



A review on adsorptive removal of dyes from wastewater by hydroxyapatite nanocomposites

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Abstract

Dye removal from wastewater is of prominence due to its hostile effects on human health and the environment. The complex structure of the dye molecule is responsible for its difficulty in removal. Adsorption is found to be a promising technique to eliminate dye wastes due to its high removal capacity at low concentration. Among different adsorbents used, hydroxyapatite is a biocompatible adsorbent that is relatively efficient in both anionic and cationic dye removal. Recently, modification of hydroxyapatite by doping with other materials to increase its removal efficiency has gained much attention. This review summarizes compilation of recent literature on the removal of anionic and cationic dye by different hydroxyapatite nanocomposites, comparison of adsorption capacities of different hydroxyapatite nanocomposites, the possible adsorption mechanism of removal of dyes, the general isotherm, and kinetic and thermodynamic studies explaining the type of adsorption and the characteristics, advantages, and limitations of adsorbents.

Keywords Adsorption · Dye · Hydroxyapatite nanocomposite · Isotherms · Kinetics · Thermodynamics

Introduction

Rapid industrialization has resulted in a detrimental effect on the environment and human health. Inevitable use of chemicals which cannot be eliminated due to growth in the economy makes it essential to ensure its safe use and disposal. One such waste is dye which is commonly used in cosmetics, food, paper, pharmaceutical, plastic, textile, and tannery industries (Nguyen and Pho 2014). Dye molecules are hazardous to human health along with aquatic and floral environments (Manatunga et al. 2018). Dye molecule contains a complex chemical structure of chromogen-chromosphere which makes it difficult to biodegrade (Shertate and Thorat 2014). Of the dye produced, 80% is used by textile industries making

them the largest consumers of dyes. India is the second-largest dye exporter after China (Bakre et al., 2005). As per the annual report of the Ministry of Textiles, 28.89 lakh kg of dye is produced in India which values around 27.02 crores (Ministry of Textile Govt of India 2018). Therefore, the treatment of wastewater containing dyestuff is very essential before discharge.

Various techniques are evolved for the treatment of dye wastes such as coagulation-flocculation (Dotto et al. 2019), biodegradation (Bharti et al. 2019), electrochemical oxidation (Shetti et al. 2019), ion exchange (Yan et al. 2019), Fenton oxidation (Sözen et al. 2019), reverse osmosis (Cinperi et al. 2019), ozonation (Venkatesh and Venkatesh 2019), electrocoagulation (Donneys-Victoria et al. 2019), and adsorption (Naushad, 2019). Researchers are under social pressure to produce eco-friendly and economic technique with relatively good efficiency. Adsorption is an efficient technique for dye removal which binds the particles on the surface of adsorbent by physical or chemical forces. India is one of the top 10 countries with documents on adsorption of dye as per Scopus as depicted in Fig. 1. Various metal oxides and waste products are used as adsorbents. Activated carbon is one of the widely used adsorbents (Jedynak et al., 2019). However, it is uneconomic; hence, we have focused our review on hydroxyapatite adsorbents.

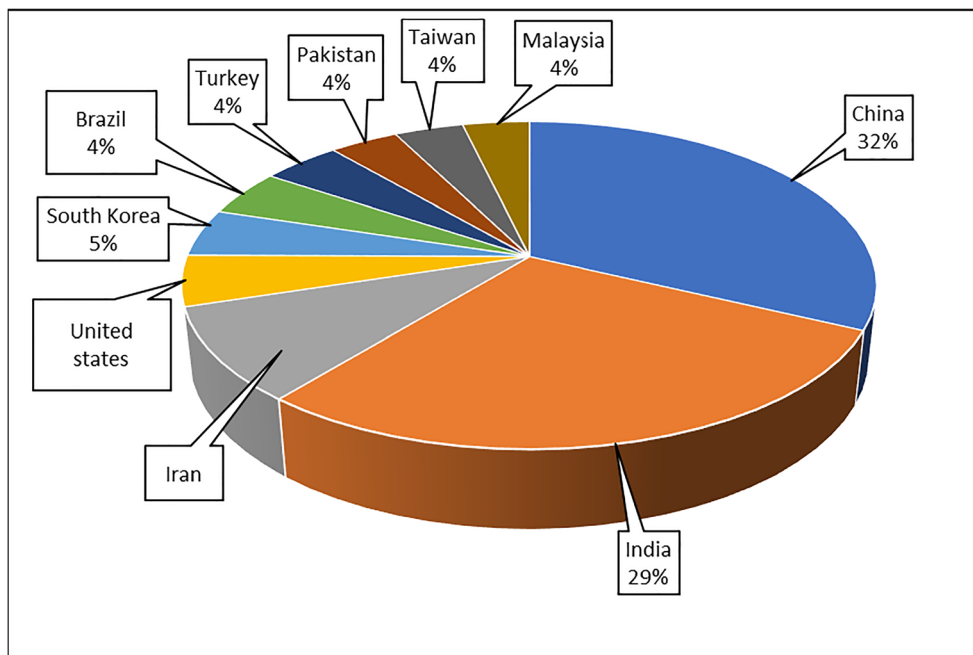
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Fig. 1 Number of articles published by various countries on “adsorption of dye”



Dyes

Due to high water solubility, it is difficult to remove dyes from wastewater by conventional methods (Yusuf 2019). Degradation of certain dye produces few products which are hazardous than the dye itself. Dye molecule adheres to the surface of the fiber by hydrogen bonding, van der Waals forces, or electrostatic interactions (dos Santos et al., 2007).

Due to the improper coloring process, the excess dyestuffs mix with water and are released as effluent. When these dyestuffs are let-off to the environment, they may cause serious hazards as shown in Fig. 2.

Toxicity analysis of various dyes is investigated in many studies which concluded dyes to be highly genotoxic and carcinogenic (Ahmed et al., 2015; Fernandes et al., 2018). The dye may enter through skin pores, inhalation, or ingestion

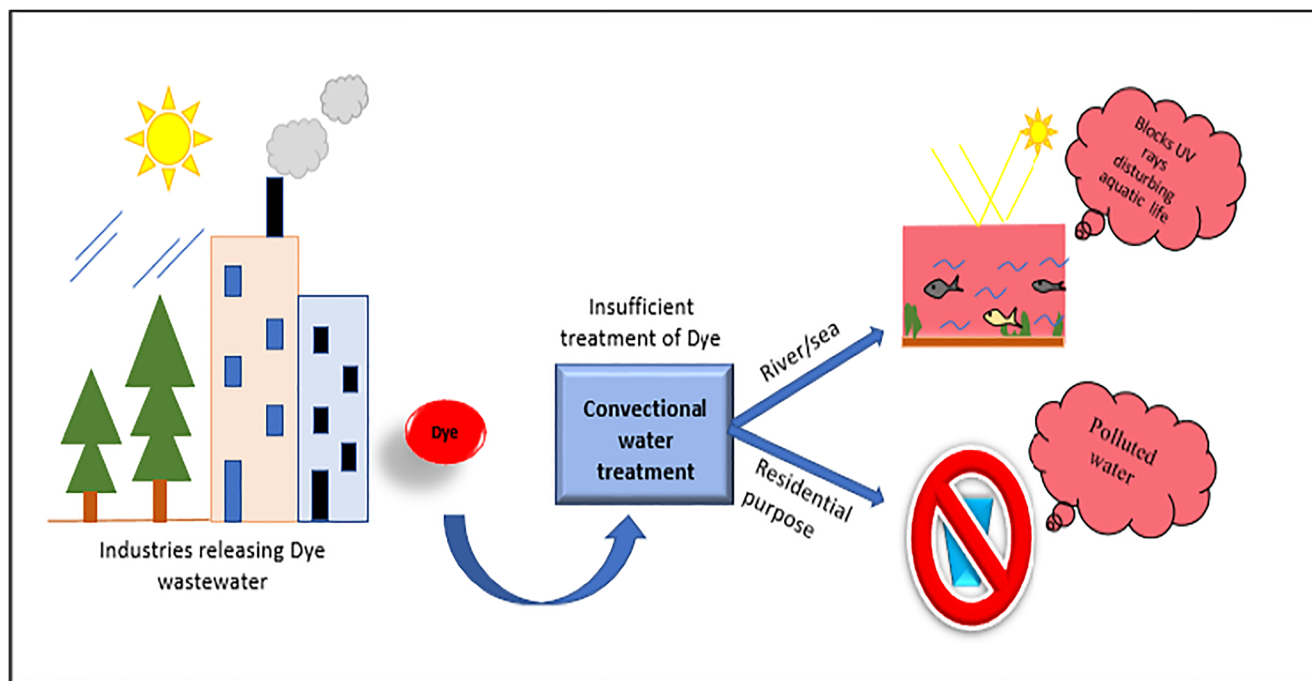


Fig. 2 Fate of dye in the environment

which causes diseases like dermatitis, kidney disorders, or even bladder cancer during long-term exposure (Akarşlan and Demiralay 2015).

Dyes are classified as ionic dye and non-ionic dyes. Dyes that form positively charged ions in the aqueous solution are cationic dyes, and those which form negatively charged ions are anionic dyes. Acid dyes, reactive dyes, and direct dyes are few anionic dyes. Rhodamine B methylene blue and malachite green are few cationic dyes. Vat dyes and disperse dyes are non-ionic dyes (Naushad 2018). Production of dye can be from natural or synthetic sources. Figure 3 demonstrates the classification of dyes with their production source. Natural dyes are eco-friendly and are used principally in food sectors limiting their use in other sectors because of their high cost (Vankar 2000).

The removal of dyes by various adsorbents is given in Table 1.

Hydroxyapatite

Hydroxyapatite (HAP) consists of calcium and phosphate mineral confirming their association with the apatite family (Fig. 4). HAP can receive a significant number of anionic and cationic substituents. HAP can either be monoclinic or hexagonal (Piccirillo and Castro, 2017). It is used widely in medicine as its composition replicates that of human bone with a Ca/P molar ratio of 1.67 (Szcześ et al., 2017). HAP is white to off-white and a soft powder-like substance which has numerous applications such as fuel-cell materials, fluorescent lamps, adsorption of pollutants, and catalysis (Fihri et al.

2017). The physicochemical properties like stability, porosity, low water solubility, high sorption capacity, and modifiable surface groups enable strong interaction between HAP and pollutant molecules (A. K. Mishra 2016).

Synthesis of HAP

The techniques commonly used for the preparation of HAP include (i) dry method, (ii) wet method, (iii) high-temperature method, and (iv) green synthesis as mentioned in Table 2.

In the dry method, precisely weighed precursors are homogenously mixed without the addition of solvent, followed by sintering to produce the porous product. The requirement of high temperature is a major drawback of this method (Chaikina et al. 2019). In a study conducted by the researches (Pramanik et al. 2007), the precursors were mixed for 16 h with the binder in a mill. The resulting slurry was dried for 3 h at 80 °C to form a powder which was cold pressed in a steel dye to produce pellets. This was heated in a furnace at 500–1250 °C followed by cooling to avoid internal cracks. The product obtained was crushed again, compacted, and heated in a furnace for further characterization.

Wet methods involve chemical precipitation, hydrolysis, sol-gel, hydrothermal, and emulsion methods. In these processes, less agglomerated products are formed by simple procedures. Chemical precipitation is one of the widely used methods for the synthesis of HAP. In a method described by Wolff et al. (2018), calcium salt solution (pH 10) was stirred and heated with a dispersant to prevent agglomeration. On attaining a constant temperature, the phosphate salt solution was added dropwise and stirred for 1.5 h. After aging for 12 h,

Fig. 3 Classification of dye based on sources with examples

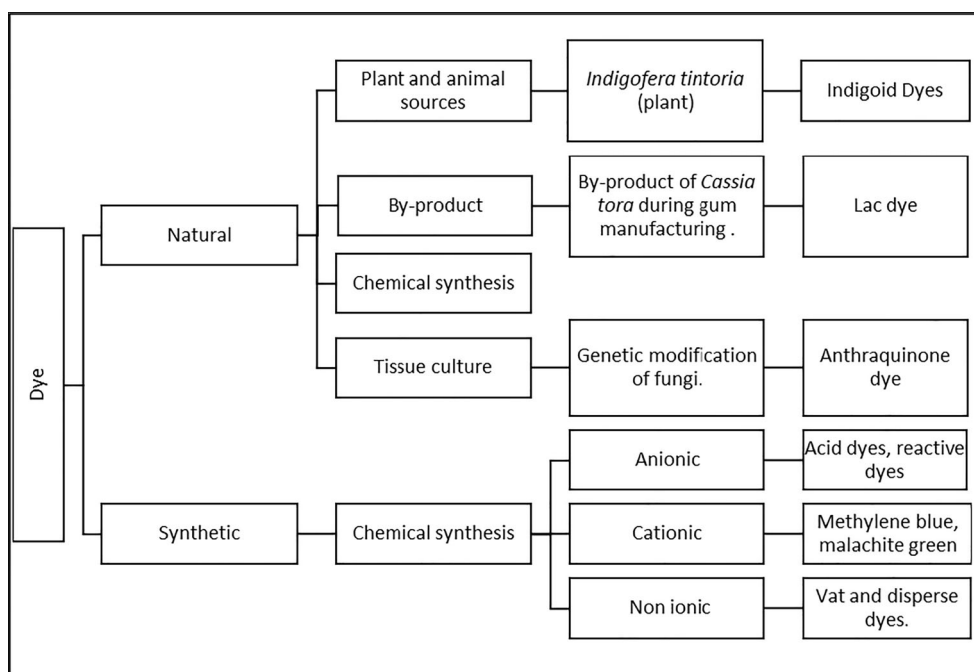


Table 1 Removal of dyes by various adsorbents

Adsorbent	Dye	Adsorption parameters			Isotherm	Kinetic model	Adsorbent capacity (mg/g)	Conclusions	Reference	
		Contact time (min)	Dose (g)	pH						Initial concentration (mg/L)
Nickel ferrite-polyaniline nanocomposite	Methylene blue	80	–	7	5	Langmuir	Pseudo second order	100	Good adsorbent for methylene blue removal with high regeneration capacity	Singh, Rachna and Agrawal (2019)
Polyethylene glycol and Ag-ZnO grafted polyaniline nanocomposites (PAPE/AZO)	Brilliant green	180	0.075	8	70	Langmuir	Pseudo second order	94.46	Doping enhanced adsorption due to large number of vacant sites	Gouthaman et al. (2019)
Metal organic framework PCN-222(Fe)	Acid red 1	720	0.003	7	200	Langmuir	–	417	Regeneration of adsorbent without much loss was observed.	Sarker et al. (2019)
	Acid blue 80	720	0.003	7	200	Langmuir	–	371		Sarker et al. (2019)
Magnetic xanthate modified chitosan	Methylene blue	60	0.1	6–11	20	Sips	Pseudo second order	197.8	Xanthate doping improves adsorption for a wider pH range	Tanhaei, Ayati and Sillanpää (2019)
	Safranin O	60	0.1	4–11	20	Sips	Pseudo second order	169.8		He et al. (2019)
Graphene hybridized polydopamine-kaolin composite	Methylene blue	1440	0.8	11	5	Langmuir	Pseudo second order	39.663	Increased surface area and large adsorption sites enhanced MB removal.	Inthapanya et al. (2019)
Calcined oyster shells (COS)	Acid green 25	60	2	11	70	Langmuir	Pseudo second order	34.1	COS has been proved to be a low-cost adsorbent with good regeneration capacity.	Chu et al. (2019)
Alumina nanoparticles	Rhodamine B	120	5	4	–	–	–	165	Surface modification of alumina by anionic surfactant enhanced its adsorption capacity	H. Hassan et al. (2019)
Chitosan/silica/zinc oxide nanocomposite	Methylene blue	120	1	7	100	Langmuir	–	293.3	Highly efficient adsorbent for dye removal.	Tan and Sen (2019)
A mixture of eucalyptus bark biomass and kaolin clay.	Methylene blue	100	0.8	9	20	Both Freundlich and Langmuir	Pseudo second order	81.3	Low-cost eco-friendly adsorbent.	Abd-Elhamid et al. (2019)
Graphene oxide-activated carbon	Methylene blue	40	0.8	12	40	Langmuir	Pseudo second order	147	Adsorbent with good thermal stability and reusability.	
	Crystal violet	60	0.8	7	20	Langmuir	Pseudo second order	70		
		10.12	0.015	4.9	37.17	Langmuir		344.827	Easily regenerable adsorbent.	

Table 1 (continued)

Adsorbent	Dye	Adsorption parameters				Isotherm	Kinetic model	Adsorbent capacity (mg/g)	Conclusions	Reference
		Contact time (min)	Dose (g)	pH	Initial concentration (mg/L)					
Magnetic activated carbon/diopside nanocomposite	Reactive green KE-4BD						Pseudo second order		Jafari Harandi, Ghanavati Nasab, and Teimouri (2019)	
Activated carbon	Indigo carmine	90	1	2	60	40	Langmuir	298.34	Adsorbent with high surface area was highly efficient in dye removal.	
Commercial activated carbon	Methylene blue	60	0.1	5	5	40	Langmuir	98	High-percentage removal of dye.	
Commercial activated carbon	Rhodamine B	180	2	–	15	42	Langmuir	87	Spontaneous adsorption is observed.	
	Acid yellow 17	180	2	–	30	42	Langmuir	71		

the product was filtered and washed many times with water and ethanol followed by calcination. This method produced HAP rapidly in a short time with poor crystallinity. The emulsion method involves the usage of precursors, specific solvent, and a surfactant at a controlled pH and temperature to obtain HAP. This method has been employed for obtaining high-purity HAP by adding CTAB, cyclohexane, and n-octyl alcohol to calcium and phosphate precursors under vigorous stirring and calcination for 4 h (Huang et al. 2019).

High-temperature processes involve the combustion of precursors at a high temperature for a specified period of time. The final products are powdered by milling to get homogeneous HAP particles (Canillas et al. 2017).

Green synthesis methods make use of waste materials as a substitution for calcium and phosphate precursors for the synthesis of HAP (Fihri et al. 2017). Limiting the use of toxic chemicals by using naturally available waste resources for the synthesis can be a solution to the arising problem of water pollution. Waste resources can be biowastes like eggshells, fishbone, and bovine bone; calcination of organic matters like a seashell, coral, starfish, and algae; and biomolecules from plants (Sadat-shojai et al. 2013). In a study conducted by researchers (Sathiskumar et al. 2019), fish scales were treated with dilute HCl to remove proteins followed by NaOH and heating to eliminate proteins. The white precipitate obtained is filtered and washed with distilled water. After drying in a hot air oven, the product is crushed and given NaOH treatment at 100 °C for 2 h with continuous stirring. The final product is obtained after drying at 100 °C after thorough washing to remove alkalinity from HAP.

Hydroxyapatite has calcium ions with a positive charge and phosphate ions with a negative charge. Therefore, it can remove pollutants by electrostatic interactions (Chahkandi 2017). However, it is difficult to obtain HAP in the required form due to its hardness and brittleness. Hence, modification of HAP by doping it with other compounds can solve this problem (Sreedhar et al. 2007). Research on the pollutants removal by adsorption has revealed that surface modification can advance adsorbent effectiveness (Darvishalipour et al. 2019). In a study conducted by researchers (Mohammad et al. 2017), adsorption capacity of chitosan doped HAP was found to be greater than that of HAP which indicated hydroxyapatite nanocomposite to be a better choice for the contaminant removal.

Hydroxyapatite nanocomposites

Enhancing the properties of HAP by doping it with other material is practiced recently by which adsorbent performance is increased. Synthesis of doped HAP can easily be obtained by mixing metal salts with calcium and phosphate salts during HAP production (Manatunga et al. 2018) or adding doping

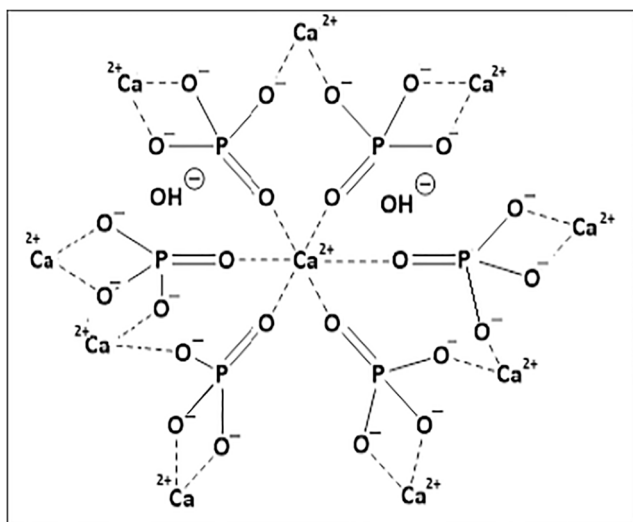


Fig. 4 Structure of hydroxyapatite

material after synthesis of HAP under controlled conditions (Hamzah and Salleh 2014). Figure 5 gives us a year-over-year increase in the number of publications in the area of HAP nanocomposites as per Scopus. Doping of HAP with magnesium (Khalil 2012), chitosan (Sadeghizadeh et al. 2019), bagasse biomass (Yan et al. 2019), zinc (El-Maghrabi et al. 2019), silver (Gottardo et al. 2019), and palladium (J. Mishra et al. 2019) for the adsorption of various pollutants is explored by various researchers.

Adsorption depends on many parameters like adsorbent dosage, contact time, agitation speed, initial concentration of adsorbate, and temperature. Recent research on HAP nanocomposite on dye removal is the focus of this review article. Adsorption of various dyes by metal/metal-oxide-based HAP nanocomposite, magnetic HAP nanocomposite, biochar-HAP nanocomposite, polymer-HAP nanocomposite, graphene-HAP is briefly discussed in the following sections.

Metal/metal-oxide-based HAP nanocomposite

The adsorption capacity of HAP increases when it is doped with metal or metal oxide. For example, doping HAP with titanium increased the adsorption of anionic reactive red dye by being positively charged at zeta potential, when compared with bare HAP which was negatively charged at zeta potential repulsing the dye molecules as shown by Asjadi, Salahi, and Mobasherpour (2016). Metal oxides in adsorbent increase the availability of hydroxyl groups which form hydrogen bonds with nitrogen atoms in dye molecules which increase the adsorption capacity. Oxygen species in metal oxides and positive charge in cationic dyes result in dipole ion interaction thereby increasing its adsorption capacity (Phasuk et al. 2018). Modification in properties of adsorbent which are prominent in enhancing adsorption capacity depends on the type of metal oxide doped (Manatunga et al. 2018).

Magnetic HAP nanocomposite

Magnetic hydroxyapatite (MHAP) is synthesized most commonly by a chemical precipitation method where the iron precursor is mixed with white precipitate formed by calcium and phosphate salt solution at high alkalinity (Sahoo et al. 2019). MHAP has a prominent advantage of easy removal by the application of external magnetic fields (Y. Wang et al. 2017). It is reported that electrostatic interactions and hydrogen bonding are the reasons for the increased adsorption capacity (Zhang et al. 2016).

Biochar-HAP nanocomposite

In general, HAP nanoparticles aggregate in aqueous solution thus reducing their dispersibility and adsorption capacity. To overcome these, few modifications can be done on the surface of HAP by doping them with biochar. Biochar produced from pyrolysis of reed straw biomass was blended with HAP which increased the adsorption of cationic dye (Y. Li et al. 2018).

Polymer/biopolymer-HAP nanocomposite

Hydrophobicity of polymer has restricted its use as a membrane for pollutant removal as it leads to membrane fouling (Lee et al. 2019). Modification of surface by doping it with nanoparticles containing hydrophilic groups can overcome this major drawback. Polymers are synthesized most commonly by the graft polymerization method where hydrogels are formed. When these polymers are soaked in calcium and phosphate salt solutions under controlled conditions, HAP/Polymer composite is produced (Hosseinzadeh and Ramin 2018). These composite membranes are efficient in the removal of dyes like Congo red (J. H. Li et al. 2019) and acid blue 113 (Varaprasad et al. 2018). The adsorption capacity depends on the quantity of HAP used in the preparation of the composite membrane (Varaprasad et al. 2018).

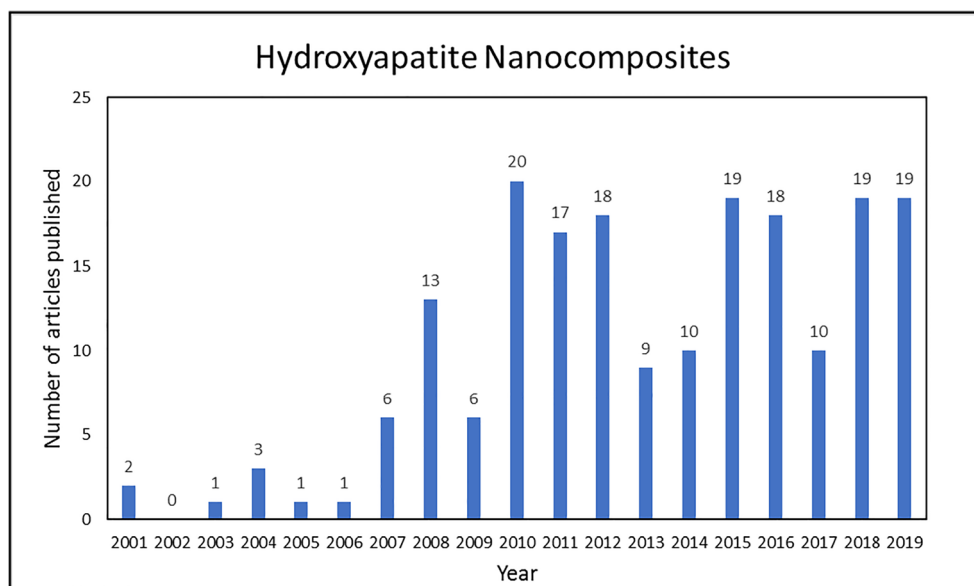
Graphene-hydroxyapatite nanocomposite

Carbon-rich materials possess a high surface area ensuing its high adsorption. Graphene has already been extensively used and is proven to be an excellent adsorbent. Doping HAP with graphene will further increase the adsorption capacity. HAP/graphene composite was successfully used as an adsorbent for the removal of methylene blue (M. A. Hassan et al. 2018). Similarly, Congo red and trypan blue dyes were removed by another HAP/graphene (Prabhu et al. 2018). These researchers have concluded that the adsorption efficiency of the HAP/graphene composite is higher than the individual components. Table 3 depicts the adsorption of different dyes by various HAP nanocomposites with their experimental conditions.

Table 2 Various HAP synthesis methods

Type	Method	Process	Advantages	Limitations	References
Dry method	Solid-state synthesis	Reactants are merged to form a homogeneous mixture which is a prerequisite for completion of the reaction. The blend is then sintered to obtain porous HAP nanoparticles	Does not require controlled conditions	Heterogeneous and irregular products are fabricated.	Guo et al. (2013), Pramanik et al. (2007)
	Mechanochemical	Precursors are blended in a ball mill under controlled conditions.	Products produced have a well-defined structure.	More energy consumption.	Chaikina et al. (2019), Amirthalingsam, Deivarajan, and Paramasivam (2019)
Wet method	Chemical precipitation	Precursors are mixed to form a precipitate which is then washed and dried after aging to form the product.	Simplest route for synthesis.	Poor crystallinity of products formed.	Yelten-Yilmaz and Yilmaz (2018), Wolff et al. (2018)
	Hydrolysis	Formation of the product by dissolution and precipitation.	It can be used to modify the characteristics of prepared HAP.	pH sensitive	M. C. Wang et al. (2015)
	Sol-gel	Precursors are mixed and aged resulting in gel formation which is then heat-treated to remove organic residues.	Chemical homogeneity.	More energy and time consumption.	Türk et al. (2019), Khan and Butt (2019)
	Hydrothermal	Blend of water and precursors at high temperature and pressure resulting in HAP of high crystallinity due to the formation of the chemical bond.	Nanosized crystalline and porous products formed.	Irregular-shaped particles are formed.	Ruffini et al. (2019)
	Emulsion	Precursors are added to immiscible solvent (surfactant) to form a transparent solution after which pH adjustment and stirring vigorously forms the product.	Simple process; agglomeration is reduced.	Type of surfactant, the ratio of immiscible solvent, pH, and temperature are the parameters to be controlled.	Huang et al. (2019)
	Sonochemical	Reactions between precursors are activated by ultrasonic irradiation.	Obtained nanoparticles with good porosity, crystallinity, and morphology.	Not energy efficient	Qi et al. (2016)
High-temperature processes	Combustion	Precursors are mixed, and the resulting white precipitate is dissolved in acid. This solution is heated with fuel to moderate temperature followed by sudden increase causing combustion in the furnace.	Inexpensive and simple process.	The use of elevated temperature indicates enormous energy utilization.	Canillas et al. (2017)
Green synthesis	Synthesis from biogenic sources	Naturally available resources for calcium and phosphate precursors are used. The synthesis process involves the extracts of plants/animals/microorganism residue.	Eco-friendly and inexpensive	The quantity of nanoparticles produced is generally less.	Sathiskumar et al. (2019), Horta et al. (2019)

Fig. 5 Trend of publication over research on “hydroxyapatite nanocomposite” as per Scopus



Dye removal by HAP nanocomposite

Dye removal by HAP nanocomposite is recently practiced. Adsorption takes place when adsorbate enters adsorbent through diffusion due to affinity between them. Adsorbate enters deep into adsorbent as time proceeds occupying all the available vacant sites (Trivedi and Mandavane 2018).

Anionic dye removal

HAP/chitosan nanocomposite was used to remove the anionic reactive blue 19 dye in which adsorption capacity was higher at low pH as anionic dyes are negatively charged (Nguyen and Pho 2014). As pH increases, the adsorbent surface becomes negatively charged which decreases adsorption. Similar results were observed in a study where an acid yellow dye was adsorbed by four different HAP nanocomposites (Manatunga et al. 2018). Congo red dye was removed by HAP/chitosan composite wherein an increase in adsorption capacity was due to hydrogen bonding between amino groups of Congo red and hydroxyl ion of the adsorbent (Hou et al. 2012).

Three anionic dyes (methyl red, methyl orange and, and methyl yellow) were adsorbed on HAP/palladium/iron composite which revealed that the adsorption was affected due to change in the structure of adsorbent due to calcination and addition of palladium degraded dye by oxidation (Safavi and Momeni 2012). Removal of methyl orange by HAP micro composite film showed an increase in adsorption with the increase in adsorbent dosage (Azzaoui et al. 2019).

HAP/CeO₂ composite was used to remove Erichrome black T. It was evident that with the decrease in pH adsorption increased as deprotonation of phosphate ions repulse adsorbent at high pH. An increase in adsorption was observed with an increase in the concentration of the dye and surface area

(Chaudhary et al. 2016). Similar results were shown in the study on the removal of lead and acid yellow dye by HAP/chitosan and HAP/carboxymethyl cellulose (Manatunga et al. 2016).

Reactive red 141 was adsorbed on HAP and HAP/titanium to check which adsorbent was best suitable for adsorption (Asjadi et al., 2016). The effect of initial concentration and the adsorbent dosage was similar to the above studies. The addition of titanium modified the structure of bare HAP making it favorable for adsorption at higher pH. Hydrogen bonding between HAP and nitrogen in dye was prominently responsible for adsorption. Doped HAP had higher adsorption capacity than bare HAP due to higher surface area.

Cationic dye removal

Two basic dyes brilliant green and crystal violet were adsorbed on kaolinite (Sarma et al., 2019). The electrostatic attraction was the main adsorption mechanism. Crystal violet had higher adsorption efficiency than brilliant green due to the larger dimension and greater number of binding sites. Methylene blue was adsorbed on MHAP (Y. Wang et al. 2017). Adsorption was mainly due to electrostatic interactions and the functional groups –OH and –COOH of carbon nanotubes.

Adsorption of brilliant green on HAP chitosan composite showed optimum adsorption at pH 7 and other factors such as dosage, the concentration of dye, and contact time which were directly proportional to adsorption (Ragab et al., 2019). Rhodamine B was adsorbed on HAP/alginate composite in a study conducted by Oladipo and Gazi (2016) where both batch and continuous studies were conducted. In a continuous study, the depth of adsorbent and flow rate of dye affected the adsorption. Malachite green was adsorbed on a

Table 3 Adsorption of different dyes by various HAP nanocomposites

Adsorbent	Dye	Specific surface area (m ² /g)	Adsorption capacity (mg/g)	Adsorption parameters				Isotherm	Kinetics	Trends and conclusions	Reference
				Contact time (min)	Dose (mg/L)	pH	Initial concentration (mg/L)				
HAP/hydroxyethyl cellulose/polyethylene glycol	Methyl orange	–	135.1	–	32.35	–	32.7	Langmuir	Pseudo second order	Multi coordination, H -bonding sites in surface resulted in high efficiency with spontaneous adsorption of MO.	Azzaoui et al. (2019)
HAP/cerium oxide	Eriochrome Black T	–	143.1	60	50	5	50	Freundlich	Pseudo first order	HAP doping enhances the biocompatibility.	Chaudhary et al. (2016)
HAP/chitosan composite	Congo red	–	769	480	50	5	400	Langmuir	Pseudo second order	Composite containing 50% of chitosan resulted in high adsorption efficiency.	Hou et al. (2012)
Zein/nHAP	Congo red	73.73	416.7	20	5.5	5.8	400	Langmuir	Pseudo second order	Surface area and number of reactive sites increased by doping zein with HAP increasing adsorption capacity.	Nasab et al. (2018)
HAP/chitosan	Acid yellow 220	119.022	303	45	10	–	500	Freundlich	–	Enhancement in properties of HAP due to chitosan resulted in rapid adsorption was observed within 30 s	Manatunga et al. (2016)
HAP/titanium	Reactive red 141	87.42	28.41	300	–	8.3	20	Langmuir	Pseudo second order	Doping enhance the surface area.	Asjadi, Salahi, and Mobasherpour (2016)
Hide substance/chitosan/H-AP	Methylene blue	5.5*10 ⁻⁵	3.8	210	50	12	–	Langmuir	Pseudo second order	A low-cost composite was produced by using a waste origin material.	Chatterjee et al. (2018)
	Sunset yellow	–	168	75	50	3	–	Langmuir	Pseudo second order		
Magnetic HAP-supported nickel oxide nanocomposite	Methylene blue	63.7	7.2	180	1000	8	7.5	Langmuir	Pseudo second order	Enhanced adsorption capacity.	Phasuk et al. (2018)
HAP-alginate composite spheres	Methylene blue	–	87.89	180	1000	9	50	Langmuir	–	HAP composite was found to have higher efficiency than bare HAP	Aslanov, Uzunoğlu, and Özer (2017)
HAP/hydrolyzed polyacrylamide 75	Methylene blue	–	435.6	180	20	5.76	400	Temkin	Pseudo second order	Spontaneous adsorption was observed with good regeneration ability of adsorbent.	Mansri, Mahrong, and Dergal (2019)

polysaccharide-based graphene HAP nanocomposite where electrostatic interactions were predominant in adsorption process (Hosseinzadeh and Ramin 2018).

Adsorption mechanism

It is well known that electrostatic interactions, hydrogen bonding, and ion exchange effects are the main possible mechanisms in the adsorption process. Hydrogen atom in HAP bonds to electronegative atom of dye to form strong hydrogen bond resulting in breaking of the complex structure of dye (Hou et al. 2012). Electrostatic interactions are principally triggered due to attraction and repulsion of counter and co-ions of HAP composites and dye molecules (Sarma et al., 2019). The description of the interactions of different functional groups in the process is surface complexation. Functional groups responsible for adsorption can be analyzed by FTIR of adsorbent before and after adsorption (Y. Wang et al. 2017). Phosphate ions in HAP composite are predominant in the ion exchange effect. Exchange of certain significant pollutant ion from the dye with this phosphate ion results in the removal of a considerable amount of contaminant from dye reducing its toxicity (You et al. 2019). Figure 6 depicts pictorial representations of mechanisms.

Adsorption isotherms, kinetics, and thermodynamic studies

The adsorption process is demonstrated by graphs showing the variation of adsorbed material with pressure at a constant temperature which is known as adsorption isotherm. Isotherms like Langmuir, Freundlich, and Temkin give the nature of adsorption. Monolayer or multilayer adsorption is depicted by isotherms. Adsorption kinetics are represented by pseudo first-order and second-order models. Determination of exothermic, endothermic, and spontaneous reaction is accomplished by adsorption thermodynamics.

Adsorption isotherms

Commonly used isotherms in the dye removal process are briefly discussed in this section. Langmuir, Freundlich, and Temkin are commonly used isotherms due to their simplicity and variable parameters. Langmuir and Freundlich isotherm equation can be altered into linear form and can be assessed effortlessly by graphical procedures (Oyekanmi et al. 2019).

Langmuir isotherm:

$$\frac{1}{Q_e} = \frac{1}{Q_o} + \left(\frac{1}{Q_o * b * C_e} \right) \quad (1)$$

Freundlich isotherm:

$$\log(Q_e) = \log K_f + \frac{1}{n} \log C_e \quad (2)$$

Temkin isotherm:

$$Q_e = \frac{RT}{b_t} * \ln(A_T) + \frac{RT}{b_t} * \ln(C_e) \quad (3)$$

where Q_e is the amount of dye adsorbed per gram of the adsorbent at equilibrium (mg/g), Q_o is the maximum monolayer coverage capacity (mg/g), b is the Langmuir isotherm constant (l/mg), C_e is the equilibrium concentration of adsorbate (mg/L), K_f is the Freundlich isotherm constant (mg/g), R is universal gas constant (8.314 J/mol/K), T is the temperature at 298 K, A_T is the Temkin isotherm equilibrium binding constant (l/g), and b_T is the Temkin isotherm constant

Langmuir isotherm depends on the rate of adsorption and desorption which is assumed to be equal at equilibrium (Patiha et al. 2016).

Freundlich isotherm is used for heterogeneous surfaces. It describes multilayer adsorption, unlike Langmuir which demonstrates monolayer adsorption. It is based on the assumption in which vacant sites for adsorption are adsorbed first depending on their binding capacity till adsorption energy is decreased exponentially (Foo and Hameed 2010).

Temkin isotherm is based on assuming that there is a linear decrease in heat of adsorption with sorption coverage (Sampranpiboon 2014). This isotherm reveals that adsorption is exothermic or endothermic. Various isotherms used by different HAP nanocomposites are cited in Table 3.

Adsorption kinetics

The adsorption kinetics demonstrates the proportion of uptake dye molecules by the adsorbent (Lin 2015). Generally, used equations are pseudo first-order and pseudo second-order equations which describe physisorption and chemisorption respectively (Patiño-Ruiz et al. 2019).

Pseudo first-order:

$$\log(Q_e - Q_t) = \log(Q_e) - \left(\frac{k}{2.303} \right) * t \quad (4)$$

Pseudo second-order:

$$\frac{t}{Q_t} = \frac{1}{k_1 * Q_e^2} + \left(\frac{1}{Q_e} \right) * t \quad (5)$$

where k and k_1 are pseudo first-order and second-order rate constants. Various dye adsorption on HAP nanocomposite shows different kinetic model as mentioned in Table 3.

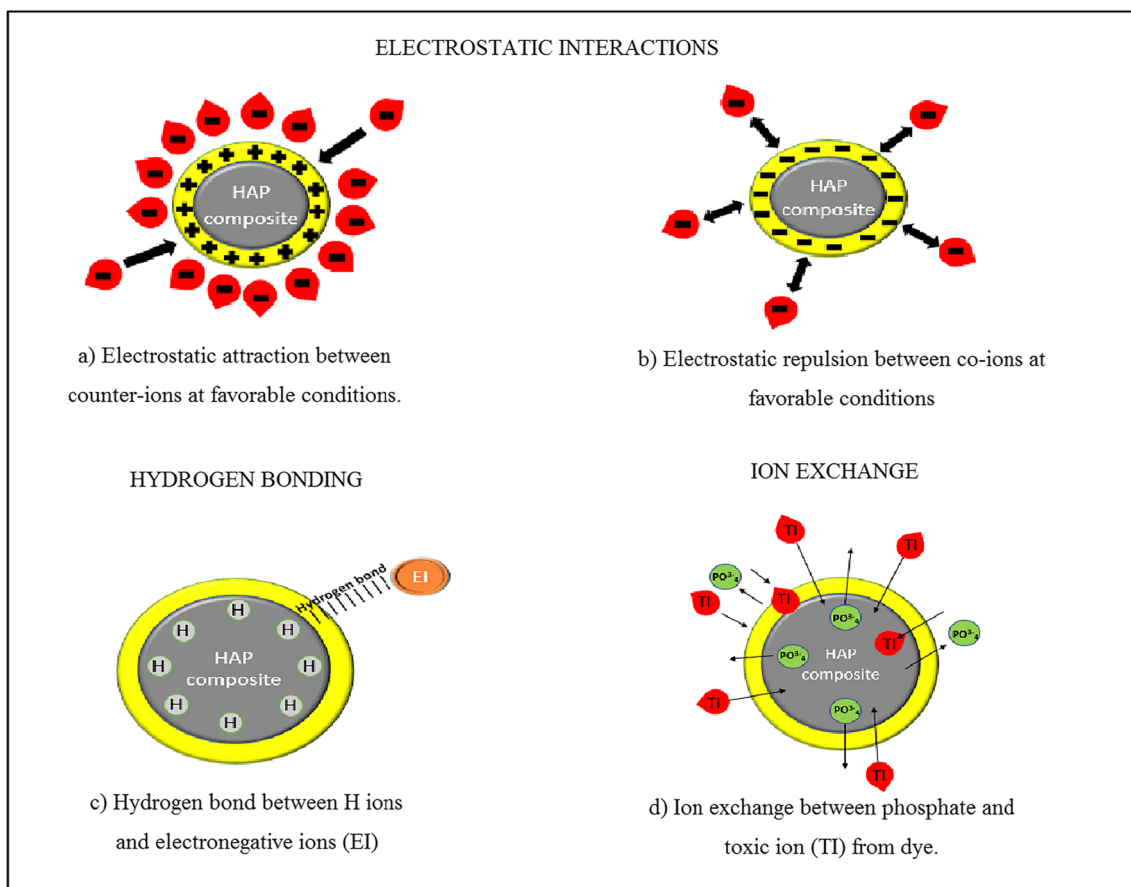


Fig. 6 Pictorial representation of a) electrostatic attraction, b) electrostatic repulsion, c) hydrogen bond, and d) ion exchange effects between dye molecules and HAP composites

Thermodynamics study

Thermodynamics relates adsorption isotherms in equilibrium and reveals the spontaneity of the process (Myers 2002). There are three main parameters considered such as (i) Gibb’s free energy, indicating spontaneity of reaction, (ii) enthalpy, indicating exothermic and endothermic nature of the reaction, and entropy which is calculated by using equations given below.

$$\Delta G = -RT \ln K_d \tag{6}$$

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{7}$$

$$\Delta G = \Delta H - T\Delta S \tag{8}$$

where K_d is the distribution coefficient.

HAP/zein composite was used to adsorb Congo red in Nasab et al., (2018). Thermodynamic parameters were calculated by Vant Hoff’s equation indicating reaction being spontaneous and endothermic. Similar results were obtained in a study where methyl orange is adsorbed on HAP composite (Azzaoui et al. 2019), methylene blue was adsorbed on HAP

composite (Y. Wang et al. 2017), and malachite green adsorption on HAP composite (Hosseinzadeh and Ramin 2018).

Methylene blue adsorption by HAP/alginate composite revealed that the adsorption process was spontaneous and exothermic, and ΔS being positive indicated nonaffinity of adsorbate extending the reaction process (Aslanov et al., 2017). Methylene blue adsorption by HAP/ polyacrylamide composite showed that the reaction is exothermic. Spontaneity reduced with an increase in the temperature, and ΔS being negative indicated a reduction in affinity of adsorbent and adsorbate at the interface (Mansri et al., 2019).

Regeneration of HAP nanocomposites

The overall waste management system is crucial in every aspect. Reduction in the amount of waste can be accomplished by three R’s “Reduce, Reuse, Recycle.” The adsorbent can be reused after desorption. Generally, a solvent is used against saturated adsorbent which causes it to release the adsorbed pollutant. In the case of MHAP, it is easy to remove adsorbent from the solution by using a neodymium magnet even though there is a slight reduction in adsorption capacity for each cycle

after adsorption (Zhang et al. 2016). Practical application is directly dependent on good reusability.

HAP/biochar composite saturated with methylene blue dye was desorbed using weak acid as a solvent. A remarkable reduction in adsorption was found in the first cycle due to the solubility of HAP in weak HCl used as solvent (Y. Li et al. 2018). HAP/chitosan composite saturated with methylene blue and sunset yellow was desorbed by washing several times with deionized water followed by water-ethanol mixture at pH 12. No adsorbent loss or reduction in adsorption capacity of desorbed samples was found up to five cycles signifying stability of composite at a wide pH range (Chatterjee et al. 2018).

Conclusion and future scope

This review is summarized to give a brief idea about both anionic and cationic dye removal by various HAP nanocomposites and study their adsorption mechanism. Electrostatic interactions, hydrogen bonding, and ion exchange effects are the three main dye removal mechanisms that are concisely discussed. The review discloses that the greater adsorption capacity is a result of either modified or composite adsorbent with a high surface area. Besides, the constraints such as pH, initial dye concentration, temperature, and adsorbent dose are vital factors which illustrate substantial effects on dyes adsorption. Frequently used isotherms, kinetic models, and thermodynamic equations that describe the adsorption process with its type and nature are conversed in this review. Future studies can be done on the simultaneous removal of different constituents from dye effluents rather than focusing only on color removal. Being eco-friendly, synthesizing different adsorbents via green route is the area of interest that can be investigated. Cost analysis is an important factor that can be done in further studies.

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