G- Journal of Environmental Science and Technology

www.gjestenv.com

REVIEW ARTICLE

Removal of organic and inorganic pollutants from the water using various adsorbents: A review

Shalu Rawat, Lata Verma, Chandra Bhan and Jiwan Singh*

Department of Environmental Science, B.B. Ambedkar University (A Central University), Lucknow, U.P. INDIA

Received: 14 June 2019; *Revised:* 11 Aug 2019; *Accepted:* 18 Sep 2019

ABSTRACT

Today purification of water is essential and to fulfil the water demand of the growing population and shrinking water resources. In last decades due to industrialization and overpopulation, the water quality is been degraded not only of surface water but also of ground water because of constant release of industrial effluent directly to the water bodies without any primary treatment and over exploitation on ground water. Among several water treatment technology adsorption is mostly considered one that is easy to manage, demand less cost and energy. However, synthesis of an effective environmentally benign and economically sustainable adsorbent is the centre of focus of researchers these days. There are various adsorbents like nanoparticles, activated carbon and zeolite etc. are being used yet for the removal of various water pollutants. In this chapter, the adsorbents are divided into three categories natural, carbonaceous and nanoparticles and their various uses in water treatment are described.

***Key words*:** water pollutant; absorbent: nanoparticles; activated carbon; zeolite

1) INTRODUCTION

Water is one of the primary needs for the entire organisms living on the earth. The need of water is growing more and more due to the increasing world population and over exploitation of the water resources [1]. Moreover, the water bodies are being polluted by several anthropogenic activities, several industrial effluents, and municipal wastewater are discharged directly into the river, oceans and other water bodies. These effluents contain different types of organic and inorganic chemical compounds. They pollute the surface water and ground water at an extreme level which is not fit for the consumption of humans and animal [2]. The coloured effluents from dyeing industries not only degrade the water quality, but it also hinders the photosynthesis phenomenon [3]. The industrial effluents contain several non-biodegradable, toxic, mutagenic and carcinogenic compounds that pose serious threat to health of all flora and fauna. Removal of these pollutants from the water is the need of the time to cope with the rising water crisis in the world. Several methods are applied for the removal of water pollutants like coagulation, flocculation, membrane filtration, reverse osmosis, ozonolysis electrostatic precipitation and adsorption among them adsorption is the widely accepted technology due to its operative ease and low cost [4]. It allows the removal of inorganic as well as organic pollutants from water. Several types of adsorbents have been utilized for water remediation till now that mainly includes activated carbons, activated alumina, zeolite, biosorbents and nanoparticles. Nanoparticles besides being a good adsorbent they also have antimicrobial activities that make them more efficient. In this chapter the adsorbents are categorised in three part i) adsorbent prepared from natural material (clay zeolite etc.), ii) carbonaceous adsorbents (biochar, activated carbon etc.) and iii) metallic nanaoparticles (iron nanoparticles; FeNPs, silver nanoparticles; AgNPs).

2) APPLICATION OF NATURAL MATERIALS AS ADSORBENT

The natural materials are known as emerging adsorbent due to their easy availability and abundance in nature, which have been used in removal of various inorganic and organic pollutants from wastewater and drinking water for decades. The clay is phyllosilicates having different types of mineral groups such as bentonite, kaolinite, montmorillonite, smectite, Illite etc. [5]. Clay minerals are mainly composed of silica and alumina having small particle size and formed by weathering of rocks [6]. Clay minerals and zeolite are considered as very effective adsorbent because they have high cation exchange capacity. Modification of natural materials for enhancement of adsorption capacity is a new development for removal of toxic pollutants from wastewater. The adsorptive behaviour of a number of natural materials and modified form of natural materials and their application for removal of pollutants are discussed as following.

* Corresponding Author: **Dr. Jiwan Singh**
Email address: jiwansingh95@gmail.com

2.1 Application of clay for adsorption of fluoride

Number of researchers studied the preparation and application of natural materials for removal of fluoride from water. Tor et al. [7] employed the red mud to prepare granular red mud (GRM) as adsorbent. GRM was synthesized by using raw red mud, fly ash and sodium carbonate, quicklime and sodium silicate and the prepared GRM used for fluoride adsorption by batch and column process. Kir et al. [8] used acid activated natural diatomite and ignimbrite for fluoride removal. Both natural materials were activated with 2 mol/L of sulfuric acid and the maximum removal of fluoride was found to be 12.03 and 8.82 mmol/g, respectively. Garcia-Snchez et al. [9] studied the adsorption effect of modified magnetite for fluoride. The magnetite was treated with lanthanum oxide and aluminum oxide and found 96 and 90% for each modified magnetite, respectively. Tang et al. [10] performed the enhancement of fluoride adsorption by using hydroxyapatite with carbon nanotubes (CNT-HAP). CNT-HAP was prepared by co-precipitation process and adsorption capacity of it was obtained to be 11.05 mg/g. Iriel et al. [11] investigated the application of laterite soil in fluoride removal from ground water. After treatment 0.48 mg/g fluoride adsorbed on the laterite.

2.2 Application of clay minerals for removal of dyes

The montmorillonite clay mineral has been modified by metals ions (Li^+, K^+, Na^+, Cs^+ and Rb^+) and used for removal of dye (Fluorescence sodium). These metal ions were used as solution of metal chloride. It was found that montmorillonite modified by Na^+ have maximum adsorption capacity (70.1 mmol/g) followed by Li^+, K^+, Rb^+ and Cs^+ modified montmorillonite clay [12]. Makhoukhi et al. [13] used modified bentonite for removal of dyes (Telon-orange, Telon-blue and Telon-red). The bentonite was modified by bis-imidazolium cations. The adsorption capacity was found to be 437.96 mg/g for Telon-Red, 108.3 for Telon-Orange and 82.4 for Telon-Blue. Eren et al. [14] investigated the use of modified bentonite for removal of basic dye (crystal violet) from aqueous solution. Magnesium-oxide was used for coating of bentonite and after treatment the maximum removal capacity was observed to be 496 mg/g of crystal violet.

The effective adsorption of acid red has been found on natural clay material without any modification. The highest adsorption of acid red was found 1133.1 mg/g on natural clay in 15 min at 2 pH [15]. Ibrahim et al. [16] applied clay soil for removal of Methylene blue and crystal violet dyes from aqueous solution. The maximum adsorption of MB and CV was found 47.8 and 35.7 mg/g, respectively by the clay soil. Various researchers were investigated that different types of natural materials are very effective for removal of dyes.

2.3 Application of zeolite for adsorption of fluoride

Ma et al. [17] applied the modified zeolite in fluoride removal from wastewater. Zeolite was modified by aluminum (III), magnesium (II) and titanium (IV) using $Al_2(SO_4)_3$, $MgSO_4$ and $Ti(SO_4)_2$. Removal capacity of Ti(IV) modified zeolite was found best than Al(III) and Mg(II) and having 1.64 mg/g. Sun et al. [18] prepared the adsorbent from natural zeolite (stilbite) and applied for fluoride adsorption. The natural zeolite powder heated at 555 °C in the presence of N_2 and obtained heated material treated with $FeCl_3$ and the removal efficiency was found 2.31 mg/g for modified zeolite. Lai et al. [19] employed the lanthanum (La^{3+}) modified zeolite at two different temperature 303 and 313 K. The adsorption capacity was 20.8 and 23.04 mg/g of both adsorbent, respectively for fluoride adsorption.

Dessalegne et al. [20] reported the aluminum hydroxide modified zeolite and the modification of it was done by aluminum sulfate. It was used in adsorption of fluoride and the adsorption capacity was found to be 12 mg/g which was higher about 12 folds than raw zeolite. Velazquez-Pena et al. [21] preformed the fluoride removal from aqueous solution using different types of modified zeolite. Mordenite, clinoptilolite and chabazite were modified with zirconium, iron and combination of both (iron-zirconium). The adsorption capacity was found to be 3.5 mg/g, 2.6 mg/g and 1.8 mg/g for FeZr modified mordenite, chabazite and clinoptilolite, respectively. Teutli-Sequeira et al. [22] used zeolite and hematite as adsorbent for removal of fluoride by batch and column process. The both materials were modified by aluminum and maximum uptake of fluoride was found 3.3 and 2.3 mg/g, respectively.

Synthesis of zeolite from fly ash is a new development of adsorbent preparation for water treatment. Panda et al. [23] synthesized the zeolite by using coal fly ash and sodium hydroxide and applied for removal of fluoride. The synthetic zeolite has good efficiency of adsorption observed. More than 85% removal of fluoride was found at normal conditions. Mukherjee et al. [24] reported 22.83 mg/g of adsorption capacity of fluoride on synthetic zeolite prepared by using rice husk ash.

2.5 Application of zeolite for adsorption of Arsenic

Lizama-Allende et al. [25] reported the use of zeolite and limestone in arsenic removal. The highest adsorption capacity was observed to be 0.17 and 1.3 mg/g of arsenic on zeolite and limestone, respectively. Melak et al. [26] evaluated the removal capacity of arsenic(V) by two types of materials stellerite and quartz tuff and the arsenic uptake was found 0.23 mg/g for stellerite and 0.42 mg/g for quartz. Clinoptilolite zeolite in the nano form used after modification with sulfuric acid and applied for adsorption of arsenic. The maximum removal was taken place 96.7% under suitable condition [27]. Khatamian et al. [28] investigated the arsenic removal capacity by using reduced graphene oxide (RGO), magnetite (Fe_3O_4) containing RGO and copper exchanged zeolite (Cu-ZEA). Graphene oxide was prepared by graphene powder, $NaNO_3$, and $KMnO_4$. Soni et al. [29] prepared the zeolite from coal fly ash and sodium hydroxide and graphene oxide (GO) also prepared by combination of graphite, $KMnO_4$, $NaNO_3$ and hydrogen peroxide. Finally, ZrGO synthesized with equal proportion of zeolite and GO and adding N-methyl-2-pyrrolidone. The synthesized ZrGO was used for adsorption of arsenic from aqueous solution and the highest removal capacity was observed to be in the range of 49.2-145.9 μg/g.

2.6 Application of natural materials for heavy metals removal from water

Various researchers investigated that natural materials have effective adsorption capacity for heavy metals and some studies related heavy metal removal are given in the Table 1.

3) APPLICATION OF CARBONACEOUS BIOADSORBENTS FOR THE REMOVAL OF ORGANIC AND INORGANIC POLLUTANTS

Water pollution and clean water availability to everyone is one of the leading problems in developing countries like India. Various treatment methods were used worldwide to tackle the problem of water contamination such as filtration, precipitation, ion exchange, membrane filtration, coagulation and adsorption. Among all these treatment methods adsorptions through carbonaceous bioadsorbent is feasibly one of the most effective treatment methods for the removal of water contaminants [36]. Carbon-based bioadsorbents like activated carbon, biochar, graphene and its derivatives and carbon nanotubes etc. are widely used for the removal of water contaminants from aqueous solution and natural water [37].

Various studies have been done by the researchers to explore the potential of these bioadsorbents for decontaminating the contaminated water and focusing on the sorption characteristics. For the treatment of water and wastewater activated carbon has been extensively used but the production cost of coal-based activated carbon is very high [38]. Biochar is an emerging low-cost alternative of activated carbon having high pore density and large surface area. The carbonaceous materials were prepared by waste biomass of rice husk, plant leave litter, sawdust, peanut peel, fruit waste residue, wood bark, solid waste etc. that solve not only the water treatment issue but also helps in managing the waste materials [39]. For the removal of organic and inorganic pollutant from water these carbonaceous biosorbents were efficiently used. The adsorption capacities of various bioadsorbents are given in Table 2.

3.1 Application of carbonaceous materials for the removal of inorganic pollutants

Verma and Singh [40] in their study shows the successful removal of As(III) and As(V) using biochar prepared from plant litter waste biomass at 800 °C. Maximum adsorption of As(III) was found to be 76.4% and 68.9% by TB-800 and LB-800, respectively. However, the removal of As(V) was 95.6% by TB-800 and 80.3% by LB-800. The adsorption capacity was found to be increased with increasing initial

Table 1. Various natural materials for the removal of heavy metals

Natural Materials	Modification	Heavy metals	Adsorption capacity/percent	References
Bentonite		Ni and Mn	90%	[30]
Clay (Polygorskite)	Mg-Al	Pb^{2+} Cu^{2+} Ni^{2+}	433.8 mg/g -	[31]
Zeolite	Fe(III)	Zn^{2+} Pb^{2+} Cd^{2+}	- 80% -	[32]
Zeolite	Zero-valent iron	Pb^{2+} Cd	154.6 mg/g 63.1 mg/g	[33]
Zeolite	Imidazolate	Pb^{2+} Cu^{2+}	99.4% 97.4%	[34]
Montmorillonite	Sodium lignosulfonate	Pb^{2+} Cu^{2+}	144 mg/g 31.4 mg/g	[35]

Table 2. Adsorption capacity of different bioadsorbent for organic and inorganic pollutants.

S.No.	Adsorbate	Adsorbent (material used)		Adsorption capacity (mg/g)	References
1.	Phenol	Activated Carbon	CHAC-250	6.468	[42]
		(corn husk)	CHAC-500	8.44	
2.	p-Nitro phenol	Activated Carbon	CHAC-250	9.930	[42]
		(corn husk)	CHAC-500	11.668	
3.	As(III)	Biochar	TB-800	0.666	[40]
		(leaves waste)	LB-800	0.454	
4.	As(V)	Biochar	TB-800	1.250	[40]
		(leaves waste)	LB-800	0.714	
5.	Fluoride	Biochar (tea waste)		52.57	[43]
6.	Fluoride	Activated carbon (*Moringa indica*)		0.23	[44]
7.	Norfloxacin	Biochar (corn stalk)		7.624	[45]

arsenic concentration. The regeneration study of the biochar materials revealed that the biochar can be reutilized up to 4 cycles effectively.

Citrus limmeta pulp residue was utilized for the preparation of activated carbon at two different temperatures i.e., 250 and 500°C, modified with $FeCl_3$ for developing magnetic properties in the activated carbon and its application for the removal of Fluoride from aqueous solution. The adsorption capacity for Fluoride by ACP-250 was 7.75 mg/g and 12.62 mg/g by ACP-500. Maximum adsorption of fluoride was observed at pH 4 i.e., 76.5% and 74% through ACP-250 and ACP-500, respectively [41].

Non- lignocellulosic material (sludge) was used to synthesize the biochar obtained from anaerobic digestion and then applied for the removal of Pb. Different pyrolysis temperature were used to prepare the biochar materials. It was found that the biochar synthesized at 600 °C temperature shows effective removal of Pb with adsorption capacity 51.20 mg/g. Langmuir model of isotherm and pseudo-second-order kinetics was best fitted to the experimental data [46].

He et al, [47] studied about the removal of As(V) using iron infused biochar and pristine biochar synthesized from corn straw and the results shows that the biochar treated with iron removed As from aqueous solution more efficiently in comparison with the pristine biochar that show less efficiency in removing As from the aqueous solution. The magnetic biochar composite showed superb characteristics like good thermal stability, large surface area, many oxygen containing functional groups etc. that enhanced the removal efficiency of the biochar for As(V).

3.2 Application of carbonaceous materials for the removal of organic pollutant

Crystal violet dye was successfully removed from aqueous solution by utilizing *Acacia mearnsii* waste for the development of an adsorbent through acetosolv method. The process of adsorption was endothermic in nature and favorable. Freundlich adsorption isotherm was well fitted to the experimental data and the maximum adsorption capacity was found to be 280 mg/g. the equilibrium was observed within 2 h and the maximum removal of crystal violet dye was found to be 95% in alkaline medium (pH 10) [48]. Hameed and Khaiary, [49] worked on the removal of malachite green dye through rattan sawdust and found that the adsorption capacity was 62.71 mg/g and the process of adsorption was homogenous in nature means followed Langmuir model of isotherm. In this study initially the rate of adsorption process was controlled by the film diffusion but after a certain time period or longer adsorption time it was controlled by the pore diffusion. Earthworm manure was used for the synthesis of biochar material at 400-600 °C temperatures and applied for the adsorption of Rhodamine B dye from an aqueous solution. The removal percentage was quite good with monolayer adsorption on homogenous surface.

4) SYNTHESIS OF METALLIC NANOMATERIALS AND THEIR APPLICATIONS FOR THE REMOVAL OF ORGANIC AND INORGANIC POLLUTANTS

Nanotechnology is an emerging and one of the fastest growing technologies. It has many advantages over other technologies. The nanotechnology use in several domestic and industrial aspects has served as a boom [50]. Nanomaterials can be defined as the particles having size within the range of 1-100 nm, in this size range the physical and chemical properties changed far from their bulk and molecular size [51], they possess characteristics features, they have a high surface to volume ratio that make them highly reactive, magnetic and electrically active. They are used because of their adsorption, catalysis, photo-catalysis, bio sensing, antibacterial, drug delivery, and optical sensation capabilities. Now a day nanoparticles have a wide field for usage such as environmental remediation, medicinal use, electrical use, uses in cosmetics and biotechnology [52]. Nanomaterials are offering advance water treatment methods. In the upcoming year the utilization of nanomaterials is expected to get increase in various industrial processes that will help in process cost reduction by enhancement of the process efficiency, use of less energy and making process more environmentally reliable. However, it may not cope with all the global problems by the increasing world population but the nanotechnology will help to have a sustainable development in many social aspects [51].

4.1. Synthesis of metallic nanoparticles

The nanomaterial can be prepared by two way firstly by broking larger bulk material into the nanosized material and secondly from the atomic size to nano-size by self-aggregation chemically or biologically [53]. The first method is referred as "top to bottom approach" which is mainly done by evaporation and condensation using tube furnace, ball milling, lithography ultrasonic and high energy irradiation and the second method is referred as "bottom to top approach" in which nanomaterials are obtained by the chemical reduction method through which the metals are reduced using a strong reducing agents like Sodium borohydride ($NaBH_4$), sodium citrate, Tollen's regent etc. Green synthesis of the nanoparticles is an emerging alternative technique that replaces the use of environmentally harsh chemicals and promises a environmentally safe and comparatively cheaper synthesis of nanoparticles. The green synthesis of nanoparticles focuses on the uses of microbial and plant entities. Lyudmila et al. [54] reported synthesis of silver nanoparticles using *Pseudomonas* Sp. Gong et al. [55] reported in his study one step synthesis of zinc sulfide nanoparticles by the use of *Desulfovibrio desulfuricans*. However, a major focus of the researches has now been shifted towards utilizing plant for the green synthesis of nanoparticles. This is due the simpler and easier process, a higher availability of plants, with less operational cost and producing nanoparticles in comparatively higher mass. Plants have so many phytochemical compounds like alkaloids, flavonoids, saponins, reducing sugars, phenolic compounds, terpenoids and many more that work as a reducing agent and replaces the toxic and hazardous chemical reducing agents. Moreover, these phytochemical compounds also serves as a capping agent that we have to provide additionally in chemical synthesis, a capping agent is a chemicals that cover ups the nanoparticles surface and give it protection from being oxidised and also provide stability to the nanoparticles. Sadeghi and Gholamhoseinpoor, [56] reported synthesis of stable silver nanoparticles with average size 20nm by using *Ziziphora tenuior* leaf extract. Various plant extracts have been used yet for the synthesis of different metallic nanoparticles a list of some of the plants have been given in the Table 3 that have been successfully used for nanoparticle synthesis. Beside plants several organic wastes have also been explored for the green synthesis, it reduces the synthesis cost more and it is also a method for the minimization organic waste. Different wastes like tea waste [57], fruit peel [58], coconut shell [59], agroforestry waste (*Moringa oleifera* petals) [60], banana peel [61], *Citrullus lanatus* rind [62], onion peel [63], Citrus maxima peel [64], sapota fruit waste [65], Almond hull [66], waste mangosteen pericarp [67] are successfully used for the preparation of extract for the fabrication of different nanoparticles. A description of some of the mostly used metallic nanoparticles and their applications are given below.

4.2. Silver nanoparticles

Silver nanoparticles (Ag-NPs) are proved to be an effective antimicrobial and anti-inflammatory agent they are mainly used in biomedical, water treatment, drug delivery and agricultural fields [78]. Today the synthesis of Ag-NPs is done by various physical and chemical processes that includes gamma rays irradiation, Laser ablation, chemical reduction, electrochemical and photochemical methods at industrial level. Silver nitrate is used as Ag precursor mainly for Ag-NPs synthesis apart from its silver chloride is also used. Different types of Ag-NPs shapes rods, sphere, triangular and cubes are obtained using different fabrication methods [79]. Shape and size of the Ag-NPs controls their antimicrobial activity, particles of 8 nm size and particles in triangle shapes are found to be most effective [80]. Immobilization of Ag-NPs on by embedding on membrane enhance their antimicrobial activity on immobilization they are found effective for both Gram negative and Gram-positive bacteria. Ag-NPs are also successfully applied for the diagnosis and treatment of cancer [53].

4.3. Gold nanoparticle

Gold nanoparticles Au-NPs have several applications bio-labelling, drug delivery, therapeutics, detection and diagnosis. They have this wide field of application due to their large surface to volume ratio, monodisperserity, low toxicity, tunable core size, multi-functionalization, simple fabrication process, high X-ray absorption coefficient, strong binding affinities with thiol, amide and sulphide groups and characteristic electronic features [81][82]. Au-NPs have also many applications in imaging and microscopy as they offer to tune their optical properties by adjustment in their diameter and shell thickness [83]. They have also emerged as an excellent material in biosensing due to their specific features they allow their safe integration into the sensing system for both in vivo and in vitro detection [84].

4.4. Titanium oxide nanoparticles

Titanium oxide nanoparticles (TiO_2) emerged as a most promising photo-catalyst they are used for the catalytic degradation organic pollutants. TiO_2 are good photo-catalyst along with it they are non-toxic the basic mechanism behind their working is the generation of highly reactive OH radicals antagonistic effects on the bacteria, fungi, algae and virus. The doping of transition metal to TiO_2 enhanced it photo-catalysis capability from UV region to the visible light region. They have shown their great potential for the disinfection of water [85]. TiO_2 films and rods are reported to be more effective photocatalyst in comparison with TiO_2 nanoparticles that are commercially available. TiO_2 is an efficient photocatalyst and disinfectant however the mechanisms behind them are still not well known.

4.5. Iron oxide nanoparticles

Since last decade the iron nanoparticles (FeNPs) are being used for the environmental remediation due to its high surface area, a wide distribution of reactive sites and unique adsorption efficiency [77]. Iron nanoparticles are also widely used in medical, environmental and other sector. Iron and iron oxide nanoparticles are used in MRI techniques, catalysis, drug delivery system, immunoassay. Iron oxide nanoparticles with the particle size less than 20 nm and composed of ferromagnetic material have super para-magnetism property. Iron nanoparticle are widely

Table 3. Different plants have been used for the green synthesis of nanoparticles

NPs	Plant extract used	Application	References
Ag-NPs	*Emblica officinalis*	Antibacterial	[68]
Ag-NPs	*Ocimum sanctum*	Antibacterial	[69]
Ag-NPs	*Trifolium resupinatum*	Antifungal	[70]
Ag-NPs and ZnO	*Heritiera forms* and *Sonnerratia apetala*	Biomedical	[71]
Cu-NPs	*Eclipta prostrata*	Antitoxicant and cytotoxic test	[72]
CuO	*Madhuca longifolia*	Water treatment and antibacterial	[73]
CuO	*Pterospermum acerifolium*	Toxicity comparison	[74]
ZVI	*Spinacea oleracea*	Wastewater treatment	[75]
Iron oxide nanoparticles	Turmeric and mosambi	Municipal wastewater treatment	[76]
FeNPs	*Azadirachta indica*	Domestic wastewater treatment	[77]

used for the adsorption as well as catalytic degradation of organic pollutants for their removal from water they are used for the removal organic pollutants, inorganic pollutants and pathogenic bacteria [86]. Nano zerovalent iron (nZVI) are also used for the removal of metal and metalloid removal from water like Arsenic [87], copper [88] chromium [89] etc. Radioactive element such as uranium dioxide were also removed by bisphosphonate modified magnetite.

5) CONCLUSION

Adsorption is an effective technique for the purification of water several types of adsorbents are been explored for this purpose. Utilization of natural materials for the preparation of adsorbents may decrease the preparation cost. The fabrication of biosorbents by the carbonization of the biomass is also an economic way and biosorbents preparation from waste biomass also helps in the reduction of waste biomass that creates a nuisance in the environment if not properly managed. Utilization of nanoparticles as adsorbents for water remediation is comparatively costly due to its synthesis method, however, this can be overcome by the green synthesis approach in addition nanopoarticles have several other properties, like photocatalytic activity and antimicrobial activity.

REFERENCES

1) Sabzoi, N., Siddiqui, M.T.H., Mubarak, N.M., Baloch, H.A., Abdullah, E.C., Shaukat, A.M., Griffin, G.J., Srinivasan, M.P. and Tanksale, A. 2018. Iron Oxide Nanomaterials for the Removal of Heavy Metals and Dyes from Wastewater. In Nanoscale Materials in Water Purification, 447-472, 10.1016/B978-0-12-813926-4.00023-9.
2) Radwan, M.A., Rashad, M.A., Sadek, M.A. and Elazab, H.A. 2019. Synthesis, characterization and selected application of chitosan-coated magnetic iron oxide nanoparticles. Journal of Chemical Technology and Metallurgy, 54(2), 303-310
3) Kouhbanani, M.A.J., Beheshtkhoo, N., Taghizadeh, S., Amani, A.M. and Alimardani, V. 2019. One-step green synthesis and characterization of iron oxide nanoparticles using aqueous leaf extract of *Teucrium polium* and their catalytic application in dye degradation. Advances in Natural Science: Nanoscience and Nanotechnology, 10:015007
4) Li, X., Yu, J., Li, G., Liu, H., Wang, A., Yang, L., Zhou, W., Chu, B. and Liu, S. 2018. TiO2 nanodots anchored on nitrogen-doped carbon nanotubes encapsulated cobalt nanoparticles as photocatalysts with photoenhanced catalytic activity towards the pollutant removal. Journal of Colloid and Interface Science, 526, 158-166.
5) Kausar, A., Iqbal, M., Javed, A., Aftab, K., Bhatti, H.N. and Nouren, S. 2018. Dyes adsorption using clay and modified clay: a review. Journal of Molecular Liquids, 256, 395-407.
6) Prabhakaran, R., Babu, K. and Suramanian, P. 2016. Characterization of clays in Trichinopoly group Tamilnadu, India. IJCS, 4(2), 75-77.
7) Tor, A., zhoglu, N., Arslan, G. and Cengeloglu, Y. 2009. Removal of fluoride from water by using granular red mud: batch and column studies. Journal of hazardous materials, 164(1), 271-278.
8) Kır, E., Oruc, H., Kır, I. and Sardohan-Koseoglu T. 2016. Removal of fluoride from aqueous solution by natural and acid-activated diatomite and ignimbrite materials. Desalination and Water Treatment, 57(46), 21944-21956.
9) Garcia-Sanchez, J. J., Solache-Rios, M., Martinez-Gutierrez, J.M., Arteaga-Larios, N.V., Ojeda-Escamilla, M.C. and Rodriguez-Torres, I. 2016. Modified natural magnetite with Al and La ions for the adsorption of fluoride ions from aqueous solutions. Journal of Fluorine Chemistry, 186, 115-124.
10) Tang, Q., Duan, T., Li, P., Zhang, P. and Wu, D. 2018. Enhanced defluoridation capacity from aqueous media via hydroxyapatite decorated with carbon nanotube. Frontiers in chemistry, 6, 104.
11) Iriel, A., Bruneel, S.P., Schenone, N. and Cirelli, A.F. 2018. The removal of fluoride from aqueous solution by a lateritic soil adsorption: kinetic and equilibrium studies. Ecotoxicology and environmental safety, 149, 166-172.
12) Belbel, A., Kharroubi, M., Marc, J., Abdessamad, M., Haouzi, A., Lefkaier, I.K., and Balme, S. 2018. Preparation and characterization of homoionic montmorillonite modified with ionic liquid: Application in dye adsorption, Colloids and Surface A: Physicochemical and Engineering Aspects, 558, 219-227.
13) Makhoukhi, B., Djab, M. and Didi, M.A. 2015. Adsorption of Telon dyes onto bis-imidazolium modified bentonite in aqueous solutions. Journal of Environmental Chemical Engineering, 3(2), 1384-1392.
14) Eren, E. 2009. Investigation of a basic dye removal from aqueous solution onto chemically modified Unye bentonite. Journal of Hazardous Materials, 166(1), 88-93.
15) Akar, S.T. and Uysal, R. 2010. Untreated clay with high adsorption capacity for effective removal of CI Acid Red 88 from aqueous solutions: Batch and dynamic flow mode studies. Chemical Engineering Journal, 162(2), 591-598.
16) Ibrahim, A., El Fawal, G.F. and Akl, M.A. 2019. Methylene Blue and Crystal Violet Dyes Removal (As A Binary System) from Aqueous Solution Using Local Soil Clay: Kinetics Study and Equilibrium Isotherms. Egyptian Journal of Chemistry, 62(3), 541-554.
17) Ma, Z., Zhang, Q., Weng, X., Mang, C., Si, L., Guan, Z. and Cheng, L. 2018. Fluoride ion adsorption from wastewater using magnesium (II), aluminum (III) and titanium (IV) modified natural zeolite: kinetics, thermodynamics, and mechanistic aspects of adsorption. Journal of Water Reuse and Desalination, 8(4), 479-489.
18) Sun, Y., Fang, Q., Dong, J., Cheng, X. and Xu, J. 2011. Removal of fluoride from drinking water by natural

stilbite zeolite modified with Fe (III). Desalination, 277(1-3), 121-127.
19) Lai, Y.Q., Kai, Y., Chao, Y., Tian, Z.L., Guo, W.C. and Jie, L.I. 2018. Thermodynamics and kinetics of fluoride removal from simulated zinc sulfate solution by La (III)-modified zeolite. Transactions of Nonferrous Metals Society of China, 28(4), 783-793.
20) Dessalegne, M., Zewge, F. and Diaz, I. 2017. Aluminum hydroxide supported on zeolites for fluoride removal from drinking water. Journal of Chemical Technology & Biotechnology, 92(3), 605-613.
21) Velazquez-Pena, G.C., Olguin-Gutierrez, M.T., Solache-Rios, M.J. and Fall, C. 2017. Significance of FeZr-modified natural zeolite networks on fluoride removal. Journal of Fluorine Chemistry, 202, 41-53.
22) Teutli-Sequeira, A., Solache-Rios, M., Martínez-Miranda, V. and Linares-Hernández, I. 2015. Behavior of fluoride removal by aluminum modified zeolitic tuff and hematite in column systems and the thermodynamic parameters of the process. Water Air & Soil Pollution, 226(8), 239.
23) Panda, L. and Kar, B.B. 2018. Preparation of Fly Ash Based Zeolite for Fluoride Removal. Asian Journal of Water, Environment and Pollution, 15(4), 105-113.
24) Mukherjee, S., Barman, S. and Halder, G. 2018. Fluoride uptake by zeolite NaA synthesized from rice husk: Isotherm, kinetics, thermodynamics and cost estimation. Groundwater for Sustainable Development, 7, 39-47.
25) Lizama-Allende, K., Henry-Pinilla, D., and Diaz-Droguett, D.E. 2017. Removal of arsenic and iron from acidic water using zeolite and limestone: batch and column studies. Water, Air, & Soil Pollution, 228(8), 275.
26) Melak, F., Alemayehu, E., Ambelu, A., Van Ranst, E. and Du Laing, G. 2018. Evaluation of natural quartz and zeolitic tuffs for As (V) removal from aqueous solutions: a mechanistic approach. International journal of environmental science and technology, 15(1), 217-230.
27) Shokrolahzadeh, A., Shokuhi, R.A. and Adinehvand, J. 2017. Modification of nano Clinoptilolite Zeolite using sulfuric Acid and its application toward removal of Arsenic from water sample. Journal of Nanoanalysis, 4(1), 48-58.
28) Khatamian, M., Khodakarampoor, N. and Saket-Oskoui, M. 2017. Efficient removal of arsenic using graphene-zeolite based composites. Journal of colloid and interface science, 498, 433-441.
29) Soni, R. and Shukla, D.P. 2019. Synthesis of fly ash based zeolite-reduced graphene oxide composite and its evaluation as an adsorbent for arsenic removal. Chemosphere, 219, 504-509.
30) Akpomie, K.G. and Dawodu, F.A. 2015. Potential of a low-cost bentonite for heavy metal abstraction from binary component system. Beni-suef university journal of basic and applied sciences, 4(1), 1-13.
31) Yang, F., Sun, S., Chen, X., Chang, Y., Zha, F. and Lei, Z. 2016. Mg–Al layered double hydroxides modified clay adsorbents for efficient removal of Pb2+, Cu2+ and Ni2+ from water. Applied Clay Science, 123, 134-140.
32) Mihajlovic, M.T., Lazarevic, S.S., Jankovic-Castvan, I.M., Kovac, J., Jokić, B.M., Janackovic, D.T. and Petrović, R.D. 2015. Kinetics, thermodynamics, and structural investigations on the removal of Pb 2+, Cd 2+, and Zn 2+ from multicomponent solutions onto natural and Fe (III)-modified zeolites. Clean Technologies and Environmental Policy, 17(2), 407-419.
33) Kong, X., Huang, G., Han, Z., Xu, Y., Zhu, M. and Zhang, Z. 2017. Evaluation of zeolite-supported microscale zero-valent iron as a potential adsorbent for Cd 2+ and Pb 2+ removal in permeable reactive barriers. Environmental Science and Pollution Research, 24(15), 13837-13844.
34) Huang, Y., Zeng, X., Guo, L., Lan, J., Zhang, L. and Cao, D. 2018. Heavy metal ion removal of wastewater by zeolite-imidazolate frameworks. Separation and Purification Technology, 194, 462-469.
35) Ma, J., Khan, M.A., Xia, M., Fu, C., Zhu, S., Chu, Y., Lei, W. and Wang F. 2019. Effective adsorption of heavy metal ions by sodium lignosulfonate reformed montmorillonite. International journal of biological macromolecules, 138, 188-197.
36) Yang, X., Wan, Y., Zheng, Y., He, F., Yu, Z., Huang, J., Wangh, H., Ok, Y.S., Jianga, Y. and Gao, B. 2019. Surface functional groups of carbon-based adsorbents and their roles in the removal of heavy metals from aqueous solutions: a critical review. Chemical Engineering Journal, 366, 608-621.
37) Ahmad, Z., Gao, B., Mosa, A., Yu, H.W., Yin, X.Q., Bashir, A., Ghoveisi, H. and Wang S.S. 2018. Removal of Cu(II), Cd(II) and Pb(II) ions from aqueous solutions by biochars derived from potassium-rich biomass. Journal of Cleaner Production, 180, 437–449.
38) Wang, B., Gao, B., Zimmerman, A.R. and Lee, X.Q. 2018. Impregnation of multiwall carbon nanotubes in alginate beads dramatically enhances their adsorptive ability to aqueous methylene blue. Chemical Engineering Research and Design, 133, 235–242.
39) Verma, L., Siddique, M.A., Singh, J. and Bharagava, R.N. 2019. As (III) and As (V) removal by using iron impregnated biosorbents derived from waste biomass of *Citrus limmeta* (peel and pulp) from the aqueous solution and ground water. Journal of environmental management, 250, 109452.
40) Verma, L. and Singh, J. 2019a. Synthesis of novel biochar from waste plant litter biomass for the removal of Arsenic (III and V) from aqueous solution: A mechanism characterization, kinetics and thermodynamics. Journal of environmental management, 248, 109235.
41) Ibrahim, M., Siddique, A., Verma, L., Singh, J., and Koduru, J.R. 2019. Adsorptive Removal of Fluoride from Aqueous Solution by Biogenic Iron Permeated Activated Carbon Derived from Sweet Lime Waste. Acta Chimica Slovenica, 66(1), 123-136.
42) Mishra, S., Yadav, S.S., Rawat, S., Singh, J. and Koduru, J.R. 2019. Corn husk derived magnetized activated carbon for the removal of phenol and para-nitrophenol from aqueous solution: Interaction mechanism, insights on adsorbent characteristics, and isothermal, kinetic and thermodynamic

properties. Journal of environmental management, 246, 362-373.
43) Roy, S., Sengupta, S., Manna. S. and Das, P. 2018. Chemically reduced tea waste biochar and its application in treatment of fluoride containing wastewater: Batch and optimization using response surface methodology. Process Safety and Environmental Protection, 116, 553-563.
44) Karthikeyan, G., Siva, S. and Elango. 2007. Fluoride sorption using *Morringa Indica* based activated carbon, Iran. Journal of Environmental Health Science and Engineering, 4
45) Wang, B., Jiang, Y.S., Li, F.Y. and Yang, D.Y. 2017. Preparation of biochar by simultaneous carbonization, magnetization and activation for norfloxacin removal in water. Bioresource technology, 233, 159-165.
46) Ho, S.H., Yang, Z.K., Nagarajan, D., Chang, J.S. and Ren, N.Q. 2017. High-efficiency removal of lead from wastewater by biochar derived from anaerobic digestion sludge. Bioresource technology, 246, 142-149.
47) He, R., Peng, Z., Lyu, H., Huang, H., Nan, Q., and Tang, J. 2018. Synthesis and characterization of an iron-impregnated biochar for aqueous arsenic removal. Science of the Total Environment, 612, 1177-1186.
48) da Silva, J.S., da Rosa, M.P., Beck, P.H., Peres, E.C., Dotto, G.L., Kessler, F. and Grasel, F.S. 2018. Preparation of an alternative adsorbent from *Acacia Mearnsii* wastes through acetosolv method and its application for dye removal. Journal of cleaner production, 180, 386-394.
49) Hameed, B.H., and El-Khaiary, M.I. 2008. Malachite green adsorption by rattan sawdust: Isotherm, kinetic and mechanism modelling. Journal of Hazardous Materials, 159(2-3), 574-579.
50) Mukherjee, R., Kumar, R., Sinha, A., Lama, Y. and Saha, A.K. 2016. A review on synthesis, characterization, and applications of nano zero valent iron (nZVI) for environmental remediation. Critical Reviews in Environmental Science and Technology, 46(5), 443–466.
51) Kyzas, G.Z., and Matis, K.A. 2015. Nano adsorbents for pollutants removal: A review. Journal of Molecular Liquids, 203, 159–168
52) Thakkar, K.N., Mhatre, S.S. and Parikh, R.Y. 2010. Biological synthesis of metallic nanoparticles. Nanomedicine: Nanotechnology, Biology, and Medicine, 6, 257–262.
53) Ahmed, S., Ahmad, M., Swami, B.L. and Ikram, S. 2016. A review on plants extract mediated synthesis of silver nanoparticles for antimicrobial applications: a green expertise. Journal of advanced research, 7(1), 17-28.
54) Lyudmila, Z., Noira, V., Sayora, R., Svetlana, K., Rokhilya, J. and Javlon, T. 2018. Microbial Synthesis of Silver Nanoparticles by Pseudomonas Sp. BioTechnology: An Indian Journal, 14(4), 169.
55) Gong, J., Song, X., Gao, Y., Gong, S., Wang, Y. and Han, J. 2018. Microbiological synthesis of zinc sulfide nanoparticles using *Desulfovibrio desulfuricans.* Inorganic and Nano-Metal Chemistry, 48(2), 96-102.
56) Sadeghi, B. and Gholamhoseinpoor, F. 2015. A study on the stability and green synthesis of silver nanoparticles using *Ziziphora tenuior* (Zt) extract at room temperature. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 134, 310–315.
57) Gautam, A., Rawat, S., Verma, L., Singh, J., Sikarwar, S., Yadav, B.C. and Kalamdhad, A.S. 2018. Green synthesis of iron nanoparticle from extract of waste tea: An application for phenol red removal from aqueous solution. Environmental Nanotechnology Monitoring and Management, 10, 377–387.
58) Nava, O.J., Soto-Robles, C.A., Gómez-Gutiérrez, C.M., Vilchis-Nestor, A.R., Castro-Beltrán, A., Olivas, A. and Luque, P.A. 2017. Fruit peel extract mediated green synthesis of zinc oxide nanoparticles. Journal of Molecular Structure, 1147, 1-6.
59) Sinsinwar, S., Sarkar, M.K., Suriya, K.R., Nithyanand, P. and Vadivel, V. 2018. Use of agricultural waste (coconut shell) for the synthesis of silver nanoparticles and evaluation of their antibacterial activity against selected human pathogens. Microbial pathogenesis, 124, 30-37.
60) Anand, K., Gengan, R.M., Phulukdaree, A. and Chuturgoon, A. 2015. Agroforestry waste *Moringa oleifera* petals mediated green synthesis of gold nanoparticles and their anti-cancer and catalytic activity. Journal of Industrial and Engineering Chemistry, 21, 1105-1111.
61) Bisauriya, R., Verma, D. and Goswami, Y.C. 2018. Optically important ZnS semiconductor nanoparticles synthesized using organic waste banana peel extract and their characterization. Journal of Materials Science: Materials in Electronics, 29(3), 1868-1876.
62) Patra, J.K. and Baek, K.H. 2015. Novel green synthesis of gold nanoparticles using *Citrullus lanatus* rind and investigation of proteasome inhibitory activity, antibacterial, and antioxidant potential. International journal of nanomedicine, 10, 7253.
63) Patra, J.K., Kwon, Y. and Baek, K.H. 2016. Green biosynthesis of gold nanoparticles by onion peel extract: synthesis, characterization and biological activities. Advanced Powder Technology, 27(5), 2204-2213.
64) Wei, Y., Fang, Z., Zheng, L., Tan, L. and Tsang, E.P. 2016. Green synthesis of Fe nanoparticles using *Citrus maxima* peels aqueous extracts. Materials Letters, 185, 384-386.
65) Vishwasrao, C., Momin, B. and Ananthanarayan, L. 2019. Green synthesis of silver nanoparticles using sapota fruit waste and evaluation of their antimicrobial activity. Waste and Biomass Valorization, 10(8), 2353-2363.
66) Rashidi, M., Islami, M.R. and Tikdari, A.M. 2019. Green synthesis of Pd nanoparticles supported on modified Nonpareil almond shell using almond hull extract: a beneficial nanocatalyst for convenient reduction of organic dyes. Journal of Materials Science: Materials in Electronics, 30(19), 18111-18122.

67) Park, J.S., Ahn, E.Y. and Park, Y. 2017. Asymmetric dumbbell-shaped silver nanoparticles and spherical gold nanoparticles green-synthesized by mangosteen (Garcinia mangostana) pericarp waste extracts. International journal of nanomedicine, 12, 6895-6908.
68) Ramesh, P.S., Kokila, T and Geetha, D. 2015. Plant mediated green synthesis and antibacterial activity of silver nanoparticles using *Emblica officinalis* fruit extract. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 142, 339-343.
69) Jain, S. and Mehata, M.S. 2017. Medicinal plant leaf extract and pure flavonoid mediated green synthesis of silver nanoparticles and their enhanced antibacterial property. Scientific reports. 7(1), 15867.
70) Khatami, M., Nejad, M.S., Salari, S. and Almani, P.G.N. 2016. Plant-mediated green synthesis of silver nanoparticles using *Trifolium resupinatum* seed exudate and their antifungal efficacy on *Neofusicoccum parvum* and *Rhizoctonia solani*. IET nanobiotechnology, 10(4), 237-243.
71) Thatoi, P., Kerry, R.G., Gouda, S., Das, G., Pramanik, K., Thatoi, H. and Patra, J.K. 2016. Photo-mediated green synthesis of silver and zinc oxide nanoparticles using aqueous extracts of two mangrove plant species, *Heritiera fomes* and *Sonneratia apetala* and investigation of their biomedical applications. Journal of Photochemistry and Photobiology B: Biology, 163, 311-318.
72) Chung, I.M., Abdul, R.A., Marimuthu, S., Vishnu, K.A., Anbarasan, K., Padmini, P. and Rajakumar, G. 2017. Green synthesis of copper nanoparticles using *Eclipta prostrata* leaves extract and their antioxidant and cytotoxic activities. Experimental and therapeutic medicine. 14(1), 18-24.
73) Das, P., Ghosh, S., Ghosh, R., Dam, S. and Baskey, M. 2018. Madhuca longifolia plant mediated green synthesis of cupric oxide nanoparticles: A promising environmentally sustainable material for waste water treatment and efficient antibacterial agent. Journal of Photochemistry and Photobiology B: Biology. 189, 66-73.
74) Saif, S., Tahir, A., Asim, T. and Chen, Y. 2016. Plant mediated green synthesis of CuO nanoparticles: comparison of toxicity of engineered and plant mediated CuO nanoparticles towards *Daphnia magna*. Nanomaterials, 6(11), doi: 10.3390/nano6110205.
75) Turakhia, B., Turakhia, P. and Shah S. 2018. Green Synthesis of Zero Valent Iron Nanoparticles from Spinacia oleracea (spinach) and Its Application in waste water treatment. IAETSD Journal for Advanced Research in Applied Sciences 5, 46-51.
76) Herlekar, M.B., Barve, S., and Kumar, R. 2015. Biological synthesis of iron oxide nanoparticles using agro-wastes and feasibility for municipal wastewater treatment. In Proceedings of the 47th Indian Water Works Association (IWWA) Convention.
77) Devatha, C.P., Thalla, A.K. and Katte, S.Y. 2016. Green synthesis of iron nanoparticles using different leaf extracts for treatment of domestic waste water. Journal of cleaner production, 139, 1425-1435.
78) Srikar, S.K., Giri, D.D., Pal, D.B., Mishra, P.K. and Upadhyay, S.N. 2016. Green synthesis of silver nanoparticles: a review. Green and Sustainable Chemistry, 6, 34-56.
79) Akter, M., Sikder, M.T., Rahman, M.M., Ullah, A.A., Hossain, K.F.B., Banik, S., Hosokawa, T., Saito, T. and Kurasaki, M. 2018. A systematic review on silver nanoparticles-induced cytotoxicity: Physicochemical properties and perspectives. Journal of advanced research, 9, 1-16.
80) Amin, M.T., Alazba, A.A. and Manzoor, U. 2014. A Review of Removal of Pollutants from Water/Wastewater Using Different Types of Nanomaterials, Advances in Materials Science and Engineering, https://doi.org/10.1155/2014/825910.
81) Han, G., Ghosh, P. and Rotello, V.M. 2007. Functionalized gold nanoparticles for drug delivery. Nanomedicine, 2(1), 113–123.
82) Elahi, N., Kamali, M and Baghersad, M.H. 2018. Recent biomedical applications of gold nanoparticles: A review. Talanta. 184:537-556.
83) Zhang X. 2015. Gold nanoparticles: recent advances in the biomedical applications. Cell biochemistry and biophysics, 72(3), 771-775.
84) Zheng, S., Yong, K.T., Roy, I., Dinh, X.Q., Yu, X. and Luan, F. 2011. A review on functionalized gold nanoparticles for biosensing applications. Plasmonics, 6(3), 491.
85) Raman, C.D. and Kanmani, S. 2016. Textile dye degradation using nano zero valent iron: a review. Journal of Environmental Management, 177, 341-355.
86) Dana, E., Taha, A. and Afkar, E. 2018. Green Synthesis of Iron Nanoparticles by *Acacia nilotica* Pods Extract and Its Catalytic, Adsorption, and Antibacterial Activities. Applied Science, 8, 1922.
87) Hokkanen, S., Repo, E., Lou, S. and Sillanpää, M. 2015. Removal of arsenic (V) by magnetic nanoparticle activated microfibrillated cellulose. Chemical Engineering Journal, 260, 886-894.
88) Vilardi, G. and Di Palma, L. 2017. Kinetic study of nitrate removal from aqueous solutions using copper-coated iron nanoparticles. Bulletin of environmental contamination and toxicology, 98(3), 359-365.
89) Xiao, Z., Zhang, H., Xu, Y., Yuan, M., Jing, X., Huang, J. and Sun, D. 2017. Ultra-efficient removal of chromium from aqueous medium by biogenic iron based nanoparticles. Separation and Purification Technology, 174, 466-473.