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CURRENT AND FUTURE PROSPECTS OF DYE CONFISCATION POTENTIAL OF INORGANIC-BASED MATERIALS: A MINI REVIEW

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Abstract – Currently, it is assumed that more than one thousand organic dyes are commercially available and utilized around the globe in enormous associated industries like textiles, paper, plastics, food and beverages as well as many others. Among all, azo-based dyes contribute about 70% of the total. However, polluted-effluent from dye-industries is highly visible and undesirable containing heavy metal ions, chemicals/dyes etc. cause the serious risks of their physical, developmental, reproductive, fatal diseases, potential human lethality and related problems on ecosystem components which circulate by the chain and web of food. Growing environmental concerns must be embraced to remove coloring components from the industrial discharges. Release of dyes into our life-saving water resources must be avoided and pressing need to treat wastewater with suitable and efficient method. Among various methods for dye removal, adsorption occupies one of the most suitable. The review highlights a literature exploration onto various adsorbents based on inorganic genera and their potential uses to remove dyes from contaminated water with recent progress and R&D.

INTRODUCTION

From the prehistoric era, people have been used their surrounding natural dyes and pigments for dyeing purposes, but the advent of the first synthetic dye 'Mauveine' in 1856 suddenly by Sir William Henry Perkin (Yusuf *et al.,* 2017), introduced a new horizon of various elegant colors of synthetic origin, and the use of natural coloring materials soon drastically reduced. The incident pioneered the dye industry origination in the UK and thereafter, worldwide (Kant, 2012). Water is considered as the most important for the survival of life on any planet and is a pivotal element of life. It has a very important role in term of Economic values, social values, and environmental values throughout the world. Numerous ventures and industrial facilities, for example, dyestuffs, material, paper and plastics etc., use colors to give shade to their items and furthermore devour significant volumes of water. Thus, they immersed a lot of hued matter into water system. It is perceived that open impression of water quality is enormously affected by the shading. Shading is the primary contaminant to be perceived in aquatic ecosystem (Kant, 2012; Abbasizadeh *et al.,* 2014). The nearness of extremely modest quantities of colors in water which is under 1 ppm for certain colors is exceptionally, noticeable and bothersome (Kant, 2012). However, polluted-effluent from dye-industries is highly visible and undesirable containing heavy metal ions, chemicals/dyes etc. cause the serious risks of their physical, developmental, reproductive, fatal diseases, potential human lethality and related problems on ecosystem components (Yusuf, 2019; Wuana and Okieimen, 2011). The intake of contaminated water containing these species is also proven to be severely hazardous to the living tissues (Khan and Malik, 2018). Besides the other industries, the textile industry was assumed to use approximately 8000 chemicals *via* various dry as well as wet processes (Kant, 2012; Abbasizadeh *et al.*, 2014), which have been discarded after application to the environment. Thereafter, the degradation processes of discarded materials by the biochemical reactions of the microbial world in an aquatic system produce unpleasant pollutants along with undesirous products that are associated with highly toxic and hazardous characteristics even carcinogenic and mutagenic nature (Fu and Wang, 2011; Sarkar *et al.*, 2020; Laraib *et el.*, 2020; Yusuf, 2019). Additionally, the organic dye contaminants and other additives have been believed to be transported easily through food chain/web due to their superior solubility index (Khan and Malik, 2018; Sher *et al.*, 2013). And thus, undoubtedly they affect the environment severely cause the degradation of aquatic life eventually. To execute these pollutants from water systems many dye degradation methodologies have been developed including physicochemical techniques such as filtration, adsorption, coagulation, flocculation, coagulation-flocculation combo, ion-exchange by resins, direct chemical oxidation etc., and biochemical methods such as phytoremediation and bioremediation technologies (usually microbial degrading were utilized by microbes (*i.e.* fungi and bacteria) (Sher *et al.*, 2013). Particularly, three types of wastewater treatments were universally accepted in terms of physical, chemical and biological (Fig. 1).

Recent decades witnessed the high use of advanced oxidation methods and processes (AOMP) through both homogeneous and heterogeneous Fenton reactions to treat industrial wastewater (Abbasizadeh *et al.*, 2014; Rodriguez *et al.*, 2012). Nevertheless, many of the dyes widely used in industrial physico-chemical processes are a rather much stable and not degrade well, also are resistant to aerobic/anaerobic digestion (Wang *et al.*,

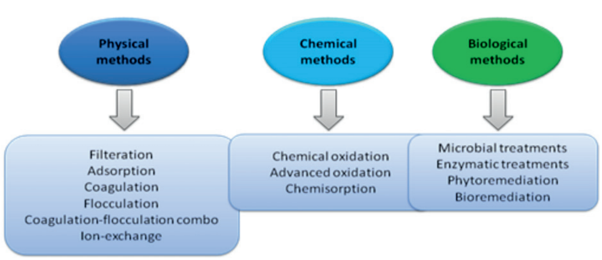

Fig. 1. Representation of dye degradation methods.

2018). Amongst all the above methods employed for the wastewater treatment, adsorption is recognized as most reliable, cost-effective, non-sensitive to toxic substances, simple, easy to use and most adapted method that have been used extensively for the separation of different industrial wastewater pollutants (Kant, 2012; Abbasizadeh *et al.*, 2014). Examples for category (a) are the sorbents from biomass such as straw, peat, hay, fibers, sawdust etc.; for class (b) examples are clay, zeolites, sand etc.; for class (c) many plastic-like examples can be given, *i.e.* polyethylene (PE), nylons, polypropylene (PP), polyurethane (PU) etc. Recently, due to eco-preservation and environmental concerns, scientific communities do not recommend the use of synthetic-based adsorbents at all. Also, natural-based materials have superior biocompatibility, less toxicity, higher eco-friendliness values (Khan and Malik, 2018; Rodriguez *et al.*, 2012) and therefore, categories (a) and (b) are entertained in the majority. Furthermore, eco-friendliness as well as low-cost nature of the adsorbents and their significant applications in the treatment of wastewater were reviewed and recommended (Rai *et al.*, 2015; Ferreira *et al.*, 2015; Zollinger, 2003). However, till date there is no any specific review published on the potential of inorganic-based materials for dye removal from wastewater. This review presents a systematic coverage with recent progress and R&D in order to discuss ecologically as well as noteworthy inorganic-based materials and their vast applications to treat wastewater.

Adverse Aspects of Dye Containing Effluents

Nowadays pollution of water contaminated with various pollutants has considered as a crucial issue globally. There are a large number of pollutants particularly various dye based-pollutants which are entering in the water ecosystems due to human activities especially by urbanization and rapid industrialization. Many industries including textiles, printing, paper, food, paint, plastic etc., release high volume of organic-based chemicals, highly acidic and basic substances and heavy metal salts in the form of effluent to the ecosystem (Yusuf, 2019; Wuana and Okieimen, 2011; Kant, 2012). More than 100,000 economically accessible colors exist and in excess of $7x10^5$ tones for every year are delivered annually to the various industrial sectors (Patel and Vashi, 2012). Because of their great solvency, manufactured colors are normal water toxins and they may oftentimes be found in follow amounts in mechanical wastewater. A sign of the size of the issue is given by the way that 2% of colors that are delivered are released straightforwardly in fluid emanating (Rai *et al.*, 2015). Because of progressively tough limitations on the natural substance of mechanical effluents, it is important to take out colors from water system before it is immersion/ discard. A considerable lot of these colors are likewise harmful and even cancer-causing. The situation represents a genuine danger to oceanic living creatures (Sher *et al*., 2013; Rodriguez *et al.*, 2012). In any case, wastewater containing colors is hard to treat, since the colors are hard-headed natural atoms, impervious to oxygen-consuming processing, and are steady to light, heat and oxidizing operators (ETAD 2002).

Lately, hued wastewater released into water has gotten one of the major ecological issues. Since it meddles with daylight transmission, and in this way diminishes photosynthetic procedure and harms the water biological system. Colors are likewise not effectively degradable as a result of their complex sweet-smelling structure, and are exceptionally harmful, mutagenic and possibly cancer-causing (Abbasizadeh *et al*., 2014). Colors added from the industrial activities can be categorized as non-ionic, anionic and cationic (Yusuf *et al.,* 2017). Cationic-based dyes are reported as significantly increasingly poisonous because they can go through the whole natural pecking order (Zollinger, 2003). Methyl violet, a cationic-based dye that is broadly utilized in the textile, material, paints and paper shading industries. Due to its hazardous nature (cancer-causing, and mitotic toxic and mutagenic) recognized as destructive to living beings just as the biological system (in human including heartbeat increment, regurgitating, stun, and jaundice cyanosis, since the methyl violet can collaborate effectively with the adversely charged layer surface of cells) (Yusuf *et al.,* 2012; Yusuf *et al*., 2017). Subsequently, it is imperative to scan for "*green*" forms with high proficiency and minimal effort to expel synthetic-based dyes with dominant negative responses added to wastewater. Sullying of water by colors is one of the significant dangers to human wellbeing just as a condition. Colors are the fragrant natural mixes having delocalization of electrons in a conjugated framework (Rawat *et al.,* 2016). Colors have a wide scope of usage in paper, mash, paints and material ventures, which requires enormous measure of water for washing and cleaning purposes. The subsequently prepared arrangements from these businesses are released without legitimate treatment into surface water which crumbles the nature of water. Manufactured colors including azo colors are viewed as increasingly harmful, mutagenic and cancer-causing in nature. Such colors are hard to expel from water as the majority of them are steady and non-biodegradable because of their complex sweet-smelling sub-atomic structure (Pandey *et al.,* 2007). Additionally, the presence of the dyes also led to low oxygen consumption and high turbidity index which strongly affect the photosynthetic ability of green plants (mainly algae and bryophytes). The toxicity of dye molecules (especially azo dyes) under ordinary conditions are highly influenced by two major factors, (i) function of their enabled-chemical moieties, and (ii) biotic and abiotic environmental components. Under normal conditions, azo dyes generate several aromatic amines with low molecular weight and high permeability to the cell walls of living beings by degradation (Khan and Malik, 2018). Therefore, the interaction of many dyes with water-borne microbes under different environmental conditions causative of several environmental risks as they produce many undesired products with acute toxicity and turbidity.

Inorganic-based Materials for Dye Confiscation

In the present era of environmental concern, eco-friendly and cost-effective methodologies are being developed to address limitations of existing physico-chemical methods (with high cost and unsafe to the environment) is on a global priority.

Adsorption is a physical process in which a particular component deposited at the surface of a substance called adsorbent and the surface phenomenon occur between two phases. The process is recognized for the removal of dyes and toxic metals, as one of the best methodology on account of its wide range of low-cost adsorbent materials available and synthesised efficiently. There are various considerable adsorbents including silica, zeolites, activated carbon, natural polymeric materials, polymer-metal-oxide composites etc. (Bafana *et al*., 2009). However, all the adsorbents are not efficient and cost-effective and have many disadvantages like low adsorption capacity and taking too much time during the adsorption process (Zee and Villaverde, 2005). Even though it has some disadvantages, yet adsorption is a recognized one of the most popular process to remove several dyes as well as metal ions from wastewater. Generally, it has an economic process that removes metal ions/dyes/ organic pollutants from water. In fact, a sole adsorbent cannot be suitable for the removal of all types of toxic metals and dyes pollutants from water. Many researchers have been searching for the development of new adsorbents that could possess a high adsorption efficiency, high-surface area, low-cost and recyclability. During the current decade, organic–inorganic hybrid materials are considered much more important due to their potential uses in catalysis, water treatment and making of optical devices (Abbasizadeh *et al.*, 2014; Sharma *et al*., 2003). Herein potentially important inorganic-based materials are discussed.

Clays

Naturally origin dirt minerals exhibit high sorption properties, found in many landmasses of the world are notable and recognizable to humankind from the soonest long stretches of progress. Morphologically, dirt materials have layered structure, are divided in few classes. For example, kaolinite, mica, vermiculite, pylophyllite (powder), sepiolite, smectites (montmorillonite, saponite), serpentine etc. (Shichi and Takagi, 2000; Abbasizadeh *et al.*, 2014; Jang and Dempsey, 2009).

Alumina

It is utilized as an adsorbent for the wastewater treatment process for expelling colors from water. It is as granules having a manufactured permeable crystalline gel and having diverse sizes. It has been seen that Alumina as an adsorbent has a property for the expulsion of colors from water and it has been read by numerous analyst for the expulsion of colors from water (Adak, 2005; Adak, 2006).

Silica Gel

It is an adsorbent for the expulsion of colors from water can be set up by coagulation of colloidal silicic corrosive which brings about the arrangement of permeable and nanocrystalline granules of various sizes with high surface zone. Basically, silica gel is mesoporous in nature made by joining SiO_2 units each-other. Because of the dependability, enormous pore channels, conceivable reuse, lower cost, incredible compound solidness, high surface territory and high mechanical opposition, it is being utilized to treat wastewaters (Unnithan and Anirudhan, 2004).

Zeolites

They are significant class among basic adsorbent and it is microporous adsorbents which are found normally and can be are arranged artificially. They are likewise considered as one of the specific adsorbents for their successful and show particle trade property just as atomic adsorption (Huang and Chen, 2009; Shichi and Takagi, 2000; Alkan, 2004).

Activated carbon

It is one of the most seasoned adsorbent utilized in many fields and it very well may be set up from coal, coconut shells, lignite, wood and so forth. It has two types of strategy and should be possible by utilizing one of the two essential initiation strategies: physical and compound. Also, the physical actuation strategy requires high temperature and take a longer time of enactment when contrasted with synthetic initiation technique however in compound actuation, the enacted carbon need an intensive washing because of the utilization of substance agents (Abbasizadeh *et al*., 2014; Babel and Kurniawan, 2003).

Graphene Oxide (GO)

Graphene oxide generally is functionalized with graphene bearing charged groups (mainy negative ions) on the surface to interact with the cationic types of contaminants such as organic/cationic dyes, toxic metal ions from wastewater by the action of industrial activities. Coherently, graphene-based materials have now become promising adsorbents (Babel and Kurniawan, 2003).

Cr_2O_3/Al_2O_3 Combination

The Cr_2O_3/Al_2O_3 combination yielded few years back the better results for the sorptive removal of dyes from water for wastewater treatment process (Espantaleon, 2003; Atun, 2003). Recently many researchers have been developed nanoscale transition metal oxides because of their physicochemical properties, which are different from other bulk metal oxides. Because of the active sites, the chemical composition of surface and surface defect of alumina, chromia is dispersed on its surface.

Composites of Na and Ca with alginate and Hydroxyapatite

Composite microspheres assumed a significant job in the fields of natural assurance with its huge explicit surface region, brilliant adsorptive property, high mechanical quality and great recovery execution. Biomaterial sodium alginate (SA) extricated from earthy colored ocean growth is a significant common polysaccharide and contains a direct square copolymer of (1,4)- connected β-D-mannuronate (M) and α-L-guluronate (G) deposits. SA has fantastic biocompatibility and degradability, and numerous analysts utilized SA as a polymer for planning composite materials with calcium chloride as a cross-connecting material. Hydroxyapatite (HA) is a permeable composite material with inexhaustible stores, great biocompatibility, ease to handle and application and soaring surface zone (Kargi and Ozmihci, 2004).

Polymer-incorporated-Carbon Nanotubes Composites (Pol-CNTCs)

In recent R&D trends, emerging new vistas based on polymer-matrix enabled materials are being considered much attention due to their proficiency and wide applicability. In order to improve surface functionalizing properties and more sorption characteristics of canbon nanotubes incorporated with suitable polymer matrices were developed for pollutant remediation from wastewater (Huang and Chen, 2009). Research targets in order to improve the water dispersibility and the adsorption performances of pol-CNTs gained using polymers-linking which have exceptional adsorption properties. Therefore, the composite of CNTs has attracted much attention to improve CNT-surface characteristics and accordingly enhance its adsorptivity towards organic counterparts, particularly dyes (Yusuf, 2019; Allen and Koumanova, 2005; Yagub *et al.*, 2014).

Mechanism of Dye Removal

Adsorption is a surface event occurred with week interactions of adsorbate molecules or ions (solid, liquid or gas) and the concentrated/adsorbed onto the solid surface entity (adsorbent) (Fig. 2). The phenomenon basically classified as physisorption or chemisorptions and particularly differentiable (Wuana and Okieimen, 2011). The associated week forces/interactions by which dye molecules adsorbed on the surface of an adsorbent have been assumed including, electrostatic, van der Waals, hydrophobic and hydrogen bonding. In general, adsorption, a surface phenomenon that deals with the utilization of surface forces through liquid-solid intermolecular forces of attraction between the pollutant (adsorbate) and the functional materials (adsorbent). Adsorption facilitates the cleaning through the conversion of a contaminated liquid to a solid or semisolid phase that adsorbed onto the adsorbent (Abbasizadeh *et al.*, 2014). The adsorbents can be classified in three main categories based on origination, for example, (a) natural organic (adsorption capacity = 3-15 times), (b) natural inorganic (adsorption capacity = 4-20 times) and, (c) synthetic (adsorption capacity = 70-100 times) (Xiao *et el.*, 2020).

Future Roadmap

Globally, organic dyes that added to mainstream wastewater are a major subject of concern amongst the scientific community due to their high persistent nature and adverse biochemical reactions. One of the serious pollutants among various pollutants in water is dyes and it can be exemplified by the

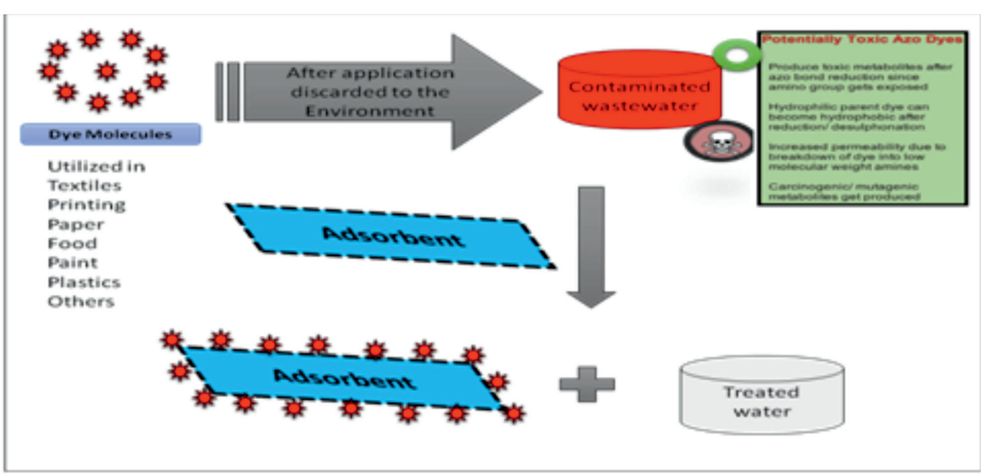

Fig. 2. Mechanistic representation for dye removal through adsorption.

international efforts of Environmental safety effectively by the use of suitable adsorbent. However, there are a large number of adsorbent-classes can be used for the sequestration of dyes contaminants from wastewater. Adsorption capacity can be increased by pre-treatment method such as physical and chemical method. Many factors influence the effectiveness of adsorption capacity include the types and chemically-active sites of both adsorbent as well as adsorbate (dye), pH, temperature, contact time and adsorbent concentration. So, there is a pressing demand to generate low-cost adsorbent alternates for dye-contaminated water treatment. Development of cost-effective substitutes with high adsorption capacity and eco-friendliness are needed and should be encouraged for commercial purposes. Therefore, inorganic-based materials show promising potential for dye removal from contaminated wastewater. For future direction polymer-incorporated and nano-assisted materials needs to be commercialized at large scale as innovative substitutes to conventional ones.

CONCLUSION

Nowadays, the commonest organic dyes utilized in several applied sectors such as textiles, printing, paper, food, paint, plastic and many more released into water, associated with the severe toxicity index that cause serious environmental as well as health issues to our ecosystem, and therefore, removal is the pressing need. In order to execute these pollutants from water systems many dye degradation methodologies have been developed including physicochemical techniques such as filtration, adsorption, coagulation, flocculation, coagulation-flocculation combo, ion-exchange by resins, direct chemical oxidation etc., and biochemical methods such as phytoremediation and bioremediation technologies (usually microbial degrading were utilized by microbes (*i.e.* fungi and bacteria). Particularly, adsorption is widely employed and accepted method to eliminate hazardous heavy metal ions as well as organic dyes. In this review, water pollution treatment process has been discussed chiefly focused on inorganic origin based on the recent literature surveys. Overall, inorganic-based materials are found easily available, cost-effective and highly efficient with considerable adsorption capacities. Many researchers have published significant reports and studies on the treatment of organic dye-contaminated wastewaters using inorganic-based materials, yet polymer-incorporated and nano-based materials do not much explored at a large scale which exhibits prominent alternation to their other counterparts, and so, more R & D works should be targeted at larger as well as commercial scale.

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Conflicts of Interest

The authors declare no conflict of interests.

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