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REVIEW

Adsorption and photodegradation of organic contaminants by silver nanoparticles: isotherms, kinetics, and computational analysis

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Abstract In view of the widespread and distribution of several classes and types of organic contaminants, increased efforts are needed to reduce their spread and subsequent environmental contamination. Although several remediation approaches are available, adsorption and photodegradation technologies are presented in this review as one of the best options because of their environmental friendliness, cost-effectiveness, accessibility, less selectivity, and wider scope of applications among others. The bandgap, particle size, surface area, electrical properties, thermal stability, reusability, chemical stability, and other properties of silver nanoparticles (AgNPS) are highlighted to account for their suitability in adsorption and photocatalytic applications, concerning organic contaminants. Literatures have been reviewed on the application of various AgNPS as adsorbent and photocatalyst in the remediation of several classes of organic contaminants. Theories of adsorption have also been outlined while photocatalysis is seen to have adsorption as the initial mechanism. Challenges facing the application of silver nanoparticles have also been highlighted and possible solutions have been presented. However, current information is dominated by applications on dyes and the view of the authors supports the need to strengthen the usefulness of AgNPS in adsorption and photodegradation of more classes of organic contaminants, especially emerging contaminants. We also encourage the simultaneous applications of adsorption and photodegradation to completely convert toxic wastes to harmless forms.

Keywords Environmental pollution · Organic contaminants · Remediation · Adsorption · Photocatalyzed degradation

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Introduction

Organic contaminants have a wider scope of coverage concerning sources of generation, present levels of contamination, current methods of remediation, and future hopes or expectations (Kruć-Fijałkowska et al., 2022). Currently, large anthropogenic and natural sources of organic contaminants have captured a large chunk of all the established contaminants and are often associated with our daily activities (Sosa-Hernández et al., 2021). This implies that over time, their aggressive impact may progress to a chronic stage. Based on the high toxicities and the future risk associated with ongoing and increasing levels of contamination, the best option is to apply remediation technology to abate the consequences of organic contaminants in water (Melo et al., 2022). To achieve this aim, a fundamental baseline must be established such as knowledge of the different methods, identification of the best or most suitable approach, economic and energy costs, availability of required raw materials or technologies, and environmental consequences of the various methods (Jesus et al., 2022; Melo et al., 2022; Ocheje Ameh et al., 2020).

Nanomaterials are generally defined as those materials that have at least one-dimensional component with a particle size, not exceeding 100 nm (Eddy et al., 2023b). These materials are known for their wider scope of industrial, agricultural, and other applications (El-Ramady et al., 2023; Mondal et al., 2023a, b). Their respective roles in various sectors are based on fundamental properties that are hardly met by other materials, such as larger surface area, high porosity, high surface area to volume ratio, low particle size, high stability, unique optical properties, and unique mechanical and electrical properties (Gandhi et al., 2021; Khan et al., 2019). Nanoparticles can broadly be classified based on several principles. For example, a consideration of their porosity and pore size fits into the differentiation of nanomaterials as microporous (for particle size range between 1 and 2 nm), mesoporous (with particle size ranging from > 2 to 50 nm), and macroporous nanomaterials (with particle size > 50 nm) (Eddy et al., 2023a). Nanoparticles can also be classified as metal-based and non-metal based. For example, graphene oxide nanoparticles (Nasrollahzadeh et al., 2021), carbon nanotubes (Júlio et al., 2022), and silicon oxide nanoparticles (Book & Backhaus, 2022) are examples of non-metal nanoparticles whereas calcium oxide nanoparticles (Garg et al., 2022a, b), magnesium oxide nanoparticles (Borgohain et al., 2020), and zinc oxide nanoparticles (Garg et al., 2022a, b) are examples of metal oxide nanoparticles.

Metal nanoparticles are nanoparticles that contain one element, individual atoms, or multiple atoms in their zero valent state. Examples of metals that can form nanoparticles without combining with other elements are silver (Torbina et al., 2018), gold (Yallappa et al., 2015), copper (Kaur et al., 2016), and platinum nanoparticles (Gama-Lara et al., 2018). Among the various classes of nanoparticles or composites, metal nanoparticles form an exceptional and interesting class of nanomaterials because only very few metals have the capacity to retain their identity in this state. This is because most metals are only stable in a combined state (Jayeoye et al., 2021). Consequently, noble metals are the only class of metals that can form such nanoparticles (Rajni Garg et al., 2021). Detailed reviews or studies of their synthesis, characterization, and application can provide some information about their chemistry and applications. Hence, the present review is centered on the investigation of the properties of silver nanoparticles, concerning their applications in adsorption and photocatalyzed degradation of organic contaminants. The review becomes necessary because of the high and unimpressive impacts of organic contaminants (in aquatic systems) at alarming levels. Consequently, the need to employ useful technology in reducing their concentrations in the environment is of significant research interest. Therefore, the study also seeks to review knowledge on adsorption and photocatalytic removal of organic contaminants from water, considering the methods as among the best-known technologies. In addition, quantum chemical studies can be used to explain the process of photodegradation using the adsorption locator model such that information obtained can serve as a predictor for contaminants that can easily be processed by adsorption and photodegradation.

Harmful impacts of organic contaminants in water

A contaminant generally refers to all forms of materials that can cause adverse impacts on the environment when present in a concentration that is no longer beneficial to man and other components of the environment (Golmohammadi et al., 2023). Organic compounds that can act as contaminants are called organic contaminants while others that are not organic are inorganic contaminants (Warren-Vega et al., 2023). According to Mandal et al. (2016), organic contaminants include pesticides and herbicides, as well as plant and animal tissues, which are known as significant causative agents for adverse impacts in the environment. Figure 1 reveals that contaminants can be generally classified as physical, biological, organic, and inorganic. However, the classes of organic contaminants, emerging and non-emerging contaminants, can be identified (Odoemelam et al., 2023).

Beyond the presented classes, there are severe forms of organic contaminants that can be treated specially (Pandey et al., 2023). For example, emerging organic contaminants cover synthetic chemicals, whose tendency towards human and ecological health has been confirmed (Rai & Shrivastav, 2021). Emerging organic contaminants may come from different sources such as personal care products, drugs, fire, endocrine-disrupting chemicals, surfactants, solvents, pharmaceuticals, and various types of agrochemicals such as soil stimulants, growth regulators, and pesticides (García et al., 2020). Overwhelming literature has been reviewed on the negative impact of organic pollutants, some of which are summarized in Table 1 along with sources of the different classes of organic contaminants.

It is evident from the above presentation that the sources depend on the identity of the contaminant; economic, domestic, and industrial activities within a given area; and natural resource distribution (such as availability of rivers, soil type, mineral deposit) (Sankar et al., 2023).

The impacts of organic contaminants in the environment depend on several factors such as (i) the identity and reactivity of the contaminants, (ii) the medium of existent, (iii) environmental identity, (iv) concentrations of the contaminants, and (v) atmospheric conditions (Khalid & Abdollahi, 2021). One general impact of organic contaminants in the water is eutrophication, which arises from a high level of concentration of nutrients such as phosphate and

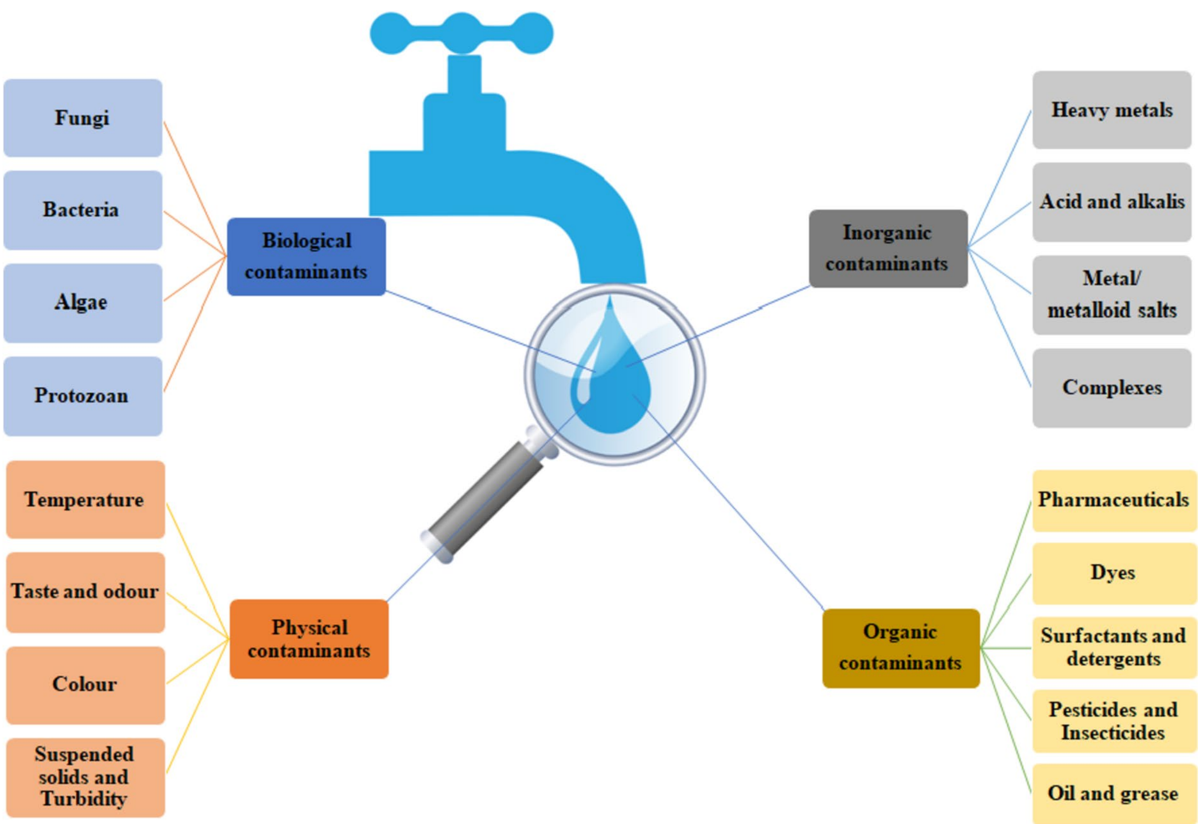

Fig. 1 Flow sheet showing major contaminants in the environment

Table 1 Some organic contaminants and their sources

Organic contaminants	Source	Examples	References
Bisphenols	Personal care products (soaps, detergents, shampoos, conditioners, shaving creams, nail polishes, lotions, and sunscreens)	Bisphenol A, B, F, AF, and S	(Khalid & Abdollahi, 2021)
Pesticides	Agriculture/horticultural practices, surface runoff, industrial effluent, fishing, etc	Dichloro diamine tetraacetic acid (DDT), garmalin, etc	(Koech et al., 2023)
Dye	Discharge of textile, paint, leather, shoe, and other dye-containing industrial wastes	Crystal violet, methylene blue, methyl orange, etc	(Ocheje Ameh et al., 2020)
Antibiotics	Hospital wastes, effluent from pharmaceutical industries	Tetracycline, ciprofloxacin, etc	(Sosa-Hernández et al., 2021)
Nutrients (P, N, etc.)	Agricultural wastes, fertilizer industrial waste, domestic wastes, etc	Biodegradable plants and animal remains	(Bijay-Singh, & Craswell, 2021)
PAHs	Petroleum industrial wastes, bitumen seepage water, coal, wood, etc	Anthracene, chrysene, pyrene, etc	(Sankar et al., 2023)

nitrates (Sosa-Hernández et al., 2021). The consequence is the flourishing of algal blooms including macrophytes and phytoplankton (Akinnawo, 2023). The consequence is excessive utilization of the dissolved oxygen in the water for the biochemical functioning of the algal blooms and subsequent depletion of available oxygen for other biological organisms (Kumar et al., 2019a, b).

As a result, the CO_2 concentration in the water will increase through the decomposition of the algae and the water becomes more acidic because of the dissolved CO_2 (Eq. (1)) (Sun et al., 2022):

$$H_2O + CO_2 \rightarrow H_2CO_3 \quad (1)$$

The lowering of the pH of seawater due to eutrophication is called ocean acidification and the consequences include the termination of aquatic life and a serious decline in aquatic productivity in addition to other chain reactions within the aquatic system, ranging from those producing adverse conditions to those generating toxic products, against public and environmental health (Shahady, 2022). Several scholars have confirmed that the deoxygenation of water is a major consequence of organic pollutants and the process can significantly increase microbial activity, enhanced production of ammonia and other mineral nutrients in the water (Xiao-e et al., 2004). Under this condition, the survival of invertebrates, fish, oxygen-sensitive insects (such as caddis flies, beetles, stone flies, and mayflies) and other aquatic organism cannot be guaranteed (Vagi et al., 2021). Many concerns have been received concerning the presence of polychlorinated biphenyls (PCBs) in water because of their high levels of confirmed toxicity (Cui et al., 2020; Cybulski et al., 2022; Wang et al., 2023). Montano et al. (2022) and Szczęsna et al. (2023) have listed some toxic impacts of PCBs including dementia, neuropsychological and neurobehavioral deficits, malfunctioning of the endocrine, cancer, cardiovascular diseases, and malfunctioning of the immune system. Also, other studies have linked infertility as a possible impact of PCB toxicity (Ermler & Kortenkamp, 2022; Neblett et al., 2020; Shirafkan et al., 2023).

Pesticide residues of different classes have been identified in several water bodies and their impacts have been extensively reviewed (Ajiboye et al., 2020; Ganaie et al., 2023; Huang et al., 2023; Nantongo et al., 2023). A review of studies conducted by El-Nahhal and El-Nahhal (2021) led to the conclusion that over 113 different types of pesticide residues were found in drinking water from 31 countries. Sources of pesticide residue in the water bodies have been reported to include leaching from agricultural soil, direct application in fishing, and other activities that use pesticides. Kruć-Fijałkowska et al. (2022) reported that pesticide residue in water can lead to cancer and neurological and reproductive-associated disorders. Other reported hazards of pesticides are the malfunctioning of the congenital system, blood dyscrasias, headache, salivation, nausea, diarrhea, wheezing, asthma, coma, and death (at acute and chronic stages) (Syafrudin et al., 2021). The presence of pesticides in water has severe consequences on the physicochemical quality of the water and can impact skin infection (through dermal contact) and direct impacts on non-target aquatic organisms (Abbassy et al., 2021).

Another set of emerging organic contaminants with severe environmental consequences is dyes (Khaliha et al., 2023; Pandey et al., 2023). Dyes can affect the color of water and subsequently reduce light penetration and can lead to a decrease in the primary productivity in the aquatic system because of low photosynthesis (Eddy et al., 2023b). Some toxic heavy metals present in water can form stable complexes with dye which can result in the enhancement of biomagnification of their toxicity, even along the food chain (Meghwal et al., 2020). A review conducted by Al-Tohamy et al. (2022) listed additional environmental consequences of toxic dyes including an increase in chemical (COD) and biochemical (BOD) oxygen demands of the water, inhibition of plant growth, increased levels of toxicity, mutagenicity, and carcinogenicity. Sources of dye contamination are numerous, some of which are listed in Table 1. Consequently, dye contamination arises from sources (such as industries, laboratories, or homes) that use one or more forms of dyes for their production, decoration, etc. (Ocheje Ameh et al., 2020).

Hydrocarbon contamination of water has received intense research concerns over the years because of the danger associated with such contamination (Srivastava et al., 2019). Apart from pesticide residues highlighted before, several other sources of hydrocarbons may include oil spillage, fossil fuels, organic pollutants, bitumen, and petroleum processing (Afzal et al., 2019; Daniel, 2021; Kponee et al., 2015; Ossai et al., 2020). In the water body, hydrocarbon contamination can impair the level of light penetration and can subsequently reduce the productivity of the aquatic system through their roles in the reduction of photosynthesis. Symptoms of hydrocarbon contamination in humans have been listed to include, headaches, fatigue, dizziness, impairment of the immune system, hematopoietic system disorderliness, decrease in blood cell count (white blood cells), and other symptoms (D'Ugo et al., 2021). Among the hydrocarbons, worse environmental consequences have been reported for polyaromatic hydrocarbons (PAHs) (Baali & Yahyaoui, 2020; Patel et al., 2020). Some impacts of hydrocarbon contamination of water include abnormality of the embryo, pulmonary disorder, immunotoxicity, gastrointestinal disorder, renal and dermatologic malfunctioning, cardiotoxicity, and carcinogenicity (Abdel-Shafy & Mansour, 2016; Jesus et al., 2022; Melo et al., 2022). Some reported PAHs in water are benzo(a)pyrene, fluoranthene, phenanthrene, pyrene, anthracene, acenaphthylene, acenaphthene, chrysene, benz[a]anthracene, etc. (Adeniji et al., 2019; Fouad et al., 2022; Muratova & Turkovskaya, 2022). The chemical structures of the listed polyaromatic hydrocarbons (PAHs) are shown in Fig. 2. The figures reveal two-, three-, and four-ring PAHs. From the chemical point of view, the toxicity of PAHs will depend on the aromaticity of the compounds, resident time, resident environment, weather conditions, and generating source as well as the reactivity of the compound. The significant impact of PAHs is their persistent and carcinogenic nature (Sankar et al., 2023).

Antibiotics are another class of emerging organic contaminants that are associated with synthesized drugs and other pharmaceuticals (Yang et al., 2021). Some toxic effects of antibiotics extend beyond the non-target organisms and may involve the termination of aquatic species and the consequence impact on man, increase in the number of antibiotic resistance microorganisms, etc. (Kovalakova et al., 2020; Zhang et al., 2022).

Challenges associated with organic contaminants

In Table 2, we present various remediation methods that have been successfully used in the removal of organic contaminants from water and their major challenges. The presented information summarizes that the listed methods have their advantages and disadvantages indicating that the most preferred methods should be those whose advantages are much more beneficial and also have the potential to outrange known disadvantages concerning performance (Zelinski et al., 2023). It is worth highlighting that the biological treatment method is not highlighted in Table 2. Biological treatment methods have been successfully used in the removal of nutrients such

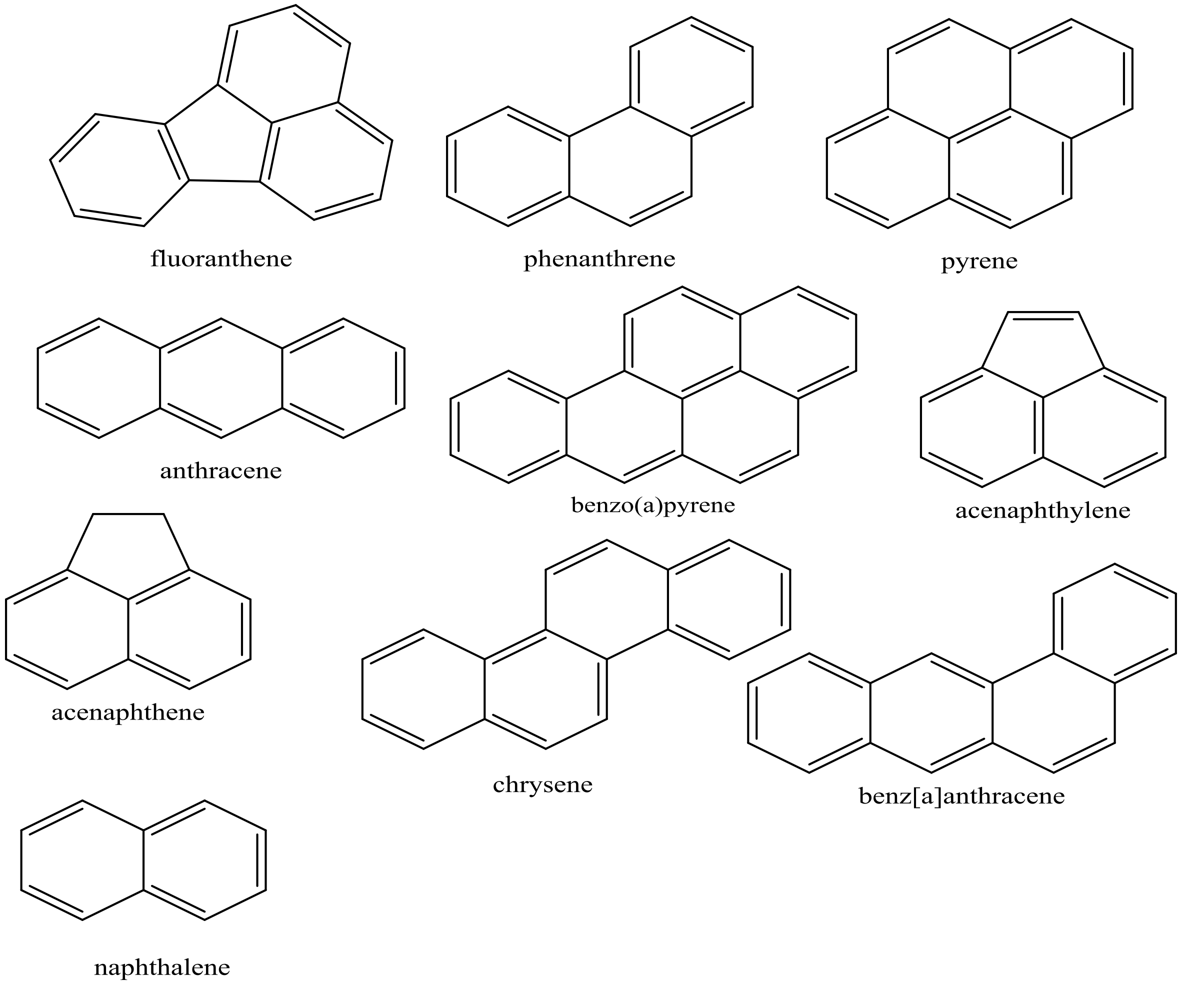

Fig. 2 Chemical structures of some common PAHs in water

as phosphate and nitrate (Oyewo et al., 2018). The three major stages in biological treatment methods are aerobic, anaerobic, and anoxic stages. The aerobic method has major disadvantages such as high energy requirements for the consumption of aeration and a cooling system, which makes the process very expensive and unrealizable when compared with other methods (Karpińska & Kotowska, 2019). Also, the anoxic stage cannot be operative in the absence of oxygen while the aerobic treatment needs no oxygen (Mateos et al., 2001). Several issues can be advanced to support the need to review the application of biological treatment methods as an ineffective approach under stressed conditions based on the consequences including (i) frequent need to vary the temperature in each state, (ii) unpredictable performance with reduced efficiency, and (iii) conversion of a reasonable amount of the COD to sludge, which may require an extra cost in managing the post-waste generated (Meghwal et al., 2020).

Biodegradation has also been seen as a method that uses some strain of microorganisms or plant materials to degrade organic waste (Zheng et al., 2013). Consequently, this method cannot be regarded as an all-around approach because the product of biodegradation, if not properly managed, can constitute a factor for secondary pollution, with a worse degree of impact compared to the original contaminants especially when interaction leads to the formation of new toxic compounds (Saleh et al., 2020).

Table 2 Literature on some remediation measures for organic contaminants, examples, and setbacks

Remediation method	Principles	Examples of contaminants	Challenges	References
Electrokinetic	Principles of electromigration and electrodiffusion	Charged particles such as metal contaminants	(i) May not be very useful for uncharged or non-ionic particles (ii) Most suitable in the soil environment (iii) May be time-consuming (iv) Change in acidity can slow down the process	(Cameselle et al., 2013)
Thermal	Steam injection and electrical resistance heating to enhance the removal of volatile and semi-volatile organic contaminants	PAHs, hydrocarbons, organic chemicals like phenol and alcohol	(i) Expensive (ii) Not easily accessible (iii) May affect the final quality of the water	(Du et al., 2014)
Reverse osmosis	Applies atomic filtration to remove organic contaminants	Emerging contaminants, nutrients, pharmaceuticals, dyes	(i) May be selective (ii) Not easily accessible (iii) Post-contamination may be difficult to manage (iv) Not suitable for organic molecules of high molecular mass and most undissolved contaminants	(Rai & Shrivastav, 2021; Zelinski et al., 2023; Zhang et al., 2023)
Non-thermal plasma discharge	Generate reactive species to degrade re-calcitrant organic contaminants	Pharmaceutical, pesticides and dyes	(i) May be selective (ii) May not be cost-effective	(Kyere-Yeboah et al., 2023)
Electrochemical advanced oxidation process: photocatalysis	Applied externally biased to an insulator to retard possible re-combination of photogenerated hole and electron	Pharmaceutical, pesticides and dyes	(i) Requires electric power (ii) May not apply to all classes of contaminants	(Alulema-Pullupaxi et al., 2021)
Photocatalysis	Employ energy of photons to cause degradation of organic contaminants to less toxic forms	Pharmaceutical, pesticides, and dyes	(i) May increase COD of the water (ii) May alter the acidity of the water (iii) Possible catalytic poisoning	(Saeed et al., 2023)
Adsorption	Separation of contaminants by removal from solution to the surface of the adsorbent	Hydrocarbons, pharmaceuticals, toxic chemicals, pesticides, dyes, pharmaceuticals	(i) May be selective (ii) Adsorbent may not easily be regenerated (ii) Success depends on some ranges concerning physicochemical parameters (iii) There may be challenges in disposing of the adsorbed contaminants (i.e., the adsorbate)	(Ajala et al., 2023; Bouafia et al., 2023; Emmanuel Awe et al., 2021; Odoemelam et al., 2018; Ogoko et al., 2023; Yousef et al., 2023)

Table 2 (continued)

Remediation method	Principles	Examples of contaminants	Challenges	References
Ion exchange	Exchange of ions associated with the contaminants with other ions	Ammonia, natural organic matter	(i) May not be useful for undissolved organic contaminants (ii) Regeneration may be expensive	(Jorgensen & Weatherley, 2003; Levchuk et al., 2018)
Ultrafiltration	Applied hydrostatic pressure forces the water to pass through the ultrafilter membrane while suspended particles do not pass through	Microorganic contaminants, pathogens, solid waste	(i) Selective and sensitive to materials (ii) Tendency to create fouling (iii) Soluble components may not be removed (iv) Not too sensitive for the removal of various types of organic contaminants except the membrane is made hydrophobic	(Kammakakam & Lai, 2023; Kotp, 2019; Saleh et al., 2020)
Microfiltration	Same as ultrafiltration but membrane pore size ranges from 0.05 to 10 μm and the operating pressure is less than 2 bar	Hyptospondium and giardia cyst bacteria, yeast cells, colloids, and smoke particles	(i) Not suitable with contaminants with sizes below the range (ii) Suitable for contaminants with molecular weight less than 400 kDa	(Cevallos-Mendoza et al., 2022)

Adsorption and photodegradation technologies using silver nanoparticles

A consideration of all the water treatment methods presented in the above review indicates that there is no method without advantages and disadvantages (Batool et al., 2022a, b). Therefore, a compromise in arriving at good results must be considered based on some factors, including (i) availability and accessibility of raw materials, (ii) types of organic contaminants to be removed, (iii) post-treatment consequences and associated cost of management, (iv) complexities of the technology, (v) eco-friendliness of the technology, (vi) economic cost, (vii) efficiency of the method, and (viii) technological requirement and availability (Gowda et al., 2022; Tran et al., 2022). Several researchers have agreed that adsorption is one of the best technologies but the management of the post-treatment consequences is the major challenge (Abbasi et al., 2014; Prabhahar et al., 2022). Photocatalysis is also a commended method because it degrades the toxic compound to non-toxic products but with the major disadvantages of (i) increasing the acidity of the water and (ii) decreasing the COD and BOD of the water (Thirumagal & Jeyakumari, 2020). It is the view of the authors that the listed setbacks aligned to adsorption and photocatalysis can be easily resolved compared to other methods (Eddy et al., 2023b; Saruchi et al., 2023). Consequently, the two methods have additional advantages because they are less selective and can be applied to almost all types of organic contaminants provided a suitable adsorbent/photocatalyst and operation conditions are selected (Yasmin et al., 2020). In addition, the methods are less expensive and do not require sophisticated technologies. Also, they can be managed in an environmentally friendly manner and a high percentage of treatment efficiencies are feasible under optimum conditions (Eddy et al., 2023a).

Silver nanoparticles (Ag-NPS) are one of the advanced classes of materials that have been documented to have excellent potential as good adsorbents and photocatalysts (Aravind et al., 2021; Yari et al., 2023a, b). Researchers have documented excellent properties of Ag-NPS as an adsorbent for the removal of contaminants (Azeez et al., 2018; Ezeuko et al., 2022). The particles of the AgNPS can easily be varied by choice of synthetic methods and precursor (Zheng et al., 2013). They have a large surface area and a high tendency to adsorb. They have a significant affinity to adsorb both positively and negatively charged contaminants (Gowda et al., 2022). They have a high degree of thermal stability that makes them suitable for high-temperature adsorption (Ezeuko et al., 2022) as well as a high degree of stability in different chemical environments that enables them not to be easily poisoned, nor constitute a toxicant at ease. They can easily be re-useable (Garg et al., 2021) and have high antimicrobial properties (Nassar et al., 2023). Also, the suitability of AgNPS as a photocatalyst is due to various unique advantages which include a high sensitivity to even visible light (Jaast & Grewal, 2021), stability within a wider range of operational temperatures and chemical environments (Muraro et al., 2020), a high tendency for reused (Ahmed et al., 2022), low bandgap (Kayed et al., 2023), electrical resistance (Islam et al., 2021), and surface plasmon resonance (Naseem et al., 2020).

AgNPS in adsorption studies

Adsorption removal of organic contaminants of different classes by AgNPS synthesized from different methods has been successfully carried out in several quarters. Two approaches to adsorption have been widely reported including (i) batch adsorption (Azeez et al., 2018) and (ii) column adsorption methods (Palani et al., 2023; Raj & Krishnan, 2023; Sundhararasu et al., 2022). Generally, most literature on the adsorption of an organic contaminant favors the batch adsorption method over the column method because the former may be time-consuming and require more expensive technology (Trinh et al., 2020a, b, c). Adsorption can be regarded as a separation method that involves the movement of contaminants (adsorbates) from the solution to a surface (adsorbent) that allows them to be held either by electrostatic or by chemical bond (Sujata Mandal et al., 2023). Results from batch adsorption study can be presented in two major forms which are (i) in terms of the equilibrium amount of contaminants removed, Q_e, or (ii) percentage concentration of contaminants removed (Trinh et al., 2020a, b, c). The expressions for the two functions are shown in Eqs. (2) and (3) respectively (Garg et al., 2022a, b):

$$Q_e(mg/g) = \frac{\left(C_{initial} - C_{final}\right) * V}{m} \quad (2)$$

$$\%\text{Removal} = \frac{\left(C_{initial} - C_{final}\right) * 100}{C_{initial}} \quad (3)$$

The initial concentration of the contaminants (C_{initial}) represents concentrations before adsorption while the final concentration denotes the concentration after adsorption (C_{final}). Therefore, once the method of analyzing the concentration of the contaminants is known, adsorption studies can be successfully implemented (Yari et al., 2023a, b). The concentration of most contaminants such as dyes can be easily determined by spectrophotometric methods, which involves the determination of measurement of absorbance of the contaminants at the wavelength of maximum adsorption (Odoemelam et al., 2023). There is success in the determination of the concentrations of most antibiotics, phenol, etc. (Ezeuko et al., 2022). However, gas chromatography–mass spectrometer (GCMS) or HPLC is most efficient in analyzing aromatic compounds such as PAHS (Wang et al., 2019). However, the cost of analysis using GCMS is more expensive than the spectrophotometry methods because (i) GCMS may require a standard whereas the spectrophotometric method can use literature maximum wavelength of absorption; (ii) sample preparation before GCMS analysis is more elaborate whereas in spectrophotometry method, the sam environmental samples can be used. Therefore, UV–visible spectrophotometric methods are most recommended when it is useful for a given organic contaminant (Vicente-Martínez et al., 2020).

The column experiment has a significant contribution to the analysis of adsorption data. The theory behind the column experiment can be analyzed through the break-through curve, which is defined as the plot of C_0/C_t against the volume of effluent or time for a given bed height. The effluent volume (V_{eff}) can be defined as the product of the total flow rate (min) and the volumetric flow rate (ml/min). The integration of a plot of the concentration of the adsorbed specie versus time gives results for the area under the breakthrough curve. The area is a reference results for the calculation of (i) the total quantity of metal adsorbed and (ii) the maximum column capacity.

Adsorption models

Kinetic model

In the adsorption process, the basic set of models includes the kinetic, isotherm, thermodynamics, and column models. A classical form of the pseudo-first-order kinetic can be expressed as Eq. (4) while its linear form is Eq. (5) (Odoemelam et al., 2018).

$$Q_t = Q_e(1 - e^{-k_1 t}) \quad (4)$$

$$\ln(Q_t - Q_e) = \ln Q_e + k_1 t \quad (5)$$

In the above equation, the kinetic rate constant of the pseudo-first-order adsorption is represented by k_1(in min^{-1}). A conformation of the fitness of a pseudo-first-order model requires high R^2 values and low error values for a linear plot of $\ln(Q_t - Q_e)$ against time (t) *j*. Also, the pseudo-second-order model can be represented by Eq. (6) while the linear form takes the form shown in Eq. (7) (Odoemelam et al., 2023).

$$Q_t\left(1 + k_2 Q_e t\right) = k_2 Q_e^2 t \quad (6)$$

$$\frac{t}{Q_e} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \quad (7)$$

Based on Eq. (7), a linear graph is expected when values of $\frac{t}{Q_e}$ versus t are plotted. Consequently, Q_e can be obtained from the slope while k_2 can be obtained from the intercept. Some literatures have ascribed the adsorption process that fits the pseudo-second-order model as an indication of the chemisorption mechanism. Another model that can be useful for the description of the chemisorption mechanism of an adsorption process is the Elovich model (Eq. (8)) (Shikuku & Mishra 2021b).

$$Q_t = \frac{1}{\beta}\ln(\beta\alpha) + \frac{1}{\beta}\ln(t) \quad (8)$$

where β (unit = g/mg) and α (unit = mg/g • min) are Elovich constants, denoting the capacity and the adsorption rate respectively. The adsorption of contaminants can be described by the Elovich kinetic when a linear plot Q_t against $\ln(t)$ gives a significant R^2 value.

The Weber Moris (W-M) intraparticle model (Eq. (9)) is also appropriate for the description of the extent of the involvement of diffusion in the adsorption process.

$$Q_t = k_{\text{intra}} t^{\frac{1}{2}} + C_{\text{int}} \tag{9}$$

where k_{inta} is the W-M intraparticle diffusion constant. The plot of Q_t versus $t^{\frac{1}{2}}$ (should be linear with slope and intercept equal to k_{intra} and C_{int} respectively. A perfect confirmation of diffusion as the rate-determining step requires an R^2 value equal to unity and a zero intercept. However, the failure or partial fulfillment of the intraparticle diffusion as a rate-determining step suggests that liquid film diffusion has some contributions. The liquid film diffusion model can be written according to Eq. (10).

$$-\ln\left(1 - \frac{Q_t}{Q_e}\right) = k_{L-F} t + C_{L-F} \tag{10}$$

The model becomes more significant when the intercept is zero; the adsorption kinetics would be controlled by intraparticle diffusion and liquid film diffusion.

Adsorption isotherm

Adsorption isotherms can provide information on the characteristics of the adsorption, surface properties, and the behavior of the adsorbent/adsorbate as well as the mechanism of adsorption. Commonly known adsorption isotherms are the Langmuir isotherm (Eq. (11)), Freundlich isotherm (Eq. (12)), Temkin isotherm (Eq. (13)), Dubinin-Radushkevish isotherm (Eq. (14)), Frumkin isotherm (Eq. (15)), Flory–Huggins isotherm (Eq. (16)), Redlich-Peterson isotherm (Eq. (17)), and the Sips isotherm (Eq. (18)) (Amrutha et al., 2023; Garg et al., 2022a, b; Kalam et al., 2021; Yari et al., 2023a, b). The symbols contained in the listed isotherms are k representing the respective equilibrium constant of adsorption, C_e is the equilibrium concentration of the adsorbate, Q_e is the equilibrium adsorption capacity, R is the gas constant, T is the temperature, n is the Freundlich or Frumkin constants, and α in the Frumkin isotherm is the interaction parameter but in the Redlish-Peterson (RP) isotherm, both α and β are the RP constants. B_T and K_T are Temkin constants.

$$\frac{1}{Q_e} = \frac{1}{Q_{\text{Lang}}} + \frac{1}{Q_{\text{Lang}} k_{\text{Lang}} C_e} \tag{11}$$

$$\ln(Q_e) = \ln K_F + \frac{1}{n}\ln(C_e) \tag{12}$$

$$Q_e = \frac{RT}{b_T}\ln(K_T) + \frac{RT}{b_T}\ln(C_e) \tag{13}$$

$$\ln(Q_e) = \ln Q_m - K_{D-R}\varepsilon^2 \tag{14}$$

$$\ln\left(\frac{\theta}{C(1-\theta)}\right) = \log k_{\text{Frumk}} + 2\theta\alpha \tag{15}$$

$$\ln\left(\frac{\theta}{C}\right) = \ln k_{\text{FH}} + n\ln(1-\theta) \tag{16}$$

$$\ln\left(k_{R-P}\frac{C_e}{Q_e}\right) = \beta \ln C_e + \ln a_R \tag{17}$$

$$Q_e = \frac{Q_{m(\text{Sip})} k_{\text{Sip}} C_e^{1/n_{\text{Sip}}}}{1 + k_{\text{Sip}} C_e^{1/n_{\text{Sip}}}} \tag{18}$$

The Langmuir isotherm, as a favorable model, can be assessed through the calculation of the separation factor (R_L) defined ((Jabar et al., 2020) as

$$R_L = \frac{1}{1 + k_{\text{Lang}} C_e} \tag{19}$$

R_L values between 0 and 1 describe favorable adsorption. Linear adsorption is defined by $R_L = 1$ while $R_L = 0$ interprets an irreversible adsorption but R_L greater than unity is for unfavorable adsorption. The Freundlich adsorption constants (i.e., K_F and n) have their respective significance. For example, K_F describes the adsorption capacity, while n is the surface heterogenous index that describes the extent of distribution of the adsorbate on the surface of the adsorbent and, hence, the adsorption intensity.

The formal form of the Temkin isotherm is $Q_e = \frac{RT}{b_T}\ln(K_T C_e)$ (Shikuku & Mishra, 2021a, b), with b_T and K_T describing Temkin constants. R is the universal gas constant and T is the temperature. Based on the Temkin isotherm, a chemisorption adsorption mechanism is most probable, (i) if the adsorption constant b_T > 80 kJ/mol and (ii) the adsorption energy ($E_{\text{ads}} = \frac{RT}{b_T}$) is within range of 8 to 16 kJ/mol. The Dubinin-Radushkevich model, Q_m, defines the saturation adsorption capacity (mg/g) while the Polanyi potential is defined as

$\varepsilon = RT\ln\left(1 + \frac{1}{C_e}\right)$. The Dubinin Raduskevich constant (K_{D-R}) is related to the mean adsorption energy, defined as $E_{\text{ads}} = \frac{1}{\sqrt{2K_{D-R}}}$mol. The mean adsorption energy greater than 16 kJ/mol represents chemisorption mechanism and vice versa.

The Flory–Huggins adsorption isotherm is useful in the prediction of the feasibility of the adsorption sites and the number of adsorbate molecules occupying the sites. The isotherm rests on the exponential relationship between the number of molecules adsorbed and the degree of surface coverage. The model can be written as $\frac{\theta}{C_0} = k_{F-H}\ln(1-\theta)^{n_{F-H}}$ with $\theta = 1 - \frac{C_e}{C_0}$, defining the surface coverage; k_{F-H}, the Flory–Huggins constant (L/mg), and n_{F-H}, the number of adsorbate ions on the adsorption sites. The validation of the Flory–Huggins isotherm relies on the plot of $\frac{\theta}{C_0}$ versus $\ln(1-\theta)$ generating a R^2 value that is very close to unity at a minimum error.

The RP isotherm is a three-parameter isotherm and has the original form given as$Q_e = \frac{k_{R-P}C_e}{1+a_{R-P}C_e^{\beta}}$. The model is suitable when a high R^2 value is observed from a plot of $\ln\left(k_{R-P}\frac{C_e}{Q_e}\right)$ versus $\ln C_e$. The RP isotherm is the limiting case of the Langmuir and Freundlich models. Therefore, between the limits of 1 and 0, the isotherm reduces to the Langmuir and Freundlich isotherms respectively.

The Sips isotherm is another form of a three-parameter isotherm. In the Sips equation, n_{Sip} is a heterogeneity parameter, $Q_{m(\text{Sip})}$ is the maximum absorption capacity, while k_{Sip} denotes the Sips adsorption constant. The isotherm can account for the exponential dependence of Q_e on concentration terms (C_e) is a combination of the Langmuir and Freundlich isotherms and is best suited for describing heterogeneous adsorption.

In summary, the following inferences can be made concerning adsorption isotherms:

(i) Any isotherm among the listed linear models (Eqs. (4)–(6)) is obeyed when the values of R^2 are very close to unity and the error parameters such as sum of square and mean square error are very minimal (Yari et al., 2023a, b).

(ii) Adsorption is favorable if the values of the Langmuir separation factor, R_L, lie between zero and 1 or the values of $1/n$ fall within the same range for the Freundlich isotherm (Garg et al., 2022a, b).

(iii) The Temkin isotherm can explain the existence of interaction between the adsorbed species and can also predict chemisorption if the adsorption energy ($b_T\ln(A_T)$ is between 8 and 16 kJ/mol or b_T values higher than 80 kJ/mol and vice versa (Shikuku & Mishra, 2021a, b).

(iv) The standard free energy of adsorption can be evaluated to determine spontaneous or non-spontaneous adsorption through the equilibrium constant values obtained from the adsorption isotherms (Tran et al., 2022). Consequently, the Gibb-Helmoltz equation would be most useful in this case, that is, $\Delta G = -RT\ln K$ (Eddy et al., 2023a).

Thermodynamic considerations

Temperature can affect adsorption and the impact of temperature on adsorption can be resolved based on the following trends".

(i) An increase in adsorption with temperature aligns with the chemisorption mechanism (Trinh et al., 2020a, b, c).

(ii) A decrease in adsorption with temperature suggests a physisorption mechanism (Tarekegn et al., 2021).

(iii) The application of the variation of the adsorption rate constant with temperature can furnish sufficient information on the evaluation of the activation energy (Eq. (20)) or thermodynamic parameters (i.e., Eq. (21)) (Bazan-Wozniak & Pietrzak, 2023):

$$\ln K = \ln A - \frac{E_a}{RT} \tag{20}$$

$$\ln\left(\frac{k}{T}\right) = \frac{R}{N} + \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{21}$$

Column adsorption model

The column experiment has several models, some of which are highlighted below. Each of these models has its break-through and limitations.

The models are useful mainly in the prediction of the kinetics of the adsorption process. Other kinetic models have not been widely utilized in most of the reported studies and reasons for such exclusion have not been reported (Saruchi et al., 2023).

The linear form of the Thomas model for column adsorption can be written as follows (Hanbali et al., 2014):

$$\ln\left\{\left(\frac{C_e}{C_0}\right)-1\right\}=\frac{k_{TH}Q_{max}M}{Q}-k_{TH}C_0t \quad (22)$$

The Thomas model expressed above contains k_{TH} as the Thomas constant (in ml/min/mg) while Q_{max} is the maximum solid phase concentration of the solute (mg/g). The major limitation of the Thomas model is the inability to predict the concentration of the effluent for zero time. Consequently, Yan et al. (2001) modified the Thomas equation to account for this and other deficiencies. Therefore, the Yan equation can be written according to Eq. (23):

$$\ln\left(\frac{C_e}{C_0-C_e}\right)=\frac{k_YC_0}{Q}\ln\left(\frac{Q^2}{k_yQ_{max}m}\right)+\left(\frac{k_YC_0}{Q}\right)\ln t \quad (23)$$

The Yan equation k_Y defines the kinetic rate constant (l/min/mg), Q_{max} is the maximum adsorption capacity (mg/g), and Q for both Thomas and Yan models is the volumetric flow rate (ml/min).

The Young and Nelson model was also developed to handle adsorption rates without reference to the physical properties of the adsorbates that are independent of their characteristics and nature. This makes the model to be relatively limited in the prediction of adsorption characteristics. The linear form of the Yoon and Nelson model can be written according to Eq. (24):

$$\ln\left(\frac{C_e}{C_0-C_e}\right)=k_{YN}t+\tau k_{YN} \quad (24)$$

In the Yoon and Nelson equation shown above, the rate constant (in /min) is represented as k_{YN}, τ is the time required for 50% of the adsorbate breakthrough (min), and t is the breakthrough time in minutes. However, for a single-component system, the determination of the breakthrough curve requires the evaluation of the constants listed in the Yoon-Nelson model.

The Clark model shown in Eq. (25) is concerned with the application of mass transfer principle and the application of the Freundlich isotherm. Consequently, n corresponds to the exponent of the Freundlich isotherm and A and r are Clark constants.

$$\ln\left\{\left(\frac{C_e}{C_0}\right)^{n-1}-1\right\}=\ln A-rt \quad (25)$$

Computational modeling

The application of computational chemistry in the interpretation or prediction of adsorption has recently received intense research commendations (Eddy et al., 2023a). Computational chemistry can be applied in adsorption studies for the calculation of semiempirical parameters, to detect the tendency towards adsorption through the frontier molecular orbital energies, to predict the sites for the adsorption through molecular modeling or simulation, and to estimate the adsorption efficiency for untested molecules through quantitative property activity relationship as well as the analysis of the toxicity or safety of chemical products to the environment (Eddy et al., 2023b).

Computational chemistry can address several problems in adsorption through the following:

(i) Calculation of quantum chemical parameters concerning the adsorbent and the adsorbates
(ii) Calculation of adsorption energy, deformation energy, rigid adsorption energy, etc.
(iii) Prediction of the site for the adsorption of the molecule
(iv) Prediction of theoretical adsorption efficiency for untested molecules
(v) Interpretation of experimental results

Detailed information on the above-listed applications are demonstrated is demonstrated for a selected molecule in the "Quantum chemical studies" section.

Literature review on silver nanoparticles (AgNPS) and adsorption

Literature on the successes of using AgNPS for the adsorption removal of some organic contaminants is presented in Table 3. The presented results confirm that AgNPS can be useful in withdrawing a good percentage of organic contaminants ranging from dyes (Aravind et al., 2021), phenol (Jilani et al., 2022), PAHs(Abbasi et al., 2014), antibiotics (Jassal et al., 2020), and nutrients (Trinh et al., 2020a, b, c). Good efficiencies were observed in all cases, extending above 80%. In most cases, the conditions for the adsorbent removal varied but generally, physicochemical conditions of the operating environments such as pH (Gowda et al., 2022), temperature (Azeez et al., 2018), dosage of adsorbent (Mandal et al., 2023), initial concentration of the contaminants (Vicente-Martínez et al., 2020), and the presence of ionic strength (Eddy et al., 2022a, b) have been reported as the major set of conditions that affects the adsorption removal of most organic contaminants by nanoparticles such as AgNPS (Batool et al., 2022a, b).

The results presented in Table 3 also reveal that most studies on the employment of AgNPS in the adsorption removal of organic contaminants are concentrated on dyes, suggesting that there is a wider research gap that needs to be overcome when considering other organic contaminants (Tam et al., 2022).

A close examination of the results shown in Table 3 reveals that different or similar adsorption efficiency may be observed for AgNPS from the same source when applied to different compounds.

For example, the reported efficiency for acid dye, methyl orange, and rhodamine blue by Yari et al., (2023a, b) was similar even if their molar masses were 604.47, 327.33, and 479 g/mol respectively. The consideration of their chemical structures (Fig. 3) suggests that the adsorption efficiency is supposed to differ for each of the compounds. However, the efficiency was the same for all because the adsorption occurs at different pH (i.e., pH = 3 for acid dye, 8 for methyl orange, and 7.5 for rhodamine blue), even when other conditions were similar. This indicates that pH can have a significant control on adsorption through its impact on the charge of the adsorbent surface.

Abbasi et al. (2014) also observed similar adsorption efficiencies for different PAHS when AgNPS from the same source was used for the adsorption experiments. Therefore, it is strongly evidenced that pH has a significant influence on the adsorption of organic contaminants. The impact of pH can be analyzed through the determination of pH at zero point charge (pHZC), which defines a value, above which the surface of the adsorbent is negatively charged and vice versa. On the other hand, the adsorption results reported by Mavaei et al. (2020) for new fuchsine, methylene blue, erythrosine B, and 4-chlorophenol (chemical structures are shown in Fig. 4) show different values for the adsorption efficiencies when the experiment was performed under similar conditions.

Some literatures have confirmed that adsorption efficiency can vary with molar mass, the presence of heteroatom, pi-bonds, the extent of aromaticity, etc. (Eddy & Ita, 2011). Heteroatom can enhance the adsorption of a chemical species because they can easily form an adsorption center due to the presence of unpaired electrons (Eddy et al., 2018).

Consideration of results obtained for the adsorption of methylene blue by AgNPS with different characters (Table 3) also reveals that their adsorption efficiencies differ, confirming that the characteristics of the AgNPS can also influence the adsorption efficiency (Gowda et al., 2022; Prabhahar et al., 2022). It should be stated that AgNPS prepared from different methods may have different particle sizes, surface area, porosity, and other surface properties. For example, different plant extracts have different phytochemicals that are needed for the reduction of silver salts to AgNPS indicating that the reduction rate and hence the expected performance may not be the same. Also, from the review of adsorption results presented in Table 3, the adsorption of organic contaminants can be influenced by the period of contact between the adsorbate and the adsorbent (Yari et al., 2023a, b), pH of the medium (Batool et al., 2022a, b), the presence of counterions, source of the nanoparticles (method of synthesis) (Gowda et al., 2022), type of the contaminants (Tran et al., 2022), operating temperature (Azeez et al., 2018), and characteristics of the nanoparticles (Saruchi et al., 2023).

Adsorption generally becomes more favorable as the particle size decreases and as the surface area of adsorption increases. This is because the smaller the particle size, the higher the number of adsorption sites that are available and that can easily be activated. Also, a higher surface area corresponds to higher number of adsorption sites and hence the availability of a wider area for the occupation of the contaminants.

In order for adsorption to be effective, sufficient time is required for the diffusion of the adsorbate to the surface of the adsorbent and subsequent adherence of the adsorbate to the surface, either by the

Table 3 Published work on the application of AgNPS for adsorption removal of organic contaminants

Reduction source	Characteristics	Contaminants	Conditions and fitted models	Optimum efficiency	References
Salvinia molesta leaf extract	λ_{max} = 430 nm Q_e = 121 mg/g	Methylene blue	pH = 4, T = 308 K,, Langmuir, Freundlich, pseudo-second order	93%	(Batool et al., 2022a, b)
Urena lobata leaf extract	PD = 20 nm, λ_{max} = 430 nm	Methylene blue	Langmuir, pseudo-first order, chemisorption	88%	(Gowda et al., 2022)
Anisomeles malabarica leaf extract		Methylene blue	Langmuir, Freundlich, Temkin, dosage = 0.1 g/l, pH = 7	98%	(Prabhahar et al., 2022)
Achillea tenuifolia flower extract	Q_e = 112.35 mg/g	Acid dye 18	pH = 3, C = 30 ppm, time = 25 min, dosage = 0.9 g, Langmuir	94%	(Yari et al., 2023a, b)
	Q_e = 90.93 mg/g	Methyl orange	pH = 8, C = 30 ppm, time = 25 min, dosage = 0.9 g, Langmuir		
Cobweb extract	Q_e = 59.85 mg/g, λ_{max} = 436 nm, PHPZC = 7.82	Rhodamine blue	Langmuir, pseudo-second order, C = 50 ppm, pH = 3.4, dosage = 1 g, time = 30 min	94%	(Azeez et al., 2018)
Citrus maxima peel extract	SA = 79.2 m^2/g, PD = 22.4 nm, PHPZC = 6.6, Q_e = 95.5 mg/g	Methylene blue	105 min	95.5%	(Tran et al., 2022)
	Q_e = 63.3 mg/g	Rhodamine blue		63.3%	
	Q_e = 51.5 mg/g	Methyl orange		81.5%	
Tri-sodium nitrate and glucose	PZC = 8.4 λ_{max} = 420 nm	bacteria DNA conveying antibiotic resistance genes	Time = 225 min, Langmuir, Freundlich, pseudo-second order, dosage = 1 molar, pH = 1, C = 13.98 µg/l	99%	(Ezeuko et al., 2022)
Oenothera biennis extract	Q_e = 101.01 mg/g	Amoxicillin	pH = 4, dosage = 0.5 g, time = 30 min, C = 30 ppm	97%	(Lotfollahzadeh et al., 2021)
Sodium borohydride	Q_e = 177.28 mg/g	Phosphorus	Time = 120 min, pH = 6, C = 10 ppm, dosage = 0.23 mg	177.28 mg/g	(Trinh et al., 2020a, b, c)
Ligustrum lucidum extract	λ_{max} = 439 nm	Phenol	pH = 3, C = 10 ppm, dosage = 0.05 g, time = 90 min, Langmuir, pseudo-second order	78%	(Khan et al., 2022)
Gum Katira and polyacrylamide	PD = 6 nm	Methyl red dye	Time = 20 h, C = 10 ppm, pH = 10, pseudo-second order, Langmuir, Freundlich	96%	(Saruchi et al., 2023)
Chitosan and *Hibiscus cannabinus* extract	PD = 3.2 nm	Congo red	pH = 6.0, time = 120 min, T = 333 K, Langmuir and Freundlich, pseudo-second order $\Delta G = -6.32\text{J/mol}, \Delta S = 12.4J/\text{mol}, \Delta H = -22.5\text{kJ/mol}$	84%	(Mandal et al., 2023)
Starch and tea residue extract	SA = 322 m^2/g PV = 0.0032 m^3/g	Phosphate	Time = 150 min, pH = 6.0 Langmuir and Sips, chemisorption, C = 10 ppm	78.50%	(Trinh et al., 2020a, b, c)
Ammonia solution	SA = 116.48 m^2/g	Ibuprofen	Time = 45 min; pH = 7.0; Langmuir, Freundlich, and Temkin isotherms;$\Delta S = 12.4\text{J/mol}, \Delta H = -22.5\text{kJ/mol}$	93%	(Vicente-Martínez et al., 2020)

Table 3 (continued)

Reduction source	Characteristics	Contaminants	Conditions and fitted models	Optimum efficiency	References
Allivum sativum extract	PD = 13 nm, λ_{max} = 400 nm	Phenanthrene, anthracene, and pyrene	C = 0.01 mg/l, pH = 3 to 7, T = 318 K	85%	(Abbasi et al., 2014)

*******SA* surface area, *PA* pore volume, *C* initial concentration of contaminants, *PD* pore diameter

formation of chemical bond (chemical adsorption) or electrostatic force (physical adsorption) or both phenomena. The period of contact can lead to an increase in adsorption, especially for adsorbents that have enough adsorption sites. Adsorption can also decrease with an increase in the period of contact when desorption sets in. This is particularly significant for materials that have fewer adsorption sites, such that after all the adsorption sites have been occupied, further increase in time may lead to desorption. Also, a decrease in adsorption with time can be much more significant when the binding energy between the adsorbate and the adsorbent is ineffective in withholding the adsorbate's molecules for a longer time.

As highlighted before, pH can affect adsorption through its effect on the surface charge of the adsorbate, which is dependent on the pH or point of zero charges (pHZC). Below the pHZC, the surface of the adsorbent would be positively charged and can readily adsorbed negatively charged contaminants, but above the pHZC, the surface of the adsorbent would be negatively charged and will preferably adsorb cation. The pHZC for AgNPS is 8.3 (Dawodu et al., 2019) indicating that AgNPS will be more active for the adsorption of anions between the pH of 0 and 8.3 but for cation above the pH of 8.3. This concept also explains why the adsorption of contaminants by AgNPS can increase or decrease with an increase in pH irrespective of the similarities of properties of the adsorbents (Table 3). For example, malachite green is a cationic dye and was reported by Dawodu et al. (2019) to show a decreasing tendency towards adsorption between the pH of 0 and < 8.3 but higher adsorption above this pH. In the presence of a dopant, the pHZC can be altered. For example, when AgNPS was doped with activated carbon produced from tea residue, the pHZC was observed to be 6.15 and the adsorption of phosphate ions (negatively charged ions) was optimized in the acidic pH.

Adsorption can be affected by temperature. As a rule, for adsorbate that follows the mechanism of physical adsorption, an increase in temperature will lead to a decrease in the degree of adsorption but an increase in temperature will favor the chemisorption mechanism (Eddy et al., 2010). For the observance of physical and chemical adsorption mechanisms for AgNPS, for example, Batool et al., (2022a, b) observed a physical adsorption mechanism for the

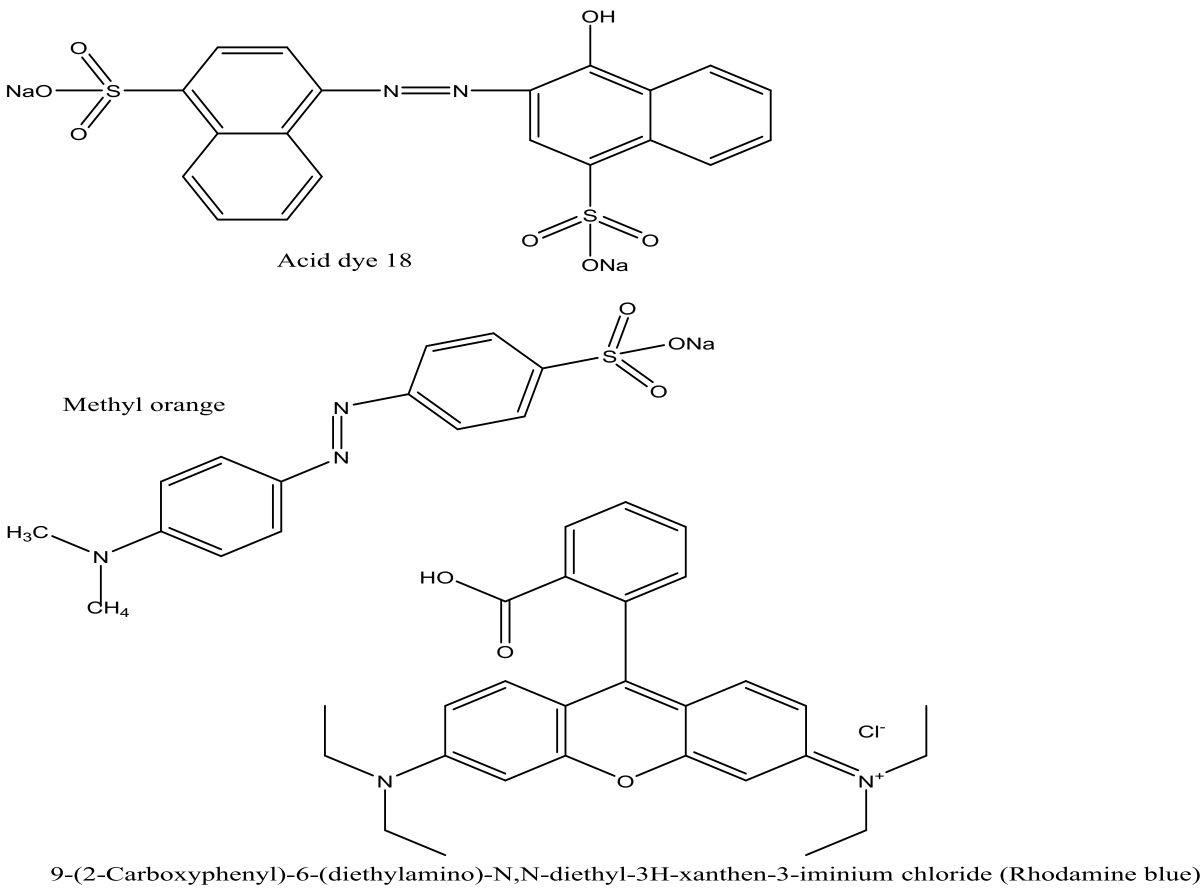

Fig. 3 Chemical structures of acid dye 18, methyl orange, and rhodamine blue dyes

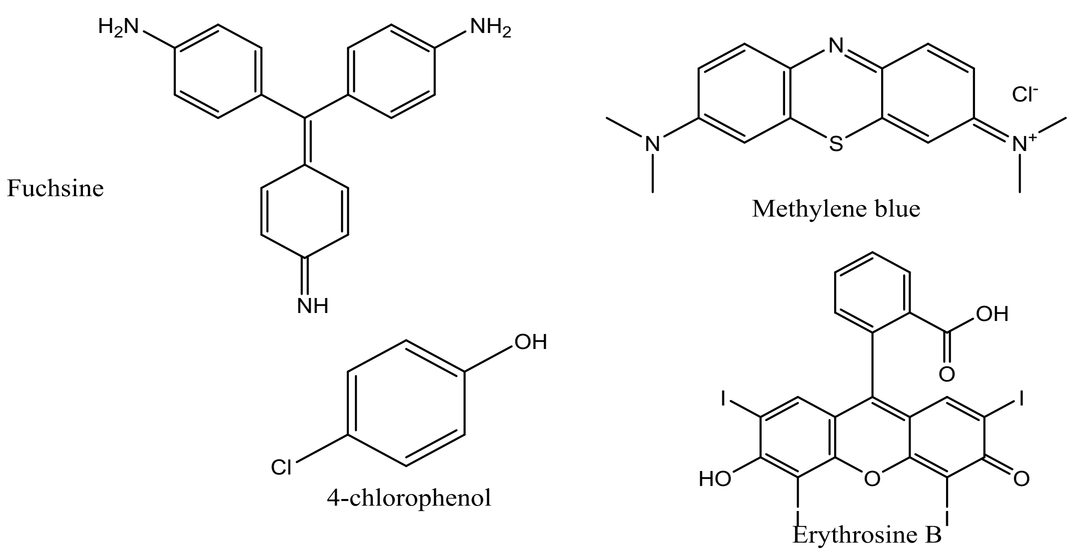

Fig. 4 Chemical structures of fuchsine, methylene blue, erythrosine B, and 4-chlorophenol

adsorption of some dyes while the adsorption of phosphate was reported by Trinh et al.,(2020a, b, c) who observed that the adsorption of phosphate by AgNPS increased with an increase in temperature because the mechanism of adsorption was chemisorption. The presence of some ions can affect adsorption through synergistic or antagonistic interactions. When synergism exists, the adsorption process will increase with an increase in the ionic strength while antagonism will lead to a decrease in adsorption. Such observations have been reported for adsorption processes concerning AgNPS (Yang et al., 2018). The amount of adsorbate molecules approaching the surface of an adsorbent can exert a significant influence that may depend on their concentration. In some cases, adsorption can increase with an increase in concentration when the number of activated adsorption sites is enough to accommodate the molecules and vice versa (Eddy et al., 2023c). Finally, an increase in adsorbent dosage may translate to a corresponding increase in the number of adsorption sites. Therefore, in most cases, the adsorption of contaminants tends to increase with an increase in adsorbent dosages (Kelle et al., 2023).

Arising from the reviewed results (Table 3), most of the listed adsorption kinetics favor the pseudo-second-order kinetic model (Eq. (9)) except methylene blue removal reported by Gowda et al. (2022), which favored pseudo-first-order kinetics (Eqs. (26) and (27)):

$$\frac{t}{Q_t} = \frac{1}{k_2} + \left(\frac{1}{Q_e}\right)t \tag{26}$$

$$\ln\left(Q_e - Q_t\right) = \ln Q_e - k_1 t \tag{27}$$

The results (Table 3) also reveal that the most widely fitted isotherms concerning the listed contaminants are the Langmuir, Freundlich, and Temkin isotherms. However, concerning column experiments, the literature is relatively scanty with AgNPS being considered an adsorbent.

Models for photodegradation

The mechanism of photodegradation involving AgNPS may be simplified to a series of steps associated with the process up to the final degradation (Singh et al., 2019). The initial step involved the adsorption of photons by the AgNPS (Eq. 28) to produce hole and electron in the valence (VB) and conduction bands (CB) respectively, followed by the production of radicals (Eqs. (29) and (30)), oxidation of the organic contaminants through radical attacks (Eqs. (31) and (32)), and lastly by oxygen reduction (Eq. (33)) (Golmohammadi et al., 2023):

$$AgNPS + hv \rightarrow h^{+}{}_{(VB)} + e^{-}{}_{(CB)} \tag{28}$$

$$OH^{-} + e^{-}{}_{(CB)} \rightarrow OH^{*} \tag{29}$$

$$H_2O + h^{+}{}_{(VB)} \rightarrow OH^{*} + H^{+} \tag{30}$$

$$ORG + OH^{*} \rightarrow Intermediate + H_2O \tag{31}$$

$$ORG + h^{+}{}_{(VB)} \rightarrow Degradation\ \text{products} \tag{32}$$

$$O_2 + e^{-}{}_{(CB)} \rightarrow O_2{}^{*} \tag{33}$$

The mechanism of the degradation of organic contaminants can be studied through the interpretation of fragmentation peaks from GCMS analysis (Mir et al., 2014). Also, kinetic models can be applied to interpret results from photodegradation including the following:

1. Langmuir–Hinshelwood mechanism (represented by Eq. (34)) (Naseem et al., 2020)
2. Modified Freundlich model (Eq. (35)) (Eddy et al. (2023a)
3. Zero-, first-, and second-order models (Eqs. (36)–(38)) (Golmohammadi et al., 2023)
4. Parabolic diffusion model (Eq. (39)) (Eddy et al., 2023b)

$$\frac{1}{rate} = \frac{1}{k_{ad}k_p[ORG]_t} + \frac{1}{k_p} \tag{34}$$

$$\frac{[ORG]_0 - [ORG]_t}{[ORG]_0} = kt^y \tag{35}$$

$$[ORG]_t - [ORG]_o = -k_o t \tag{36}$$

$$\ln\left(\frac{[ORG]_t}{[ORG]_o}\right) = -k_1 t \tag{37}$$

$$\frac{1}{[ORG]_t} - \frac{1}{[ORG]_o} = k_2 t \tag{38}$$

$$\frac{1 - \frac{[ORG]_t}{[ORG]_o}}{t} = -k\sqrt{t} + a \tag{39}$$

where $[ORG]_0$ and $[ORG]_t$ are the initial and final concentrations of the organic contaminants in the solution. k is the rate constant in each case and t is time.

Application of AgNPS as photocatalysts

In Table 4, literature on reported works on photodegradation using AgNPs and some composites as catalysts are presented. The presented results indicate that the literature is dominated by the photodegradation of dyes (Thirumagal & Jeyakumari, 2020). An overview of the presented information reveals the following:

(i) Photodegradation catalyzed by AgNPS shows a strong response to the energy bandgap (Khatoon et al., 2018).
(ii) The particle size, surface area, surface area to volume ratio, porosity, bandgap, and other properties of the nanoparticles (Nagar & Devra, 2019).
(iii) The energy bandgap of AgNPS observed in this review seems to show strong dependence on the method of synthesis and the presence of dopant (Tam et al., 2022).
(iv) Doping seems to significantly lower the bandgap of AgNPs in most of the recorded works (Aravind et al., 2021).
(v) Photodegradation also shows strong responses to time, catalyst load, and initial concentration of the organic contaminants (Sunkar et al., 2013).

Quantum chemical studies

Also, in our research group, we have technically applied some computational chemistry tools to explain the photodegradation process through the adsorption locator model (in Materials Studio), Monte-Carlo simulations, Fukui function analysis, frontier molecular orbital analysis, and the prediction of redox or oxidation potential and other models (Eddy et al., 2023a, b; Ogoko et al., 2023). Computational calculations can also be effective in producing information on the photodegradation process through the following:

(i) Calculation of bandgap and theoretical absorption spectrum.
(ii) Calculation of the valence band and conduction band potential using Eqs. (40) and (41) respectively (Eddy et al., 2023b).

$$VB_p = \chi + \frac{1}{2}E_{BG} - E_{e^-} \tag{40}$$

$$CB_p = VP_p - E_{BG} \tag{41}$$

(iii) Calculation of the Fermi level.
(iv) Determination of the mechanism of photodegradation which may include degradation via reduction or oxidation.
(v) Evaluation of the sites for electrophilic, nucleophilic, and radical attacks using Fukui functions presented as Eqs. (23, 24) and (25) respectively.
(vi) Fukui function calculations are based on atomic charges of the neutral (N), cation ($N-1$), and anionic ($N+1$) forms of the respective atoms.

$$f_x^- = q_N - q_{N-1} \tag{42}$$

$$f_x^o = \frac{q_{N+1} - q_{N-1}}{2} \tag{43}$$

$$f_x^+ = q_{N+1} - q_N \tag{44}$$

Technically, the site with the highest positive value of the respective Fukui function is the preferred site for the respective attack. A simple practical analysis of the application of computational methods in the analysis of adsorption and photodegradation of benzene by AgNPS is considered in this section. Benzene is a carcinogenic aromatic compound whose environmental consequences have been widely investigated and reported (Gao et al., 2023). The crystal structure

Table 4 Published work on the application of AgNPS for photocatalytic degradation of organic contaminants

Synthetic method	Characteristics	Contaminants	Reaction parameters	Removal efficiency (%)	References
Trigonella foenum-graecum leaf extract	$\lambda_{max}=428$ nm, PD = 24 nm	Reactive dye 19	Time = 180 min., $C=10$ ml	86	(Singh et al., 2019)
Ocimum sanctum leaf extract	$\lambda_{max}=468$ nm, $E_{BG}=$ 2.88 eV, PD = 13 nm	Reactive orange	40 min, $C=2.5$ µg	62	(Khatoon et al., 2018)
		Reactive blue		73	
		Reactive red		46	
		4-Nitrophenol	$C=50$ mg/l, time = 20 min	100	
Artemisia annua leaf extract	$\lambda_{max}=434$ nm, $E_{BG}=2.86$ eV, PD = 30 nm	Reactive orange	Time = 40 min, $C=2.5$ µg	27	
		Reactive blue		33	
		Reactive red		16	
Phaseolus vulgaris pod extract	$\lambda_{max}=435$ nm, $E_{BG}=2.85$ eV, PD = 30 nm	Mordant black 17	$C=25$ µl, time = 24 h	5	(Sunkar et al., 2013)
		Congo red		55	
Anas platyrhynchos eggshell extract	$\lambda_{max}=430$ nm, $E_{BG}=2.88$ eV, PD = 9 nm	Rose bengal	Dosage = 10 mg, $C=200$ ml, time = 1 h	98	(Sinha & Ahmaruzzaman, 2015)
		Methyl violet 6		98	
		Methylene blue		97	
Disporopsis Longifolia plant extract	$\lambda_{max}=422$ nm, $E_{BG}=2.94$ eV, PD = 14 nm	Methylene blue	Time = 240 min, dosage = 5 mg, $C=100$ ml	100	(Tam et al., 2022)
Crataegus pentagonal fruit extract	$\lambda_{max}=500$ nm, $E_{BG}=2.48$ eV	Methylene blue	Dosage = 30 mg, $C=15$ ml, time = 90 min	78	(Ebrahimzadeh et al., 2020)
Morinda tinctoria leaf extract	$\lambda_{max}=470$ nm, $E_{BG}=2.64$ eV	Methylene blue	Dosage = 10 mg, $C=10$ mg/l	95	(Vanaja et al., 2014)
Jasminum flower extract	$\lambda_{max}=440$ nm, $E_{BG}=2.82$ eV, $D_{cry}=22$ nm	Methylene blue	Dosage = 10 mg, time = 120 min, $C=100$ ml	72	(Aravind et al., 2021)
Cauliflower leaf extract	PD = 35.08 nm, SA = 19.22 m^3/g	Methylene blue	Dosage = 5 mg, time = 150 min, $C=50$ ml, pH = 8.5	95	(Kadam et al., 2020)
Isoimperatorin solution	$\lambda_{max}=439$ nm, $E_{BG}=2.82$ eV	New fuchsine	Time = 60 min	97	(Mavaei et al., 2020)
		Methylene blue		96	
		Erythrosine B		92	
		4-Chlorophenol		95	
Melia azedarach fruit extract and rice husk extract	-	Ciprofloxacin	Time = 180 min, pH = 6.2, $C=0.12$ g	98	(Golmohammadi et al., 2023)
Pleurotus ostreatus fungal mass extract	$\lambda_{max}=435$ nm, $E_{BG}=2.85$ eV, PD = 12.9 nm	Ampicillin	Time = 4 h, $C=10$ ppm, pH = 7.3	97	(Jassal et al., 2020)
Mesua ferrea seed extract	$\lambda_{max}=459$ nm, $E_{BG}=2.7$ eV, PD = 15 nm	Congo red	180 min, $C=100$ mg/l	92	(Thirumagal & Jeyakumari, 2020)
Diospyros lotus leaf extract	$\lambda_{max}=407$ nm, $E_{BG}=3.07$ eV, PD = 27 nm	Industrial wastewater	pH = 6.6, time = 54 h	73	(Yasmin et al., 2020)
Azadirachta indica leaf extract	$\lambda_{max}=433$ nm, $E_{BG}=2.86$ eV, PD = 9 nm, Zeta potential = −22.4 eV	Methyl orange	Time = 40 min, pH = 6.3	88	(Nagar & Devra, 2019)
		Wastewater	Time = 80 min, pH = 6–7	88	

of silver (Fig. 5a) was developed through the employment of Materials Studio software using three steps (namely, cleaving of the cell, building super cell, and crystal slap) and is shown in Fig. 5a while Fig. 5b shows the structure of benzene, which was optimized using Forcite package in the studio of the same

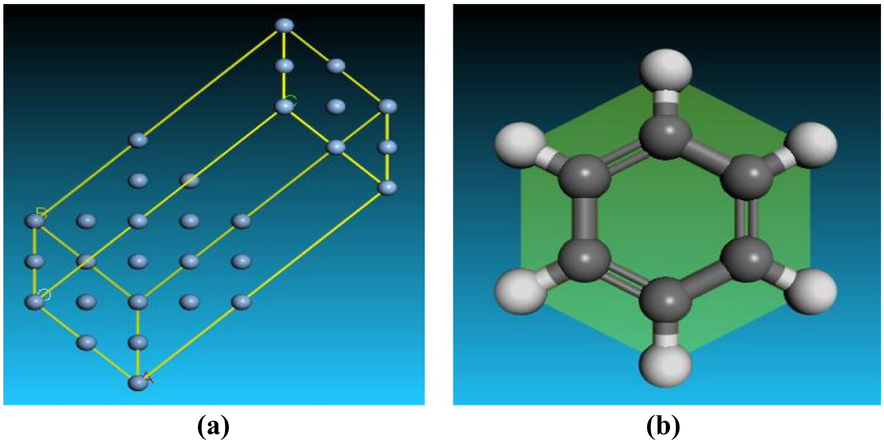

Fig. 5 **a** Crystal structure of AgNPS. **b** Optimized structure of benzene

materials. An optimized structure is the most stable structure of a compound that represents the state with the minimum energy.

The adsorption of benzene on silver can occur through several configurational positions which can be modelled using the Fukui function analysis (Eqs. (25)–(27)). The results of Fukui function calculations for the electrophilic (f_x^-) and nucleophilic (f_x^+) attacks on atoms in benzene are shown in Table 5. The presented data concerning the Fukui function were evaluated using Hirsfeld and Mulliken's charges calculated from the DFT method. The results clearly show that all the carbon atoms in benzene are equally likely concerning electrophilicity because for a given Hirsfeld or Mulliken charge–based Fukui function, the values are the same. A similar observation is seen for nucleophilic Fukui function.

A further probe into the investigation of identifying the atom or group of atoms that will facilitate the adsorption of benzene on AgNPS, a Monte Carlo simulation calculation, was also implemented. Three different conformational positions were observed (Table 6) and the corresponding total energy, adsorption energy, rigid adsorption energy, and deformation energy were computed (Table 6). The evaluated adsorption energies for the three possible conformations are negative, indicating that the adsorption of benzene on the AgNPS surface is spontaneous. However, conformations 1, 2, and 3 (Fig. 6) are associated with adsorption energies equal to −21.48, −20.84, and −13.85 kcal/mol. Therefore, conformation 1 is the most likely conformation that can be advanced to describe the adsorption of relaxed benzene on AgNPS because it requires the least amount of energy. The adsorption of the unrelaxed benzene molecules on the AgNPS also requires the release of the least energy under the same conformation. Therefore, benzene is

Table 5 Hirsfeld and Mulliken charges calculated Fukui Functions for benzene

Atom	Hirsfeld	Mulliken	Hirsfeld	Mulliken	Hirsfeld	Mulliken
C(1) to C(6)	0.057	0.109	0.600	0.106	0.059	0.059
H(7) to H(12)	0.109	0.058	0.107	0.06	0.108	0.108

Table 6 Monte Carlo simulation results showing possible positions for the adsorption of benzene onto AgNPS and associated energies

Conformation	Total energy	Adsorption energy	Rigid adsorption energy	Deformation energy
1	−21.4797	−29.3112	−29.3465	−0.0353
2	−20.8395	−28.6710	−28.6694	−0.0016
3	−13.8530	−21.6845	−21.6457	−0.0388

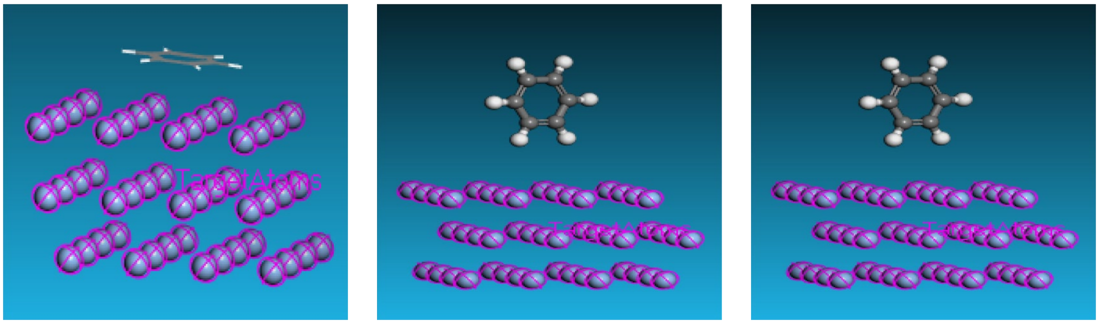

Fig. 6 Three different conformational positions for the adsorption of benzene on the AgNPS surface

believed to lie flat on the surface of the AgNPS as shown by conformation 1, which supports the benzene being adsorbed on a laying down configuration, unlike a configuration that suggests a vertical position. The drawn conclusion also agrees with the Fukui function analysis that proposes equally likely positioning, and this can only be fulfilled if the benzene molecules lie horizontally as shown by configuration 1.

The energy of the highest occupied molecular orbital of benzene was evaluated as −5.534 eV while that of the lowest unoccupied molecular orbital was evaluated as −0.3156 eV. This implies that the energy gap is 4.924 eV. This represents the minimum energy needed to move an elementary particle such as an electron from the HOMO to the LUMO. On the other hand, CASTEP calculations indicated that the AgNPS is a cubic crystal with $a = b = c = 2.89$ Å while $\propto = \alpha = \beta = \gamma = 60°$ and cell volume = Å^3. These results are in agreement with experimental data. The Dmol^3-based calculated optical properties of the AgNPS crystal indicated Fermi energy (E_{Fermi}) = −2.824 eV, DFT energy gap (E_{BG}) = 4.209 eV, valence band edge (VB_E) = −0.2584 eV, and conduction band edge (CB_E) = −2.824 eV consequently; the AgNPS is shown by computational computation that its wavelength of maximum absorption should be in the UV region, which is also in agreement with literature (Zaman et al., 2023).

Optical properties such as E_{BG}, E_{Fermi}, CB_E, and VB_E are significant factors in the evaluation of the efficiency of AgNPS as a photocatalyst for the degradation of organic contaminants, which has been successfully reported for several contaminants as listed in Table 3. The observed results show that the Fermi level is almost in the conduction band which suggests a high tendency for the AgNPS to behave as a conductor or a semiconductor, which is a basic requirement for the materials to act as a photocatalyst. The above analysis, concerning the behavior of AgNPS as an adsorbent and a photocatalyst for remediation of organic contaminants, shows that computational evaluation can provide preliminary information on the vast number of contaminants that can be processed by AgNPS and thus, adsorption and photodegradation prediction can be achieved through computational chemistry treatment.

Comparative overview of literature

Literature is not scanty concerning some excellent properties of AgNPS over other nanoparticles especially concerning their electrical conductivity, chemical stability, catalytic properties, antimicrobial properties, and cytotoxicity against cancer cells (Zhao et al., 2022). In adsorption technology, the required material properties are porosity, surface area, chemical stability, thermal stability, reusability, high selectivity, etc. (Pourhakkak et al., 2021). Consequently, the evaluation of the suitability of an adsorbent can be conducted based on the listed properties. In Table 7, some reported properties of AgNPS and those of popular adsorbents such as activated charcoal, biochar, and other metal nanoparticles are presented.

The information presented in Table 7 shows that among the popular adsorbents, silver nanoparticles have some excellent adsorbent properties. The

Table 7 Literature on adsorption properties of AgnPS and other popular adsorbents

Adsorbent	Surface area (m^2/g) and *a*	Particle size/Q_{max} (mg/g)	Stability	Selectivity	Ref
AgNPS	30 to 90 m^2/g	7 to 524	Stable against chemical attack	Very high selectivity	Jeung et al., 2021) Darweesh et al. (2022)
Biochar	46.32–99.91	0.05–1.00 mm 2.00–4.00 mm low porosity compared to AgNPS	May be thermally stable but easily attacked by several chemicals	Selectivity is far lower than that of AgNPS	Elnour et al. (2019), Sigmund et al. (2017)
Activated carbon	Very high surface area which can approach 3000	0.15–0.25 mm low porosity compared to AgNPs	Low thermal stability compared to AgNPS	Selectivity is far lower than that of AgNPS	Bazan et al. (2016) Pan et al. (2017), Saeidi and Lotfollahi (2016)
Silica	200–1200	200–1000 nm	High thermal stability up to 1200 °C	Relatively fair	Huo et al. (2019), Szekeres et al. (2022) Davenport et al. (2020)

**Q_{max} is the adsorption capacity in milligrams per gram

nanoparticles are thermally stable because they have perfect atomic planes that resist the detachment of atoms (Gould et al., 2015). The challenges facing the other listed adsorbents also include low particle size, which does not fit them to the nanodimension unlike that of AgNPS, which can be adjusted based on the method of synthesis, the type of precursor, seeding time, etc. (Garanbohm et al., 2018; Iravani et al., 2014). Chemical stability is also a unique feature of AgNPS that can hardly be matched by other adsorbents (Nguyen et al., 2023a, b). The high selectivity of AgNPS has also contributed to its comparative advantages over some adsorbents. For example, activated carbon is a popular adsorbent with a very high surface area but its adsorption capacity for some allergens and do not exhibit antimicrobial activity, which could limit some useful function in some applications, for example, in the removal of some drugs and microorganism from contaminated water. Also, activated carbon has a poor capacity for the adsorption of polar molecules, some of which are significant as environmental contaminants (Park et al., 2023). AgNPS do not exhibit such resistance but have rather shown significantly higher adsorption capacity against polar compounds (Al-Jubouri et al., 2023). However, Qiu et al. (2022) reported that biochar has the potential to remove polar compounds through adsorption but with relatively low efficiency when compared to AgNPS. Biochar also has other limitations when compared to AgNPS when considering particle size, surface area, and other properties listed in the above table. Silica is also known for exhibiting high surface area compared to AgNPS as indicated in the above table. However, silica suffers from large particle size, low water exchange, low packing density, poor heat transfer, etc. (Hassan et al., 2023). It is worth pointing out that AgNPS are unique because most of their properties can be improved through doping or composite formation (Soni & Biswas, 2019).

As a photocatalyst, AgNPS have significant advantages compared to most photocatalysts that have been reported, especially concerning pollution management. The efficiency of a photocatalyst can be evaluated based on the amount of contaminants that have been degraded over a given time. Photodegradation requires catalysts with good optical properties.

Literature on the efficiency of some compounds (especially nanoparticles) as photocatalysts for the degradation of organic contaminants is not scanty. In Table 8, literature on the degradation of methyl orange dye by some nanoparticles is presented to establish the uniqueness of AgNPS as a photocatalyst. Methyl orange is chosen as a representative contaminant because of its broad spectrum of toxicity and the availability of a large volume of literature regarding the need for the degradation of the dye. The values of the bandgap of the dye (methyl orange)

Table 8 Bandgap and photocatalytic degradation efficiencies for AgNPS and some nanoparticles

Photocatalyst	Dye	Bandgap (eV)	Degradation efficiency (%)	References
AgNPS	Methyl orange	2.88	98.00	Trieu et al. (2023)
Ag doped ZnO	Methyl orange	2.97	96.74	Bhosale et al. (2023)
NiONPS	Methyl orange	4.00	46.00	Ashfaq et al. (2023)
Bi_2O_3NPS	Methyl orange	2.85	67.00	Ashfaq et al. (2023)
Bi_2O_3-NiO	Methyl orange	2.30	100.00	Ashfaq et al. (2023)
SiO_2NPS	Methyl orange	4.18	95.00	Biradar et al. (2021)
TiO_2@UiO-66	Methyl orange	2.90	97.56	Yang et al. (2023)
TiO_2NPS	Methyl orange	3.00	45.98	Yang et al. (2023)
TiONPS	Methyl orange	3.37	40.00	Raliya et al. (2017)
ZnONPS	Methyl orange	3.18	40.70	Algarni et al. (2022)
CuONP	Methyl orange	3.71	65.08	Aroob et al. (2023)

and reported degradation efficiency for the different photocatalysts are also presented in Table 8.

The most remarkable observation based on the information presented in Table 8 above is the high degradation efficiency that characterizes AgNPS against methyl orange. The degradation efficiencies recorded for other nanoparticles are low except when doped with other materials. It is also evidenced from the results in the above table that bandgap has a significant influence on the photocatalytic degradation efficiency of organic compounds. Consequently, the lower the bandgap, the higher the expected photodegradation efficiency. AgNPS absorb in the visible region while most of the listed photocatalysts absorb in the ultraviolet region. Excitation within the visible region requires lower photon energy compared to excitation in the ultraviolet region; hence, the observed trend in the variation of the efficiency of the listed photocatalysts strongly depends on the bandgap. The doping of nanoparticles with other components can reduce their bandgap and consequently enhance their degradation efficiency. For example, it can be seen in Table 8 that the bandgaps and photodegradation efficiencies of NiONPS and Bi_2O_3NPS are very low but when combined, a significantly higher degradation efficiency was obtained due to the reduction in bandgap. However, doping of silver with ZnO did not produce a similar observation but a higher bandgap and relatively reduced efficiency. This may be due to the nature of the doping materials, some of which may enhance hole-electron recombination. Therefore, to improve the bandgap of AgNPS through doping, careful selection of the proper semiconductor is necessary.

Also, in Table 9, the adsorption capacity or efficiency of AgNPS and other adsorbents reportedly used for the removal of methyl orange from aqueous solution is presented.

From the information presented in Table 9, it is indicative that silver nanoparticles have a good adsorption capacity for the removal of methyl orange dye when compared to other known adsorbents. However, biochar and activated carbon seem to have better adsorption capacity than AgNPS because of their large surface area, which was reported in Table 6. When compared with information observed for photocatalysis, it is indicative that AgNPS can function better as a photocatalyst than as an adsorbent.

Table 9 Adsorption capacity of some adsorbent for methyl orange dye removal from water

Adsorbent	Adsorption capacity (mg/g)	References
AgNPS	90.90	Yari et al., (2023a, b)
Biochar	136.67	Hanoon and Ahmed (2019)
Activated carbon	107.53	Abolle et al. (2022)
Silica	45.05	Hassan Boushara et al. (2022)
Alumina	56. 50	Rahim et al. (2023)

Challenges and the way forward

From the forgone review, it is most indicative that AgNPS have unique properties as an adsorbent and photocatalyst for the remediation of contaminated environment. However, some challenges may operate to limit the application of these nanoparticles. Some of these challenges may include the cost of production and market value, the management of toxicological impact arising from its usage, and raw material availability.

Market value

In Table 10, the market value of AgNPS and other adsorbents is presented. The results show that, although the market value for AgNPS is the least among the presented adsorbents, it is the most expensive nanoparticle because of the high cost of production. Consequently, forces of demand and supply for other adsorbent seem to compete higher than those of AgNPS. Given this, there is a serious need to engage in research that can be implemented to reduce the high cost of silver nanoparticles. For example, Mondal et al., (2023a, b) have reported success in the recovery of silver from electronic waste as an option towards reducing the high cost of silver. It is most certain that there could be other sources of silver in the environment. Some researchers have also suggested that industries involved in the application of silver do experience some leakages during the production or application. Consequently, the resource recovery approach should also be considered as an essential policy of such industries.

Toxicity

Another challenge that may likely face the AgNPS industries is reported toxicity. Although the biocompatibility and cytotoxicity of AgNPS have not been conclusively found, some studies have shown that its toxicity depends on particle size, concentration, and duration of exposure with consequences such as impaired proliferation, lymphocyte in humans, and mononuclear cell functions. In as much as numerous advantages can be harnessed from AgNPS, toxicological management is a crucial factor that must be thoroughly considered during the application of silver nanoparticles. Perhaps, a viable remediation approach may involve an efficient detection mechanism and system design to reduce leakage and recover such if they exist. Some levels of toxicity may arise when the chemical synthetic method is used. Fortunately, efforts in overcoming toxicity arising from synthetic methods have received huge success, especially the application of green synthetic routes (Algarni et al., 2022; Ali et al., 2023; Mondal et al., 2023a, b).

Regeneration of used AgNPS

AgNPS is a toxic metal, which can be oxidized to Ag_2O. The dissolution of Ag_2O in water can lead to the release of $Ag+$, which has the potential to impact biological systems and exert their toxic impact. Given the known toxicity of AgNPS in the environment, experimental approaches involving their application must have an inherent design for remediating their impact. In adsorption and photocatalysis, used AgNPS

Table 10 Global market values for some adsorbent

Adsorbent	Market value ($)	Reference
AgNPS	6.101 million	Imarci Group (2023)
Activated carbon	4.98 billion	Thr Business Research Company (2023)
Biocahr	220.27 million	YahooFinance (2023a)
Silica	2982.70 million	YahooFinance (2023b)
TiONPS	10.68 billion	Emergene Research (2023)
SiO_2NPS	4.65 billion	Research and Market (2023)

can be recovered and re-used, otherwise, the process will not be economically and environmentally viable.

In both adsorption and photocatalysis, it is necessary to recover AgNPS after the experiment, otherwise, the process will not be cost-effective and may have a toxic effect on the environment. Some methods have been employed to recover silver from solution after adsorption and photodegradation. One such method involved the use of a magnet since silver nanoparticle is paramagnetic (Alzahrant, 2017). The use of solvent to regenerate the AgNPS has also been reported (Akl et al., 2023). For example, Kumar et al. (2023) used ethanol to regenerate AgNPS which was used in the adsorption removal of methyl red dye. However, the choice of solvents will depend on the solubility of the adsorbate but the solvent must not be the form that reacts with the nanoparticles. The centrifugation method has also been used in the recovery of AgNPS.

The solvent extraction method has also been reported as an effective process that can be applied to recover silver nanoparticles from the solution. This method seems to be a good approach that can be used to recover silver nanoparticles from leached solution. Successful recovery of silver from HNO_3 solution using calix arene tetramine and its thio analogue dissolved in dichloromethane was reported. The recovery efficiency was reported to be 99%.

Summary, conclusions, and recommendations

The current review has gathered substantial information on classes of organic contaminants that need to be removed from the global water flow because most of them tend to cause toxic impacts. The application of adsorption and photocatalysis in the removal of organic contaminants has present and future hopes. Several factors can operate to influence the efficiency of given adsorbents, for example, surface properties such as surface area; pore size; pore volume; thermal, mechanical, and chemical stability; and selectivity. Also, factors such as porosity, particle size, bandgap, and electrical conductivity can significantly affect the performance of a given material as a photocatalyst.

Considering the present literature search and review, the knowledge gap concerning research in the application of adsorption and photocatalysis is still open. Consequently, literature on adsorption and photocatalyzed degradation of organic contaminants is dominated by those concerning dyes but scanty regarding similar applications for antibiotics, toxic chemicals, and other emerging contaminants. As an observation of the information presented on the adsorption and photocatalysis concerning AgNPS, it can be stated that the photocatalytic ability of AgNPS is better than its adsorption capacity concerning the tendency to remove contaminants.

Most study on the application of AgNPS as an adsorbent and photocatalyst seems to neglect the toxicological aspect of the nanoparticles. This implies that information such as the impact of the untreated and treated medium may not be obtainable from most of the reported studies.

Since AgNPS have great potential as an effective adsorbent and photocatalyst for the remediation of water polluted by organic contaminants, it is needful to recommend the following:

1. There is a need for extensive research on the applications of AgNPS in the remediation of water contaminated by organic pollutants not yet tested.
2. The need to align the behavior of AgNPS as an adsorbent and a photocatalyst to their associated quantum chemical properties.
3. The need to apply theoretical models to further investigate the mechanism involved in the remediation of different classes of organic contaminants and to engage measures (based on such information) towards improved efficiency.
4. Theoretical calculations can also be used to predict the fate of untested contaminants towards the action of AgNPS as an adsorbent or photocatalyst.
5. In designing research for the applications of AgNPS as an adsorbent and a photocatalyst, effort should also be directed towards environmental impact and ameliorative measures.
6. Research on the improvement of the efficiency of AgNPS, without the alteration of its environmental friendliness, is highly encouraged.

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Nnabuk Okon Eddy: Conceptualization; Funding acquisition; Project administration; Resources; Software; Supervision; Validation; Roles/Writing—original draft; Writing—review & editing

Rajni Garg and Rishav Garg: Software; Data curation; Formal analysis; Roles/Writing—original draft; Writing—review & editing

Richard Alexis Ukpe and Hillary Abugu: Investigation; Roles/Writing—original draft; Writing—review & editing.

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Data availability The datasets used or analyzed during the current study are available from the corresponding author upon reasonable request.

Declarations

Ethics approval All authors have read, understood, and have complied as applicable with the statement on "Ethical responsibilities of Authors" as found in the Instructions for Authors and are aware that with minor exceptions, no changes can be made to authorship once the paper is submitted.

Consent for publication All authors have consented to publish this paper.

Competing interests The authors declare no competing interests.

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