metals removal stated that different heavy metals had maximum adsorption capacities at different pH conditions. The findings reported that the adsorption mechanism followed Langmuir isotherm and pseudo-second-order kinetics model with spontaneous and endothermic process (Ain et al., 2019). The advantages of using magnetic nanocomposite could be easily separated from treated water and reduce recontamination. However, in terms of separation of pure graphene and GO it would be difficult (Khan et al., 2017). Several types of carbon-based nanoadsorbents and their optimum conditions with adsorption capacity are summarized in Table 5 below.

Table 5. Comparative table on carbon-based nanoadsorbents on optimum parameters and removal efficiency

Carbon-based nanoadsorbent	Heavy metals	pH	Contact time	Adsorbent dosage	Initial metal concentration	Removal efficiency/maximum adsorption capacity	Reference
CNT	Pb	5	20 min	-	30 mg/L	35 mg/g	Li et al., 2005
CNT	Cu Co Zn Mn Pb	9			20 mg/L	99% 85% 82% 58% 87%	Stafiej & Pyrzynska, 2007
Oxidized MWCNT	Pb	NA	35 min	0.05 g	-	20 mg/g	Robati, 2013
MWCNT	Ni	8	0.6 min	0.6 mg		85 %	Elsehly et al., 2016
MWCNT	Cu	3	60 min	10 mg	20 mg/L	93 %	Gupta et al., 2017
Polyhydroxylbutyrate Functionalized Carbon Nanotubes	Fe Ni Cd Pb Cu Zn Cr As	5.65	10 min	20 mg		15.92% 77.95% 99.34% 98.85% 83.08% 18.34% 98.19% 99.95%	Bankole et al., 2019
GO-EDTA	Pb	6.8	20 min	-	0.1 g/L	479 mg/g	Madadrang et al., 2012
GO	Cu Zn Cd Pb	5	60 min 30 min 60 min 60 min	-		294 mg/g 345 mg/g 530 mg/g 1119 mg/g	Sitko et al., 2013
GO GO-COOH	Cu	6	60 min	-	50 mg/L	97%; 277.77 mg/g 99.4; 357.14 mg/g	White et al., 2018
GO-MgO nanohybrid	Pb	6.5	30 min	-	0.4 g/L	190 mg/g	Mohan et al., 2017
GO	Pb	7	10 min	0.1 mg	100 mg/L	99%; 500 mg/g	Nik-Abdul-Ghani et al., 2019
Magnetic GO	 Pb Cr Cu Zn Ni 	5 6 6 7 8	25 min 35 min 25 min 35 min 25 min	 0.014 g/L 0.016 g/L	-	200 mg/g 24.330 mg/g 62.893 mg/g 63.694 mg/g 51.020 mg/g	Ain et al., 2020

Briefly, carbon-based nanoadsorbents that had been utilized in the adsorption for heavy metals have different adsorption mechanisms in aqueous solutions based on the physical, chemical and electrostatic interaction. Mainly, adsorption process on GO and CNTs are dominated by ion exchange mechanism due to presence of surface functional groups that allow interaction and provide high adsorption sites to heavy metals (Khan et al., 2017). Many findings estimated the reusability of the carbon-based nanoadsorbents by adsorption/desorption process. The reusability of graphene oxide-chitosan nanofibers is reported by Hadi-Najafabadi et al., (2015) which is up to fifth cycles of regeneration process. The regeneration properties of GO and GO–COOH were also reported that copper removal efficiency only reduced by 4.50% and 3.96%, respectively after five cycles of adsorption/desorption process (White et al., 2018). The reusability of magnetic-GO was evaluated, and the results showed that the total adsorption capacity of MGO for heavy metals ions remained in the range of 87.51 % - 78.12 % after four successive adsorption/desorption cycles (Ain et al. 2019). These findings supported that GO-based nanoadsorbents possess good reusability and regeneration properties (White et al., 2018; Ain et al., 2019).

Despite all the exceptional properties of the carbon-based nanoadsorbents, the applications of CNTs in wastewater are

limited due to low volume of production and high cost. Besides, CNTs cannot be used alone without any supporting or matrix to form structural components and the effective techniques for regeneration or reuse of CNTs have not been elucidated yet (Ihsanullah et al., 2016; H. Lu et al., 2016). In addition, some limitations of utilization of GO are high water absorption and poor performance of the solid–liquid separation, thus GO might remain in the filtered water and will cause a risk of exposure to humans, animals, and other aquatic organisms (Pérez-Ramírez et al., 2016). Moreover, these nanomaterials of CNTs and GO also have limitations when used in the packed bed column process due to high pressure drop when the small particles were tightly packed and leading to the low adsorption rates because of loss of active adsorption sites (Zhang et al., 2019).

Metal oxide-based nanoadsorbent
Metal oxides nanoparticles provide high removal capacity, high surface area and specific affinity towards heavy metal adsorption and become a great potential as nanoadsorbent for wastewater treatment applications (Hua et al., 2012; Yang et al., 2019). Metal oxides-based nanoparticles are nanosized materials (in range 1-100 nm) including manganese oxide, zinc oxide, nickel oxides, iron oxides, aluminium oxides, titanium oxide, magnesium oxides and zirconium oxides. These metal oxide-based nanoparticles are the promising nanoadsorbents to remove heavy metals from aqueous system due to their high adsorption capacity and large surface areas (Hua et al., 2012; Taman, 2015; Yang et al., 2019). All of these nanosized metal oxides have been utilized in various heavy metals removal from wastewater. The adsorption mechanisms of metal oxides were governed by complexation between dissolved metals and the oxygen in metal oxides with two step process; firstly the adsorption of metal

ions on the external surface and secondly by the rate limiting intraparticle diffusion along the micropore (Koeppenkastrop & Decarlo, 1993; Trivedi & Axe, 2000; Wang et al., 2020).

Nickel oxide
The adsorption study of nickel oxide in nanopowder form is reported for the removal of lead and zinc with enhanced catalytic activity and high adsorption capacity with 50.5 mg/g and 63.7 mg/g respectively (Abd El fatah & Ossman, 2014). The authors reported that lead removal by nickel oxide fitted well with Langmuir isotherm and pseudo second order kinetic models while zinc removal followed Freundlich isotherm and pseudo first order kinetic model (Abd El fatah & Ossman, 2014). Mahmoud et al., (2015) reported that nickel oxide prepared by organic solvent is capable of lead removal and the equilibrium was achieved at 2-hour, and the adsorption mechanism fitted to Langmuir model and pseudo-first order reaction. The green synthesis of nickel oxide from lemon juice extract also showed the capability to remove chromium, copper and nickel from aqueous solution. The results obtained showed that the adsorption was highly pH dependent and well defined with Langmuir isotherm and pseudo second order kinetic models (Panji et al., 2016). Recent finding by Krishna et al., (2018) reported that chromium doped nickel oxide nanoparticle offers a great potential for heavy metals removal including lead, cadmium and copper. The cation removal and high adsorption capacity in aqueous solution by chromium doped nickel oxide is due to the formation of hydroxide on the surface nanoparticle with the adsorption kinetic and isotherm models were well fitted using pseudo-second-order kinetic and Freundlich isotherm model, respectively (Krishna et al., 2018).

Copper oxide

Previous findings using copper oxide as nanoadsorbent showed high removal of heavy metals including iron and cadmium with adsorption capacity of 94.34 mg/g and 131.33 mg/g, respectively (Taman et al., 2015). Moreover, Hassan et al., (2017) reported that copper oxide also has high capability to remove other heavy metals such as cadmium and nickel with respect to 64.935 mg/g and 322.50 mg/g of adsorption capacity, respectively.

Titanium oxide

Titanium oxides had been well studied for the removal of heavy metals from aqueous solution (Gebru & Das, 2017; Y. Lu et al., 2016; Moon et al., 2014; Youssef & Malhat, 2014). Gebru and Das (2017) reported that highest removal capacities of lead and copper were obtained by electrospun cellulose acetate/titanium oxide nanoadsorbent which were at maximum removal efficiency of 99.7% and 98.9%, with adsorption capacity of 25 mg/g and 23 mg/g, respectively as compared to pure cellulose acetate. The adsorption mechanism process was well fitted with the Langmuir isotherm model and pseudo-second order kinetic model for both lead and copper ions (Gebru & Das, 2017). Other finding from Li et al., (2014) stated that titanium oxide was used for chromium removal using magnetic mesoporous titanium dioxide–graphene oxide. The study showed that the adsorption process followed Freundlich isotherm and pseudo second order kinetic models with maximum adsorption capability of 117.4 mg/g (Li et al., 2014). Thus, it demonstrated that titanium oxide is a potential nanoadsorbent for wastewater application.

Zinc oxide

In addition, zinc oxide is a nanoparticle that has been synthesized and applied widely in heavy metals removal due to its characteristics of high surface area, low cost and extraordinary removal capacity (Ghiloufi et al., 2016; Khan et al., 2019; Le et al., 2019). A study conducted by Ghiloufi et al., (2016) compared the adsorption capacities of doped gallium-zinc oxide nanopowders in different concentrations for cadmium and chromium removal from aqueous solution. The results showed high percentage removal of heavy metal ions was at 1wt% of doped gallium zinc oxide compared to the bare zinc oxide indicated that the incorporation of gallium in zinc oxide nanoparticles could improve the uptake effect of these heavy metals. Green synthesis of zinc oxide also exhibited maximum removal efficiencies up to 93% of lead ion at pH 5 and Langmuir isotherm fits with the adsorption data indicated the favourable surface adsorption on the metal ions (Azizi et al., 2017). Le et al., (2019) also reported that zinc oxide nanoparticles can removed effectively various heavy metals including Cu (II), Ag(I) and Pb (II) ions with removal efficiency more than 85%.

Iron oxide

Iron oxide nanoparticle has been extensively studied and reviewed as nanoadsorbent for heavy metals removal due to their high surface area, small size, superior adsorption capacity, easiness of isolation method and magnetic property (Dave & Chopda, 2014; Nizamuddin et al., 2019; Vélez et al., 2016). Baalousha, (2009) had studied the aggregation properties of iron oxide at different parameters including particle concentration and pH. Arsenic adsorption by Magnetic γ-Fe_2O_3 biochar exhibited Langmuir isotherm and pseudo-first order kinetic models adsorption mechanism with the maximum adsorption capacity 3.147 mg/g (M. Zhang et al., 2013). Lin and Chen, (2014) also reported that carbonized Fe_3O_4/phenol–formaldehyde resins were capable for the maximum adsorption of arsenic at 216.9 mg/g. Furthermore, iron oxide nanoparticles i.e. Fe_3O_4 and γ-Fe_2O_3

were successfully synthesized and removed mercury from water with 87 % removal efficiency (Vélez et al., 2016).

However, metal oxides nanoadsorbent such as titanium oxides, zinc oxides and iron oxides have several disadvantages when they are used in the suspension especially in wastewater treatment (Lu et al., 2016; Nizamuddin et al., 2019). These nanoparticles are difficult to recover from the treated water due to small size, complicated production procedure of metal oxides and production cost would hinder the upscaling process for water application (Lu et al., 2016;

Nizamuddin et al.; 2019). Therefore, researchers suggested that functionalization of metal oxides based nanoadsorbent could be implemented to overcome these limitations and enhance their adsorption properties. For example, addition of ligands such as ethylenediamine tetraacetic acid, L-glutathione and mercaptobutyric acid or addition of copolymers might increase the adsorption capacity of metal oxides (Ge et al., 2012; Lu et al., 2016; Warner et al., 2010). The summary of metal oxide-based nanoadsorbents and its optimum operating parameters are shown in Table 6.

Table 6. Comparative table on metal-oxides nanoadsorbent and their optimum operational parameters

Metal oxide	Heavy metals	pH	Contact time	Adsorbent dosage	Initial metal concentration	Reference
Nickel oxide nanopowder	Pb Zn	6 9	120 min	NA	Independent of initial concentration	Abd El fatah & Ossman, 2014
Nickel oxide nano catalyst	Pb	5.8	120 min	0.2 g	5 mg/L	Mahmoud et al., 2015
Nickel oxide	Cr Ni Cu	3 7 7	10 min 5 min 10 min	25 mg 10 mg 6 mg	NA	Panji et al., 2016
Chromium doped nickel oxide	Cd Pb Cu	9	45 min	0.15 mg	NA	Krishna et al., 2018
Copper oxide	Fe Cd	6	20 min	0.3 mg 0.4 mg	NA	Taman et al. 2015
Copper oxide	Cd Ni	6	30 min	0.1	15	Hassan et al., 2017
Cellulose acetate/titanium oxide	Pb Cu	5.2 5.8	300 min 300 min	2.5 wt.%	NA	Gebru & Das, 2017
Magnetic mesoporous titanium dioxide–graphene oxide	Cr	2	40 min	NA	NA	Li et al., 2014
TiO_2 and γ-Al_2O_3 nanoparticles	Cd	8	NA	NA	80 mg/L	Shirzadeh et al., 2020
Doped gallium-zinc oxide	Cd Cr	5 3	10 min 760 min	1 wt.%	NA	Ghiloufi et al., 2016
Zinc oxide-green synthesis	Pb	5	60 min	0.1 g	25 ppm	Azizi et al., 2017
Magnetic γ-Fe_2O_3 biochar	As	NA	240 min	NA	10 ppm	Zhang et al., 2013
Iron oxide	Hg	NA	24 min	8 mg/L	NA	Vélez et al., 2016
Granule iron oxide	As	5	49.9 min	8 mg/L	30 ppm	Tabatabaei et al., 2020

NA: not available

Polymer based nanoadsorbent

Conventional adsorbents have limitations such as lack of specificity, lower adsorption capacity and poor recyclability (Burakov et al., 2018; Siddiqui & Chaudhry, 2017). Therefore, numerous organic-inorganic hybrid polymers with stronger adsorption capacity, greater thermal stability and higher recyclability have been developed to overcome the issues of conventional adsorbents (Lofrano et al., 2016). Polymeric based nanoadsorbents having high specific surface area, porous structure, and presence of functional groups on the surface are identified to have the capability of binding efficiently towards organic dyes and heavy metal ions including lead, arsenic, cadmium and zinc from wastewater (Lofrano et al., 2016; Baruah et al., 2019).

Different types of polymers which are categorized based on materials used (i.e:, chitosan, dendrimers, cellulose), methods of preparation of a good nanoadsorbent, adsorption process and mechanism have been reviewed and demonstrated that the polymer-based absorbents are good potential to remove various kinds of heavy metal ions from wastewaters and aqueous solutions (Samiey et al., 2014; Wadhawan et al., 2020; Zare et al., 2018; Zhao et al., 2018). The study of Dubey et al., (2016) investigated the role of chitosan-alginate nanoparticle in removal of mercury. This study showed that maximum adsorption capacity of 217.39 mg/g is achieved at optimum conditions of pH 5 at 90 minutes contact time with 4 mg/L of initial ion concentration. Chitin nanofibrils, a derivative of chitosan was fabricated by Liu et al., (2013) to remove wide range of metal ions such as cadmium, nickel, copper, zinc, lead and chromium.

Dendrimers are another organic polymer based nanoadsorbents with highly branched and star shaped macromolecules in nanometer scale dimension. They consist of three components which are a central core, an interior dendritic structure (the branches), and an exterior surface with functional surface groups (Vunain et al., 2016) (Fig. 8).
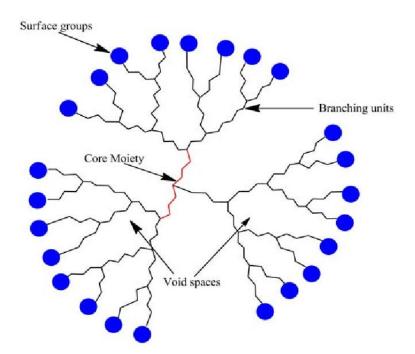

Fig. 8. Structure of dendrimers (Vunain et al., 2016)

Mainly, the functional groups on dendrimers in polymer based nanoadsorbent are chelating functional groups (Wadhawan et al., 2020). Previous report stated chelating agents such as 3-aminobenzoic acid 1, 2-diaminoethane or 1, 3-diaminopropane were used for modification of poly (styrene-alt-maleic anhydride) and the percentage removal efficiency of heavy metals were reported in the descending order of Fe (II)>Cu (II)>Zn (II)>Pb (II) (Hasanzadeh et al., 2012). Polyacrylonitrile is selected as base polymer to prepare three ion selective nanofibers modification with chelating groups of ethylenediamine (EDA), ethyleneglycol (EG) or diethylenetriamine (DTA) by (Martín et al., 2018). In this study, obtained values of adsorption capacity for Cu (II), Pb (II) and Zn (II) are 6.1, 8.8 and 7.2 mmol/g, respectively which are higher than other materials due to large surface area and high degree of surface functionalization as a results of greater number of chelating groups accessible for metal adsorption (Martin et al., 2018).

Biopolymer based nanoadsorbents such as cellulose had been studied for uptake of heavy metal ions. Previous finding by Mautner et al., (2016) stated that cellulose nanofibrils with phosphate groups adsorbed Cu (II) ions efficiently from aqueous solution due to existence of functional groups on the surface of the nanopapers. Other cellulose based nanoadsorbents such as cellulose gels, cellulose composites and derivatives as well as nanocrystalline cellulose had been reviewed by Jamshaid et al., (2017) and results exhibited the adsorption capacity of heavy metals were enhanced successfully. Furthermore, other polymer based nanoadsorbents such as chitosan, polyaniline, polypyrrole, poly(1-amino-5-chloroanthraquinone) have been fabricated for heavy metals removal and the adsorption studies and mechanism have been reported (Dubey et al., 2016; Huang et al., 2016; Mahmud et al., 2017; Piri et al., 2016).

Nanocomposite adsorbents
As mentioned above, every nanoadsorbent has its own disadvantages. Hence, to overcome all these problems it is an effective strategy to fabricate novel nanocomposites for water and wastewater treatment. New strategy in nanoadsorbent modification by incorporating nanoparticles with polymer/metal/carbon based has been introduced to produce various types of nanocomposites. Recently, there are several types of nanocomposite that have been developed which are inorganic-polymer, organic-polymer and magnetic nanocomposites that take advantages from different nanomaterials (Yang et al., 2019). These nanocomposites would improve the adsorption performance and provide more specific interaction with the targeted contaminants, thus, better adsorption capacity and high efficiency removal of heavy metals from wastewater would be achieved (Yang et al., 2019; Zhao et al., 2018). Nanocomposites have many advantages in terms of low cost, stability, better mechanical properties, low energy consumption, susceptible to high temperature and harsh chemical environments (Barak et al., 2018). Moreover, the development of hybrid nanocomposite adsorbents also provides amazing advantages in terms of physiochemical stabilities and magnetic characteristics for wastewater treatment applications (Nizamuddin et al., 2019). Several works on nanocomposites, their adsorption mechanisms and remarkable discoveries are summarized in Table 7 below. The reusability and longevity of the nanocomposite adsorbents also had been reported by several findings that the nanocomposite adsorbents possess a very good regeneration properties as the key factor for the cost-effective strategy of heavy metals removal from wastewater (Ahmaruzzaman, 2019; Ge et al., 2012; Hadi-Najafabadi et al., 2015; Mahmoudi et al., 2019; Nasir et al., 2019; Razzaz et al., 2016).

Table 7. Summary of efficacy for various nanocomposite adsorbents for heavy metals removal

Nanocomposite	Heavy metals	Parametric conditions	Results/Findings	Remarks	Reference
Magnetic iron oxide modified with copolymers (acrylic acid and crotonic acid) and 3-aminopropyltriethoxysilane	Cd Zn Pb Cu	pH 5.5 30 minutes of contact time initial concentration of metal ions, 20–450 mg/L T = 298 K	Adsorption capacities for cadmium, zinc, lead and copper were 29.6, 43.4, 166.1 and 126.9 mg/g, respectively. Langmuir isotherm Pseudo-second order kinetics	The metal ion adsorption capacity remained constant for 4 cycles, indicates no irreversible sites on the surface of Fe_3O_4@APS@AA-co-CA MNPs	Ge et al., 2012
Graphene oxide–$MnFe_2O_4$ magnetic nano-hybrids	Pb As	pH = 5 for Pb(II) pH = 4 for As(V) pH = 6.5 for As(III)	Langmuir isotherm Pseudo-second order Surface complex formation theory -spontaneous and endothermic	Superior adsorption capacity property is due to the combination of the unique layered nature (allowing maximum surface area) of the hybrid system and the good adsorption capabilities of both the GO and NP. Magnetic separation	Kumar et al., 2014
Hydrous cerium oxide–graphene composite	As	Contact time: 20 minutes Maximum adsorption at pH 4.0 (As (III)) and pH 7.0 (As (V))	Maximum adsorption capacities were 62.33 and 41.31 mg/g for As(III) and As(V) Langmuir isotherm Pseudo-second order	X-ray photoelectron spectroscopy analysis indicated that the major chemical state of cerium (Ce) element in the adsorbent was +IV and the hydroxyl group might be involved in the adsorption process.	Yu et al., 2015
Electrospun PVA/ZnO nanofiber	U Cu Ni	Contact time 6 h, temperature 45 °C, adsorbent concentration 1 g/L and pH 5	Double-exponential kinetic model D–R isotherm model indicated that the mechanism of U(VI), Cu(II) and Ni(II) sorption on the nanofiber adsorbent was physisorption Endothermic and spontaneous	The sorption process occurs in two steps: i) external diffusion (transport of the metal ion to the external surface of the adsorbent) which is a rapid phase, ii) the pore diffusion (sorption of the metal ion on the interior surface of the adsorbent) which is a slow phase	Hallaji et al., 2015
Reduced GO-Fe_3O_4 composite	Pb	pH=7.0 with the initial concentration of Pb(II) ions of 80 mg/L	Adsorption capacity was 30.68 mg/g Langmuir isotherm	The composite with absorbed Pb(II) can be easily collected by magnetic separation from wastewater because of the excellent magnetism of Fe_3O_4	Cao et al., 2015
Chitosan-GO	Cu Pb Cr	Equilibrium time of 30 min and temperature of 45 °C	Adsorption capacity of Pb^{2+}, Cu^{2+} and Cr^{6+} metal ions using chitosan/GO nanofibers was found to be 461.3, 423.8 and 310.4 mg/g Redlich–Peterson isotherm models Double-exponential kinetic Endothermic and spontaneous reaction	Reusability studies indicated chitosan/GO nanofibers could be reused frequently without any significant loss in adsorption performance	Hadi-Najafabadi et al., 2015
Magnetite–graphene oxide and magnetite-reduced graphene oxide composite	As (III) As(V)	As (III) adsorption at pH 7 As (V) adsorption at pH 4 temperature = 25 °C, adsorption time = 12 h	Adsorption capacity of M-GO and MrGO for As(III) and As(V) were 85 mg/g (M-GO for As(III)), 38 mg/g (M-GO for As(V)), 57 mg/g (M-rGO for As(III)), and 12 mg/g (MrGO for As(V)) Freundlich isotherm Pseudo-first order Surface complexation	Electrostatic interaction between the positively charged surface of Fe_3O_4–graphene-based adsorbents and anionic As(V) -adsorption mechanism of As(III) was strongly affected by a surface complexation,	Yoon et al., 2016
Chitosan/TiO_2	Cu Pb	Equilibrium time of 30 min Temperature= 45 °C,	The maximum adsorption capacities of Cu and Pb ions were 710.3, 579.1 and 526.5, 475.5 mg/g pseudo-first order and Redlich–Peterson isotherm models endothermic/spontaneous	The selectivity of metal sorption using chitosan/TiO_2 nanofibrous adsorbent was in order of Cu > Pb. Five cycles of adsoprtion/desorption	Razzaz et al., 2016
Hydrated manganese oxide (HMO) on GO nanocomposite (HMO@GO)	Pb	pH 6.7 sorbent dose = 0.2 g/L Temperature = 298 K	High adsorption capacity >50 mg/g Freundlich isotherm Pseudo-second order Intraparticle diffusion	GO offered the preconcentration of Pb for enhanced sequestration through the Donnan membrane effect	Wan et al., 2016
α-FeOOH decorated graphene oxide-carbon nanotubes aerogel	As	Maximum As adsorption at pH 9.5	Adsorption capacities of 56.43, 24.43 and 102.11mg/g^1 for As(V) Langmuir isotherm Pseudo-second order Endothermic reaction	Arsenic interact with α-FeOOH@GCA to form inner-sphere complexes which could be interpreted through ligand exchange mechanism	Fu et al., 2017
graphene oxide-MgO nanohybrid	Pb	Adsorbent dose: 0.4 g/L 30 min of equilibrium time temperature: 30 °C, pH 6.5	Langmuir, and D-R isotherm model Spontaneous and endothermic Pseudo-second-order kinetic Intraparticle diffusion	The lead adsorption was governed by the external mass transfer which was followed by intraparticle diffusion	Mohan et al., (2017)
Polyaniline/ZnO nanocomposite	Cr	Optimum pH 2 optimum temperature 60 °C	Adsorption capacity was found to be 346.18 mg/g -Langmuir Pseudo-second order endothermic and spontaneous	Electrostatic adsorption coupled reduction of adsorption mechanism	Ahmad & Hasan, 2017
GO-blended Polysulfone (PSf) ultrafiltration membrane	Pb	Lead concentration = 50 mg/L and pH = 5.5	Maximum rejection of 98% was achieved -high flux of 43.62 L/m^2 h, higher porosity membrane	GO and NMP in obtaining a highly porous membrane that provides improved flux and enhanced rejection of lead ions	Ravishankar et al., 2018
Functionalised mesoporous KCC-1 and chitosan-oleic acid	Pb	pH: 9 Adsorbent dose = 20 mg, contact time = 100 min, initial concentration: 100 mg/L	Maximum adsorption was 168 mg/g Langmuir and pseudo-second-order models were found to be the best fit models to predict isotherms and kinetics of adsorption, respectively.	Green synthesis of pure mesoporous KCC-1 was prepared through the facile hydrothermal-assisted sol-gel process in a Teflon-lined stainless steel autoclave at 393 K	Zarei et al., 2019
Polydopamine/metal organic framework thin film nanocomposite	Cd Ni Pb	0.01 % of metal organic framework concentration	the removal rate was in the range of 94% to 99.2% for Ni^{2+}, Cd^{2+} and Pb^{2+}, respectively	None of nanocrystal aggregation, poor stability and large MOF loss when a MOF is applied to membrane separation new application of nanocrystals in heavy metals removal	He et al., 2020

Limitations and future perspective

Recently, several nanotechnology products have been applied in water purification as well as wastewater treatment. There are differences in opinions of several researchers regarding the use of nanomaterial for wastewater treatments. Although all types of nanoadsorbent exhibited extremely large specific areas and promising adsorption capacity towards heavy metals from wastewater, there are some limitations that need to be addressed for improving their properties to make them more suitable in real wastewater applications. Moreover, the nanoparticles utilized in the waste management process are expected to have an adverse effect towards human and living things. Exposure to the risk of toxicity might be happened in a long-term exploitation due to leaching out of nanoparticles. Yet the risk and the response of nanoparticles towards human health are still unclear because only few reports are available on this matter. Therefore, assessing the risk of the nanomaterials in the environment is necessary to understand the mobility, reactivity persistency and toxicity of the nanomaterials. In addition, the cost analysis on the preparation of nanoadsorbent materials should be addressed before the application in the real wastewater. Therefore, the adsorption capacity of each nanoadsorbent should be considered along with the cost aspect because a good nanoadsorbent not only satisfies the cost aspect but should also provide a competitive adsorption capacity. Besides that, one of the crucial factors to develop a cost-effective nanoadsorbents is reusability of the nanoadsorbent where good regeneration properties of nanoadsorbents still give a high efficiency of heavy metals removal after recycles for many times.

Further work needs to be done to clarify whether nanocomposite adsorbents have more advantages compared to single use of polymer, carbon-based and metal based nanoadsorbent. Numerous studies have been conducted and developed on fabrication of nanocomposite throughout the world. Thus, the necessary procedure and proper management are important prior to large-scale nanocomposite for water and wastewater treatment. It is very crucial to design the devices that curb the nanomaterials from leached out and can regenerate after a period time of usage. The previous studies on existence of nanoadsorbent regarding the adsorption mechanism might be utilized and applied in the real wastewater effluent from industries related with the heavy metals production. The present and latest nanocomposite systems for wastewater treatment can be improved further by improving and enhancing the effectiveness of the material used as well as the applicability of nanocomposites towards wide range of heavy metals and other pollutants species. Considering all the features stated above, it is very promising that nanocomposite adsorbent can be opted as one of the leading nanotechnologies for various applications especially for heavy metals removal from wastewater.

CONCLUSIONS

Challenges in the global water situation resulting from population growth, climate change, rapid urbanization and industrialization require an innovative water purification technology to overcome water scarcity and meet the demand of drinking water to people. Recent engineering knowledge has led to the recognition of nanotechnology application to sustain and preserve the environment. To date, this work presented a brief review of a wide range of nanoadsorbents had been successfully utilized for heavy metals adsorption from wastewater with excellence and high removal. However, the reports on the nanoadsorbents utilization on the real wastewater are insufficient and highly in need of further investigations on pilot and industrial-scale studies. Thus,

much more investigation is required to show that, the optimization of nanoadsorbents considering the removal capability, reusability, their synthesis, cost and appropriate strategies are required to improve the efficiency and practicability of the nanoadsorbents in real wastewater treatment.

CONFLICT OF INTEREST
The authors declare that there is no conflict of interests, regarding the publication of this manuscript. The authors declare that there is not any conflict of interests regarding the publication of this manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/ or falsification, double publication and/or submission, and redundancy have been completely observed by the authors.

LIFE SCIENCE REPORTING
No life science threat was practiced in this research.

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