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Wastewater treatment and dye sequestration using potential magnetic composites – A comprehensive review

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Abstract

Water is an excellent solvent as a wide variety of chemical substances dissolved in during number of industrial processes. The quality of water has been adversely affected by several anthropogenic influences during past few decades due to the addition of huge quantities of organic pollutants, inorganic impurities and toxic heavy metal ions. Therefore, development of potential treatment technologies and exploration of natural or synthetic bio adsorbents for the effective removal of colored impurities, hazardous contaminants and undesirable components is dire need of the hour. To solve these environmental problems, magnetic particles have been widely used in recent few years as potential adsorbents for treatment of polluted water as aqueous and gaseous contaminants are adsorbed on the surface of magnetic particles. This review is attempted to compile scattered available information about magnetically active metallic compounds including iron, copper, cobalt, chromium, nickel, zinc, manganese and zirconium as central metal atom that can be used as effective adsorbents. Iron based magnetic composites are used for removal of both organic and inorganic contaminants, various metal ions and organic pollutants such as Cu(II) from water, Sr(II), cationic dyes and Pb(II), chromium ions, neutral red (NR), methyl orange (MO) and methylene blue (MB), metal ions or residual dyes from wastewaters, phenols, chloro-phenols and pesticides, several gases, heavy metal cationic contaminants and azo-dye acid red B (ARB). Nickel based composites are widely used for removal of nitrogen compounds and sulfur from liquid fuels and model dyes such as indigo carmine and methylene blue. Copper based composite are used in power engineering, spintronics, instrument making and microelectronics etc. Zinc based adsorbents are used in efficient and fast magnetic purification of dyes, strong anti-bacterial activity and photo-catalytic degradation of methylene blue dye. Manganese possesses outstanding mechanical and ferromagnetic properties. Zirconium composites are used for oil recovery from oil-in-water emulsion while cesium composites are used in wastewater treatment and automotive exhaust treatment.

Key words: Wastewater, magnetically active components, methyl orange, methylene blue, azo-dye acid red B, neutral red, anthropogenic sources

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1. Introduction

Now-a-days, development of modern and advance methods for treatment of wastewater is of great importance and a hot topic of current scientific investigations all across the globe in order to deal with every day arising environmental problems. In recent years, more attention is paid towards application of magnetic particles to solve different environmental problems. In order to adsorb pollutants from aqueous or gaseous effluents, magnetic particles are widely used. After the process of adsorption, adsorbent can be easily separated with the help of magnetic particles from the reaction mixture. There are different examples of such technologies like magnetic particles are used to accelerate coagulation of sewages [1], functionalized polymer coated with magnetite are used in milk to remove radio nuclides, for the adsorption of organic dyes poly(oxy-2,6-dimethyl-1,4-phenylene) is used [2] and for remediation of oil spill magnetic particles coated polymer are used [3].

Magnetic materials have great impact on our life as they are widely used in computers, telecommunication and in electronic industries. Different types of magnetic materials have been used during the past few decades including pure iron and its alloys such as Fe–Ni–P, Fe–Ni, Fe–Si and Fe–Nd–B and ferrites including soft and hard, such as Mn–Zn, Ba ferrites and Ni–Zn. Different aspects including properties, processing, applications of ferrite and effect of additives, such as MoO_3 in Mn–Zn–ferrites and V_2O_5 for high frequency application and low consumption lamps were discussed by many researchers. In the magnetic history, soft magnetic composite materials such as amorphous wires, nano-crystalline materials and amorphous materials are one of the latest developments [4].

The process of adsorption is surface based and exothermic in which the molecules in liquid or gas are accumulated at the surface of adsorbent [5]. Adsorbate is the compound that is adsorbed of the adsorbent. Another term is called "desorption" in which the adsorbed molecules are released from the adsorbent surface, this phenomenon is opposite to the adsorption. There are two ways through which adsorption occurs one is called "physiosorption" and the other is called "chemisorption". Both these processes depend on the interaction of molecules with the surface of the adsorbent. The weak forces of attraction such as Van der Waals forces and electrostatic interaction are involved in physical adsorption. While in chemical adsorption, strong bonding occurs between the surface and adsorbed molecules. In chemical adsorption, monomolecular layer is formed and it is slower than physical adsorption. Moreover, a thick multilayer is formed on the surface during physical adsorption [6]. A schematic representation of the monolayer and multilayer adsorption on the adsorbent surface is shown in the following figures.

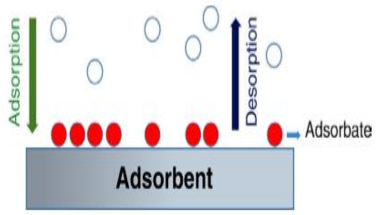

Fig 1 Depiction of adsorption and desorption processes

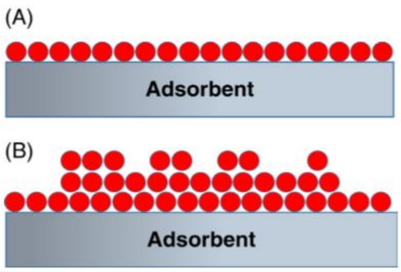

Fig 2 (A) Monolayer and (B) multilayer adsorption

2. Adsorption Isotherms

For any adsorption system, the adsorption isotherm is referred to as a curve of the amount of adsorbed molecules to the adsorbent surface as a function of partial pressure or concentration of the adsorbate at a constant temperature [7]. According to the IUPAC classification, there are six types of adsorption isotherms for gas adsorption on the surface of solid adsorbents [8] as shown in figure 3. The adsorption isotherm in type I demonstrate the adsorption of gas molecules to the adsorbent which are having micropores including activated carbon and the adsorbents surface is covered with a monolayer of adsorbed molecules. While in type II, the adsorption of gas molecules to the adsorbents having macroporous is shown below. In type II, no saturation point is seen as in type I and after coverage of the adsorbent surface with monolayer adsorbed molecules a multilayer of adsorbed molecules is formed.

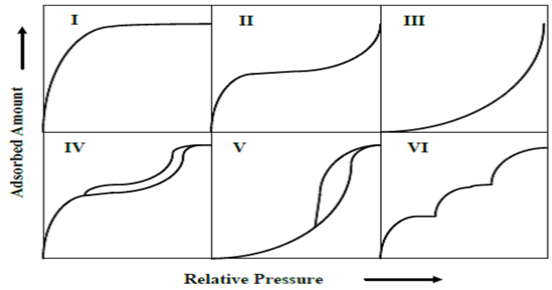

Fig 3 Adsorption isotherms

Type III adsorption isotherm show weak interactions with low energy between adsorbed molecules and adsorbent surface having macropores. The multilayer adsorption together with capillary condensation to the mesoporous adsorbents is shown in Type IV and Type V. Type VI adsorption isotherm demonstrate the stepwise formation of a multilayer on the surface of nonporous adsorbent. Different adsorption isotherm models including Dubinin–Radushkevich, Freundlich, Harkins–Jura, Langmuir, BET (Brunauer, Emmett, and Teller) and Redlich–Peterson are used to get detailed information about the interactions between the surface of the adsorbents and molecules to be adsorbed [9].

3. Magnetic Composites

There are many potential technological applications of magnetic particles including adsorption processes, magnetic resonance imaging, environmental remediation, support for catalysts and drug delivery. To improve their stability and to introduce new surface properties and functionalities, magnetic particles can be coated with protective layer of different materials. Some of these coating materials are alumina, silica, gold and polymer such as polyaniline, methacrylate, polystyrene, polyacrylamide and poly-methyl. Carbon is a highly versatile coating material due to its biocompatibility, pore creations, chemical stability and widely used as efficient adsorbent in different applications [10].

3.1 Iron Based Composites

For soft magnetic applications, the idea of using iron based resin is not new. More than 100 years ago, it was appeared, but there are many reasons due to which iron based resins have been rarely used such as difficult processing technology for making parts, real need for these materials was not sufficiently developed and their properties were not completely determined. However, with the help of new shaping technologies and improved raw materials, such types of limitations were being overcomed. The use of these composites, are increasing by replacing existing laminate materials and in electrical motors. The purpose of these materials is to provide high electrical resistivity and to provide materials with competitive magnetic properties (magnetic saturation and good relative permeability) [11]. In some applications, insulated iron powder offers several advantages over traditional steel. In recent years, particle composition (Fe–Ni–Co, Fe–Ni and Fe–Si), effects of particle size, resin, compaction parameters such as pressure, warm compaction and lubricant and for creation of insulation layer around particles wet chemical methods have been verified [12].

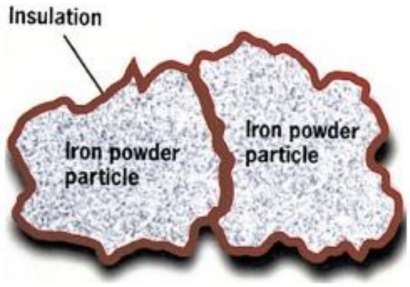

Fig 4 Representation of component elements of powdered core

3.1.1 Classification of Soft Magnetic Composites

Soft magnetic parts which are produced by powder metallurgy processes can be broadly divided into sintered magnetic cores and powder compressed magnetic cores. Sintered magnetic cores are manufactured by the conventional powder metallurgy process nevertheless powder compressed magnetic cores are those which are manufactured without sintering [13].

3.1.1.1 Sintered Soft Magnetic Materials

The direct current magnetic properties of sintered compacts are determined by the density and chemical composition of material and crystal grain size of the sintered part. A comparatively high magnetic flux density is seen in pure iron sintered compacts. Generally the flux density of iron-based materials shows a strong relationship with the density of the sintered part and purity of the material. By using high purity iron powders, high flux density can be obtained and by applying die wall lubricant, high compaction techniques and warm compaction, a high density sintered compact can be manufactured. In sintered parts, grain growth can be encouraged by addition of a small amount of phosphor (P) to pure iron (Fe) powder and making it possible to produce sintered compacts with a coarser grain size. In addition to the density of the sintered compact and material composition, the shape of the part is also strongly related to alternating current magnetic properties of sintered components. Some of the examples are electromagnetic actuators, alternating current magnetic fields used in various kinds of motors. In an alternating current magnetic field when soft magnetic materials are used, core loss occurs [13].

3.1.1.2 Powder Cores

Magnetic powder particles are used in manufacturing of powder cores which are insulated individually and are approximately 100 m in size. In manufacturing of cores, the powder is mixed with a small amount of an organic resin as a binder and the iron-based powders with a size of around 100 m are insulated with an inorganic insulating layer. The mixture is then compacted and treated with heat. In this case, the heat treatment must be done at a temperature that will not destroy the organic resin binder and the inorganic insulating layer. During the process of compaction, high density must be realized [13].

3.1.1.3 Soft Magnetic Composites

These are basically pure-iron powders which are coated by electrically insulating materials. Isotropic magnetic behavior improves high-frequency performance with soft magnetic composites and by using different particle sizes and insulations these can be compacted into the 3D and complex-shapes [14].

3.1.2 Zeolites with Iron Oxides

Magnetic properties of iron oxides with the adsorption features of zeolites have been combined in a composite to produce a novel magnetic adsorbent. For the removal of both organic and inorganic contaminants [15], zeolites offer an inexpensive and attractive option [16]. Several organic contaminants in water including phenols, pesticides and chloro-phenols has been reported to be strong adsorbents recently in the literature [15]. Natural zeolites are functioning as excellent cation exchangers of low cost and often used to adsorb metallic contaminants. Due to the net negative charge on their channel structure, which attracts and holds cations such as heavy metals and a high surface area, zeolites offers strong adsorption capacity [15]. Pore diameter of about 7.8 A of NaY zeolites present the highest cation exchange capacity, one of the largest surface areas and have been studied as adsorbent for heavy metals [17].

Common pollutants in environment are heavy metals like Pb, Cd, Cr and Hg. There are two stable oxidation states of chromium metal such as Cr(III) and Cr(VI). Since first successful trial by Augustus Schultz, an American dye chemist, in his two-bath method mentioned that the sole leather-tanning chemical that is left behind in whole process is chromium. Basic chromium sulfate ($CrOHSO_4$) is used by many tanneries in which the chrome exist in trivalent oxidation state. In chromium pollution, other main sources are glass industries, cement ceramics, production of steel and other metal alloys, mining, electroplating, corrosive paints and photographic material [18].

3.1.3 Carbon Nanotubes (CNTs)

Carbon nanotubes (CNTs) have already been investigated to be promising adsorbents for various metal ions and organic pollutants due to small, layered structures, hollow and a large surface area. In order to increase the capacity of adsorption, different modifications are done by chemical treatments [19]. For the treatment of heavy metals contaminations in aqueous solutions, CNTs have been widely used. CNTs possess different features unlike many other adsorbents that contribute to the superior removal capacities; including large accessible external surface area, well developed mesopores and fibrous shape with high aspect ratio. Due to high van der Waals interaction forces along the length axis, these pores have been reported to be mostly mesopores [20]. As a support of metallic oxides, CNTs have still been reported [21]. The advantages of these materials are large surface area, supported metallic oxides and high sorption capacity. To produce iron oxide-impregnated magnetic CNT composites, chemical oxidation polymerization followed by the process of carbonization. In order to synthesize CNT iron oxide composites a solvo-thermal method has also been used. To prepare CNT-based functional materials other effective approaches such as electrolysis deposition and arc-discharge technique have been developed [22]. The behavior of carbon nanotube iron oxides magnetic composite as adsorption for the removal of Cu(II) from water [23], Sr(II) [24], cationic dyes [24] and Pb(II) has been investigated too.

3.1.4 MWCNT/Nano-Iron Oxide

Characterization of multiwalled carbon nanotubes/nano-iron oxide magnetic composites through XRD suggests that magnetic phase formed is magnetite and maghemite. Clusters of nano-iron oxides attached to a network of MWCNTs are seen in SEM images. For chromium ions, the adsorbents show good adsorption capacity. The composite has adsorption capability higher than activated carbon and MWCNTs. It was revealed that the adsorption capability is increased in the batch mode by the speed of agitation and it depends on pH. In fixed bed mode, performed experiments revealed that the removal capability of the composites for chromium increases with decreasing the flow rate. Results shows that the MWCNTs/nano-iron oxide magnetic composites, with large surface area are very promising materials as adsorbent with good performances for removal of contaminants from water. In the process of reverse osmosis, materials reported could be used as a base for encapsulation. It is required to have a small material with good ability to remove pollutants and large surface area especially for compact columns used in water filtration [18].

3.1.5 Iron Oxide with Halloysite Tube

To prepare the magnetic sorbent HNT–Fe_3O_4, on the halloysite nanotube (HNT), iron oxide nanoparticles are synthesized which adsorb three dyes, such as neutral red (NR), methyl orange (MO) and methylene blue (MB). HNT–Fe_3O_4 was characterized by FTIR, thermo gravimetric analysis, TEM and XRD. After analysis, it was revealed that the synthesis of Fe_3O_4 occurred mostly on HNT. Adequate hydroxyl groups of HNTs, large surface area and large pore volume made metal ions to adsorb on HNTs, thus Fe_3O_4 nanoparticles formed on HNTs. HNT–Fe_3O_4 adsorption behavior for NR and MB could be described well by the pseudo second-order model whereas HNT–Fe_3O_4 shows better adsorption for MB than NR, but for anionic MO the adsorption was very little. At neutral conditions, this may be related to the surface of HNTs which is negatively charged. Because of their hydrophilic surface, HNTs can disperse in water. Rather than the centrifugation processes or filtration, magnetic separation will be applied on HNT–Fe_3O_4 if it is used as sorbent for dyes. Moreover, HNT–Fe_3O_4 is an efficient and an economical sorbent. Thus it will have potential applications for removing heavy metal ions or residual dyes from wastewaters [25].

3.1.6 Activated Carbons

For the removal of organic and inorganic contaminants from water, activated carbons offer an inexpensive and attractive option. Adsorption of several organic contaminants in water, such as phenols, chloro phenols, pesticides and several gases occur efficiently due to its porous structure and high surface area. Moreover, for heavy metal cationic contaminants, activated carbon can easily be used as an efficient adsorbent and can be functionalized. The magnetic composites of activated carbon with a high adsorption capacity can be prepared by a very simple procedure using low cost and available chemicals. Mossbauer data having Fe^{+3}/Fe^{+2} ratios, magnetization measurements and XRD, suggested that the main magnetic phase formed in the composites is maghemite, possibly with small amounts of hematite, goethite and magnetite. Controlled TPR experiments showed that Fe_3O_4 enhances the magnetization of the composites and Fe_2O_3 oxides in the materials can be selectively reduced to produce magnetite. There is no significant decrease in the porosity of the activated carbon or in the surface area was evident as generally caused by the presence of Fe oxides in composite. Composites showed high adsorption capacities for chloroform, drimarine red dye in aqueous solution, phenol and chlorobenzene. More importantly, in adsorption, no reduction was produced by the formation of the composite. Moreover, good resistance is showed by the magnetic composites over the pH range 5–11 [26].

3.1.7 MnO–Fe_2O_3

It is found that MnO–Fe_2O_3 composite-manganese ferrite possesses good magnetic properties. The specific saturation magnetism is 40 emu/g. This value shows that these materials can easily be separated and recovered by using magnetic separation technology. The use of powder MnO–Fe_2O_3 composite as catalyst/adsorbent is shown to combine the excellent adsorptive properties, high catalytic activity of manganese oxide and iron oxide by magnetic separation technique for highly effective recovery. Moreover MnO–Fe_2O_3 composite can easily be prepared and proved to be a low cost material. However, in its application in water treatment, little research has been conducted with this material so far. For the removal of azo-dye acid red B (ARB), four magnetic powder MnO–Fe_2O_3 composites of different Mn:Fe mole ratios were prepared and characterized.

It is estimated that the azo-dye with approximate concentration of about 15% is produced worldwide and is directly released into the environment. ARB was selected as a model pollutant in a recent research activity because azo-dyes comprise approximately half of all the textile dyes used today. Unfortunately, there is some difficulty in treatment of these dyes due to their properties that make them excellent in application to fabrics, having adequate resistance to biodegradation or oxidation. For the removal of these dyes, catalytic oxidation and adsorption are promising alternative technologies. Under acidic condition, magnetic powder MnO–Fe_2O_3 composites possess good adsorptive properties toward azo-dye ARB. With increasing the surface area of adsorbent and Fe content, adsorption capacity usually increases. By magnetic separation technology, these magnetic powder composites can be conveniently recovered that make it quite easy to apply powder materials as catalyst or adsorbent for treatment of water and therefore these fine powder materials take the full advantages of excellent catalyst or adsorption properties. In air, combustion of adsorbed ARB was observed by the catalytic activity of MnO–Fe_2O_3. Using catalytic combustion method it is effective to regenerate powder MnO–Fe_2O_3 composites [27].

3.1.8 Graphene

An emerging carbon material, graphene, owing to its superior properties and unique two-dimensional structure has attracted tremendous attention of upcoming researchers all across the globe. Graphene oxide (GO, one derivative of graphene) and graphene have been reported as efficient adsorbents. For the decolouration of methylene blue (MB), some scientists indicated that graphene oxide was proven to be a promising adsorbent. For the removal of Cd(II) and Pb(II) from water, a functionalized graphene is fabricated by researchers which presents a high adsorption capacity. In adsorption of pollutants another fascinating nanomaterial, CNTs, exhibits high performance in adsorption and possesses one dimensional structure. It was revealed that it has a high adsorption capacity toward different metal ions and organic chemicals. Researchers have attempted to fabricate their composites as new adsorbents based on adsorption properties of CNTs and graphene which towards MB have a maximum adsorption capacity of approximately 81.97 mgg^{-1}. Adsorption capacity of new composite adsorbent may be high due to synergistic effect of different carbon nanomaterials.

It can also be found that binary adsorbents, graphene-CNTs shows enhanced adsorption performance than single ones alone (i.e., graphene and CNTs). One important issue is removal of nano-sized adsorbents that requires high cost. An approach to imparting magnetic properties onto adsorbents, the application of magnetic particles has been proposed. And by a simple magnetic process, these can be separated from treated water. Due to its low toxicity, eco-friendliness and low cost, ferriferous oxide (Fe_3O_4) nanoparticles have become most popular magnetic material. For preparing magnetic adsorbents, some investigators have applied Fe_3O_4 nanoparticles with great separability. For removal of MB in water some researchers synthesize magnetic graphene composite by a solvothermal method that shows extraordinary adsorption capacity and magnetic separability. Magnetic hybrids based on CNTs can be used as adsorbents which show excellent adsorption capacity of dyes, good dispersibility and magnetic properties. Thus in the adsorption of dyes, magnetic CNTs and magnetic graphene have superior performance.

However, in the removal of dyes, no reports have been found about magnetic graphene-CNTs as an adsorbent. By a solvothermal method, magnetically separable composite adsorbent for effective MB removal has been prepared. It was observed that the adsorption was affected by temperature and pH in both adsorption experiments. It is proved by kinetic studies that the adsorption process takes place with intra particle diffusion model kinetics and pseudo-second-order reaction. With the Langmuir isotherm model, the equilibrium study was well fitted. The highest adsorption capacity (65.79 mg g^{-1}) was with optimum ratio of graphene to MWCNTs 1:4. In the dyeing wastewater treatment, the ternary hybrid could be used as a potential adsorbent for its good adsorption performance and magnetic separability [28].

3.1.9 Magnetic Cellulose/Activated Carbon

Some cellulose based bio-adsorbents are difficult to be separated and recovered except by filter or high speed centrifugation. Practical application of these bio-adsorbents is limited due to their relatively low adsorption capacities towards azo dyes. It is significant and necessary to explore environment friendly bio-adsorbents for above-mentioned reasons that are based on cellulose and possess excellent separation property along with higher Fe_3O_4/adsorption capacities. For organic dyes, activated carbon (AC) is the most common adsorption process but on a large scale, its use is limited due to its correspondingly expensive nature. At the same time, a new biomaterial can be created by combining iron oxide nanoparticles and bio-adsorbents which will possess easy recovery by applying a magnet from treated effluents with high adsorption capacity. By a co-precipitation technology, magnetic cellulose/activated carbon composites (m-cell/Fe_3O_4/ACCs) were prepared and characterized with thermo gravimetric analysis (TGA), x-ray diffraction (XRD), scanning electron microscopy (SEM), vibrating sample magnetometer (VSM) and Brunauer–Emmett–Teller (BET). To investigate the effect of some parameters such as temperature, initial dye concentration, adsorbent dosage, the pH and contact time on the adsorption efficiency of azo dye from aqueous solutions onto m-cell/Fe_3O_4/ACC, the congo-red (CR) with azo structure was selected as model dye. For the removal of azo dyes from wastewater, adsorption is a promising route with high performance to graft functional polymer on the surface of solid supports [29].

Some recent investigations showed that [26] magnetic multiwall carbon nanotube nano-composite were prepared by Gong and coworkers [30] as an effective adsorbent for removal of dyes from aqueous solution which are cationic in nature. Some scientists reported that organic dyes could efficiently be adsorbed by magnetic composites with activated carbon. Researchers found that for removal of amaranth (AM) from water solution, iron oxide nanoparticles coated with cetyl-tri-methyl-ammonium bromide (CTAB) proved as an efficient adsorbent [31]. While another group of researchers revealed that the removal ability of reactive black 5 and hazardous azo dye were greatly improved when the iron oxide nanoparticles cross-linked with chitosan were used. For adsorption of acid orange and similar dyes with high efficiency, other magnetic particles such as magnetic alginate beads cross-linked with epichlorohydrin and magnetic silica modified with amine groups could be used [32]. However few studies are evident on magnetic particles cross-linked with carbon which is environment friendly, easily synthesized and particularly economic.

Table 1 Comparison between physical adsorption and chemical adsorption

Physical Adsorption	**Chemical Adsorption**
Electrostatic interactions and Van der Waals forces are involved	Covalent bonds are formed between the surface and the adsorbed molecules
Fast	Slow
Reversible	Irreversible
Not very specific	It is specific
Multilayers are formed	Monolayer is formed
Activation energy is not required	Activation energy is required
It usually occurs at low temperature values and decreases with increasing temperature	High temperature is needed

Table 2 Role of some nanocomposites in removal of dyes

Removed Dyes	**Nanocomposites**	**References**
Cationic Dyes	Magnetic Multiwall Carbon Nanotube Nanocomposite	[30]
Organic Dyes	Magnetic Composites with Activated Carbon	[33]
Amaranth (AM) from Water Solution	Iron Oxide Nanoparticles Coated with Cetyl-tri-methyl-ammonium bromide (CTAB)	[31]
Reactive Black 5 and Hazardous Azo Dye	Iron Oxide Nanoparticles Cross-Linked with Chitosan	[32]

Table 3 Use of magnetic composites for removal of dyes

Magnetic Composite	**Dyes Removed**	**References**
Zeolites with Iron Oxides	Removal of both Organic and Inorganic Contaminants	[15]
Carbon Nanotubes (CNTs)	Various Metal Ions and Organic Pollutants such as Cu(II) from water, Sr(II), cationic dyes and Pb(II)	[23-24]
MWCNT/Nano-Iron Oxide	Chromium Ions	[18]
Magnetic Sorbent HNT–Fe_3O_4	Neutral Red (NR), Methyl Orange (MO) and Methylene Blue (MB), Metal Ions or Residual Dyes from Wastewaters	[25]
Activated Carbons	Phenols, Chloro-phenols and Pesticides, Several Gases, Heavy Metal Cationic Contaminants	[26]

$MnO–Fe_2O_3$	Removal of Azo-Dye Acid Red B (ARB)	[27]
Graphene	Decolouration of Methylene Blue (MB)	[28]
Magnetic Cellulose/Activated Carbon	Azo Dyes from Wastewater	[29]
Iron with Glucose	Organic Dyes or Other Pollutant	[34]
Fe_3O_4@Graphene Composites (FGC)	Removing Cationic and Anionic Dyes in Water Solution	[35]

Table 4 Role of different magnetic composites on removal of dyes

Magnetic Composite	Removed Dyes	References
Ni/Mo_2C	Removal of Nitrogen Compounds and Sulfur from Liquid Fuels and Model Dyes such as Indigo Carmine and Methylene Blue	[36]
Al_2O_3/Ni Composite	Have both Magnetic and Superior Mechanical Properties	[37]

Table 5 Cupper based composites and their properties

Composites	Properties	References
Cupper Based Composites	Power Engineering, Spintronics, Instrument Making and Microelectronics	[38]

Table 6 Zinc based composite materials and their absorptive potentials [41]

Composites	Properties
Zinc Ferrite	Efficient and Fast Magnetic Purification of Dyes
Zinc/Iron Oxide Composite	Strong Anti-Bacterial Activity
ZnO/Ag	Photocatalytic Degradation of Methylene Blue Dye

Table 7 Manganese, zirconium and cesium based metal composites

Composite	Properties	References
Manganese Mono-Boride	Outstanding Mechanical and Ferromagnetic Properties	[46]
Zirconium-Chitosan Hybrid	For Oil Recovery from Oil-in-Water Emulsion	-
Fe_3O_4/CeO_2 Composite	In Wastewater Treatment and Automotive Exhaust Treatment	[48]

3.1.10 Iron with Glucose

For removal of organic dyes from aqueous solution, glucose is often used as a carbon source and $FeCl_3·6H_2O$ as an iron source for synthesis of superparamagnetic Fe_3O_4/C core–shell nanoparticles as potential adsorbents. From aqueous effluents, these composites displayed high efficiency to adsorb contaminants. By applying a discontinuous magnetic field they can be easily separated from the water after the completion of adsorption. To test the adsorption performance of the nanoparticles, two typical dyes, cresol red (CR) and methylene blue (MB) were employed as model organic pollutants and their adsorption kinetics were fully investigated. For removal of the cationic dyes from water with average size ∼250 nm in the diameter, super paramagnetic Fe_3O_4/C nanoparticles have been synthesized. In the aqueous solution after adsorption, prepared magnetic nanospheres can be well dispersed and using an external magnet can be separated from the solution in 10 s. The adsorption capacities are 44.38 mgg^{-1} and 11.22 mgg^{-1} for MB and CR respectively. Using magnetic nanomaterials, the process of purifying water pollution presented here is safe and clean. Hence, for removal of organic dyes or other pollutants, it provides an environment friendly and simple tool [34].

3.1.11 Fe_3O_4 Graphene Composites (FGC)

For preparing FGC, a simple approach is used in which chemical deposition of Fe_3O_4 NPs onto GO is practiced followed by reduction of GO to graphene using a hydrazine hydrate solution for removal of dyes. These magnetic materials were characterized by FESEM, FTIR, EDS, TGA and TEM techniques. The size of 30 nm Fe_3O_4 nanoparticles was homogeneously dispersed onto graphene sheets through a chemical deposition method. For removing cationic and anionic dyes in water solution, FGC had great potential as an effective absorbent. To describe MB and CR adsorption data onto FGC, both Freundlich and Langmuir were applied, providing a better fit to the Langmuir isotherm model. Kinetic data of CR and MB can be described by a pseudo second-order kinetic model [35].

3.2 Nickel Based Composites

Nickle based composite materials have recently been known as potential adsorbents for treatment of different types of contaminants from industrial and domestic wastewater. In this review, various nickle based composite materials are discussed in detail with their wide range of applications and shortcomings on utilization on commercial scale.

3.2.1 Ni/Mo_2C

With catalytic chemical vapor deposition from ethanol, new magnetic composites based on metallic nickel and molybdenum carbide (Ni/Mo_2C) have been recently produced. Raman spectroscopy, scanning electron microscopy, X-ray diffraction and thermal analysis revealed that CVD process occurs in a single step. This process includes the reduction of NiMo oxides at different temperatures (700°C, 800°C and 900°C) with catalytic deposition of carbon from ethanol thereby producing molybdenum carbide on the surface of nickle. The formation of Ni/C was observed in the absence of molybdenum. Removal of nitrogen compounds and sulfur from liquid fuels and model dyes such as indigo carmine and methylene blue was evident by adsorption through magnetic molybdenum carbide. The great advantage of these carbide composites is that they may be reused and easily recovered magnetically [36].

Based on metallic nickel and molybdenum carbide, the preparation and characterization of new magnetic composites covered with carbon was ensured and their use as adsorbent of nitrogen and sulfur compounds was evident by using quinoline and dibenzotiophene as a model dye. Organic dyes adsorption has also been investigated by many recent researchers. Other new promising catalysts are transition metal carbides and in recent years they have been widely investigated due to their high selectivity in hydrogenation, hydro-de-nitrogenation in petroleum refining, hydro-desulfurization and good catalytic activity. Due to its unique physical and chemical properties, molybdenum carbide has extensively been studied including thermal stability, surface reactivity, mechanical hardness and superconductivity. Also, it is reported that catalytic behavior of molybdenum carbide is comparable to the noble metals [36].

3.2.2 Al_2O_3/Ni Composite

Since the dispersed Ni particles may cause toughening of alumina by plasticity of metal, Al_2O_3/Ni composite system has already been studied. In particular cases, due to micro-structural refinement by incorporating the Ni, strengthening of Al_2O_3 has also been observed. For this composite, another interesting point is that nickel is a ferromagnetic material. It is known that ferromagnetic properties depend on crystalline size of materials. Therefore, for the nanometer-sized Ni-dispersed composites particular magnetic properties are expected. The main purpose is to develop the dense Al_2O_3/Ni nanocomposites having both magnetic and superior mechanical properties. The composites were fabricated by hot-pressing and by reducing Al_2O_3/NiO mixtures which were prepared by the "solution-chemical process". This method allows one to fabricate metal/ceramic nanocomposites with homogeneous and fine metal dispersion. The effect of soft Ni particulate dispersion and the effect of the micro-structural characteristics on the mechanical properties have also been clarified. However, there is compatibility between mechanical and functional properties of present composites when their magnetic properties were assessed [37].

3.3 Cupper Based Composites

Copper based binary systems in which no intermetallic compounds are formed with limited solubility (Cu–Fe, Cu–Ag, Cu–Nb, Cu–Cr,) belong to a class of materials that combine high electrical conductivity with high strength of material. The priority fields of their use include power engineering, spintronics, instrument making and microelectronics due to their unique complex physico-mechanical properties. The broad spectrum of application of Cu–Fe composites is found e.g., excellent thermal and electrical conductivity, high wear and corrosion resistance, good mechanical properties in combination with the good manufacturability and the low cost of iron compared with other possible materials such as Ag, Nb, Au and Cr. In the field of creating composites, the most important task is the development of methods of the directional regulation of their properties and structure, which would ensure the required operating characteristics [38].

During constructing composites, in addition to appropriately selecting the geometry of their arrangement and the material of components, which determine the opportunity of achieving the required complex of properties, economical technology of their production and the correct selection of most efficient method is also of exceptional importance. At present, for obtaining composite materials, several thousand methods are known. The expediency of applying a given technological process is determined by the requirements to their surface quality, the specific features of the materials of composites and accuracy of sizes, as well as based on the economical, technical, ecological and other indices. For obtaining Cu–Fe composites, traditional methods include vapor phase methods, liquid phase methods and chemical methods that use powder metallurgy and gases during operation [38].

3.4 Zinc Based Magnetic Composites

A novel carbon allotrope with a single-atom thick sheet, graphene, has attracted much broadened interest in various scientific areas such as material science, electronics, biology and spintronics as well as technological areas such as fast DNA sequencing, nanomedicine, ultra high sensors and tissue engineering [39]. In the area of environmental remediation, graphene shows promising applications due to its unique physicochemical characteristics including composition, diverse functionalization, easy fabrication, anti-bacterial properties, less cytotoxicity compared with carbon nanotubes and excellent specific surface area. Recently, in water purification as well as nematicidal, anti-viral and bactericidal applications graphene-based composites were used. For adsorption of dye molecules, which are widely used in textile and chemical industry, graphene or graphene oxide (GO) was applied in recent reports. However, in removing the dyes from their aqueous solutions, efficiency of graphene or its oxide is extremely low so that a long reaction time is usually required. In adsorption of dyes, magnetic nanoparticles not only show a relatively low reactivity but also they tend to aggregate thereby resulting in low decolorization efficiency. In order to enhance the decolorization efficiency and to prevent agglomeration of the nanoparticles, graphene is selected as a template or support for magnetic nanoparticles [40].

Zinc ferrite is a normal spinel structure among various magnetic materials that is usually indicated as (Zn) [Fe_2]-O_4 in which square brackets contain the octahedral sites and parenthesis show the cations in tetrahedral sites. Due to its contrasting magnetic properties as compared with other spinel ferrites, zinc ferrite has long been attracted interests, e.g., anti-ferromagnetic ground state with a Ne´el temperature at 10 K, narrow band gap of 1.9 eV, low ordering temperature and paramagnetic behavior at room temperature. By using a one-step hydrothermal reaction method, graphene-based nanostructures were synthesized with superparamagnetic property. This method provided both attachment of zinc ferrite spinel nano-particles onto reduced sheets and effective reduction of GO sheets. In composite, by increasing the graphene contents, significant decrease in size as well as saturated magnetization of the nanostructures and the number of the $ZnFe_2O_4$ nanoparticles has been observed. Concerning this, for magnetic separation of the $ZnFe_2O_4$/rGO (40 wt %) composite from its solution (2 mg/mL in ethanol) the time needed was too long (60 min) but a short time (only 2 min which is comparable to the separation time of pure $ZnFe_2O_4$ nanoparticles) was required while using the $ZnFe_2O_4$/rGO (15 wt %), in the presence of a magnetic field (1 Tesla). For aqueous solutions containing dyes, efficient and fast magnetic purification is provided by superparamagnetic $ZnFe_2O_4$–graphene nanostructures (with optimum ratio of graphene to $ZnFe_2O_4$, i.e., 15 wt %) [41].

3.4.1 Zinc/Iron Oxide Composite

In several industries, anti-bacterial agents are of great importance e.g. textile units, construction sites, water disinfection plants, medicine industry, packaging assemblages and food factories. For disinfection, traditionally used organic compounds pose several disadvantages such as high sensitivity to high temperatures, toxicity to the human body and pressures that are present in many industrial processes [42]. For these above reasons, the interest is increasing in using inorganic disinfectants such as metal oxides. At low concentrations, these inorganic compounds show strong anti-bacterial activity. Under extreme conditions, they are also much more stable, considered as non-toxic and even contain mineral elements essential to the human body. Among all metal oxide powders, zinc/iron oxide composite demonstrated significant growth inhibition to broad spectrum of bacteria. For the anti-bacterial activity of ZnO, the suggested mechanism is based on oxygen that disrupt the integrity of bacterial membrane and mainly on catalysis of formation of reactive oxygen species (ROS) from water, although additional mechanisms have also been suggested. Since on the particle surface, catalysis of radical formation occurs, stronger anti-bacterial activity is demonstrated by particles with larger surface area. Thus anti-bacterial activity increases as the size of the ZnO particles decreases [43].

3.4.2 Polyaniline-Coated Manganese–Zinc Ferrite

Upto the present time, in ferrites the resonance phenomena have been studied extensively and described by two different mechanisms of domain-wall motion and magnetization–spin resonance. The permeability spectra for polycrystalline ferrite can be described by superposition of both contributions. Moreover, in high-frequency region, the complex permeability is greatly affected by spin-rotation component. In ferrites, it has been found that the relaxation of magnetic oscillations is strongly affected by structural disorder, both geometrical and crystallographic, including cracks, surface roughness, defects and pores. Composite materials introduce an additional disorder in form of filler–matrix interfaces in which magnetic particles are embedded in insulating binders. Having different sorts of magneto-crystalline anisotropy, there are many technologically important ferrite materials.

Manganese–zinc (Mn-Zn) ferrites have selected due to low value of effective magnetic-field anisotropy, high initial permeability and low core losses. In electronic devices, ferrites of this type have widely been used. On the level of permeability, particle size and the effect of ferrite content is recently been reported. The shift of frequency resonance from the MHz to the GHz-frequency region is resulted by the surface modification of ferrite particles with conducting PANI coatings. For the preparation of composites with a polyurethane matrix, polycrystalline Mn-Zn ferrite and the same material after coating with PANI have been used. Ferrite particles based composites had higher permeability with the average size 60 mm than those with 30 mm particles.

The layer of conducting polymer, PANI was coated in former particles. The conductivity of the PANI coating deposited on the surface of ferrite particles is greatly affected by resonance frequency. In composites containing ferrite coated with conducting PANI, hydrochloride, a higher resonance frequency, enhanced approximately 6-fold that is observed by comparing with those based on uncoated specimens. Changes in magnetic properties of composites containing PANI-coated ferrite are due to the changes of boundary condition of the microwave field at the interface between polymer matrix and ferrite particle and to the demagnetizing field generated by magnetic dipoles. It is found that depending on conductivity of PANI, simple mixtures of ferrites with PANI powders in a polyurethane matrix do not exhibit resonance frequency shifts [44].

3.4.3 ZnO/Ag

In presence of Fe_3O_4 nanoparticles, the Fe_3O_4/ZnO/Ag nanocomposite is synthesized by a sequence formation of silver and zinc oxide nanoparticles. The results of XRD analysis showed that nanocomposite composed of hexagonal quartzite ZnO and Ag nanomaterials, face centred cubic structured Fe_3O_4. To study the morphological features, the nanomaterials were characterized by TEM and FESEM imaging. Based on the morphological and structural analysis, plausible formation mechanism of nanocomposite was studied. By using the VSM measurements, saturation magnetization (Ms) value of about 57.2 emu g^{-1} has observed for this nanocomposite. To study the band edge absorption characteristics, the optical absorption spectra were recorded. For the incorporation of Ag nanoparticles, the quenching of emission intensity of ZnO nanoparticles is indicated by photoluminescence graph. Due to SPR, the energetic electrons produced by Ag NPs are trapped into Fermi level of ZnO nanoparticles and are further trapped to Fe ions.

Efficient inhibition of electron hole pair recombination facilitates the series of electron trapping. Under visible light, illumination of nanocomposite has showed the degradation of photocatalytic methylene blue dye however for six reaction cycles the rate of degradation was consistent. The vessel containing colloid of nanoparticles well dispersed in water is placed with a permanent magnet in order to evaluate the magnetic separability of nanoparticles. Manifesting the convenient separation of materials from liquids using an external magnet, ZnO/Ag hetero-structures attached to Fe_3O_4 nanoparticles were noted for their magnetic attraction within 5 sec. The homogeneous dispersion of the composite in solution allowed the removal of magnet piece. This indicates that nanocomposite can be effectively used for rapid separation of nanomaterials back from the medium at the end of reactions and heterogeneous catalytic reactions [45].

3.5 Manganese Mono-Boride

Metalloid compounds of transition metals typically present outstanding mechanical properties owing to strong covalent bonds between atoms of metalloids and transition metals. Manganese borides were one of the most promising transition metal borides because of their low compressibility, wear resistance, high melting point, high hardness, high electrical conduction, excellent magnetic properties and thermal conduction. Furthermore, it is noteworthy that, from a more technological point of view, high glass forming ability (GFA) to form bulk glass materials (BGMs) and their INVAR behavior may be more useful in industrial applications. However, the higher boron content in manganese borides basically exhibit weak paramagnetic behavior and lower boron contents generally contribute to relatively soft mechanical properties. Consequently, suitable crystal structure constituting proper boron content may facilitate outstanding mechanical and ferromagnetic properties. In 1950, the synthesis of orthorhombic manganese MnB was first reported by Kiessing. Among transition metal borides (TMBs), MnB was reported to have high Curie temperature, Tc, due to the proper boron contents. Outstanding ferromagnetic property is shown by FeB-type MnB. The combined mechanical, electrical conductivity, room temperature ferromagnetic and chemical inertness make these material promising candidates for engineering and technological applications [46].

3.6 Zirconium-Chitosan Hybrid

For oil recovery from oil-in-water emulsion, the bio-polymeric hybrid sorbent, Zr-CS-HC was found to be a new adsorbent. At acidic pH, the adsorption capacity of Zr-CS-HC was found to be higher due to de-emulsification which takes place in acidic condition. For oil sorption, the Langmuir isotherm was best fit as compare to other isotherm models according to equilibrium data. The nature of oil sorption was endothermic and spontaneous which is proved by thermo-dynamic studies. When zirconium is incorporated onto chitosan, hydrophobic property of chitosan increases which in turns helps to adsorb hydrophobic compounds effectively. The prepared sorbent and oil sorption were confirmed by the XRD, DSC, contact angle, FTIR, TGA, heat of combustion and SEM with EDAX. The results showed that oil particles were effectively adsorbed by prepared hybrid sorbent and zirconium was successfully entrapped onto chitosan polymeric matrix. In oil sorption followed by electrostatic interaction, hydrophobic-hydrophobic mechanism plays a vital role. For oil recovery from oil-in-water emulsion, zirconium-chitosan hybrid has identified as an environmental friendly and effective adsorbent [47].

3.7 Fe_3O_4/CeO_2 Composite

A rare earth element of the lanthanide series is cerium. It provides a high oxygen storage capacity and has a redox cycle between the +3 and +4 oxidation states. In wastewater treatment and automotive exhaust treatment, this property enhances the performance of transition metal catalysts. For Fenton's depuration of phenolic wastewaters, the catalytic activity of Fe−Ce−O particles was investigated by Martins' group with diameters in the range of 250−500 μm. Zhang and coworkers reported that in heterogeneous Fenton reaction for decolorization of reactive brilliant red X-3B, nano-scaled Fe-Ce oxide hydrate catalyst showed a relatively low rate which was assisted by UV irradiation in order to achieve almost complete removal of dye within 30 minutes.

By impregnation method, magnetic nano-scaled Fe_3O_4/CeO_2 composite was prepared and characterized as a heterogeneous Fenton-like catalyst for 4-chlorophenol (4-CP) degradation. In view of the effects of various processes, catalytic activity, hydrogen peroxide concentration, temperature, pH value and pseudo-first-order kinetic constant of 0.11 min^{-1} was obtained for 4-CP degradation at pH 3.0 and 30°C temperature with catalyst addition.

In the oxidative degradation of organic pollutants, the high utilization efficiency of H_2O_2 showed a promising application of catalyst. After six successive runs, reusability of Fe_3O_4/CeO_2 composite was also investigated on the basis of the results of the effects of radical scavengers, x-ray photoelectron spectroscopic (XPS) analysis, metal leaching, intermediates determination and dissolution of Fe_3O_4 facilitated by CeO_2 played a significant role and 4-CP was decomposed mainly by the attack of hydroxyl radicals ($OH^•$), including surface-bound $OH^•$ ads generated by the reaction of Fe^{2+} and Ce^{3+} species with H_2O_2 on the catalyst surface and $OH^•$ free in the bulk solution mainly attributed to the leaching of Fe ions [48].

Conclusion

Magnetic composites have great impact on our lives as they are widely used in removal of different contaminants from wastewater. Depending upon the pollutant, different metals are used to form composite to treat wastewater and remove specific dyes under specific conditions. If the wastewater is not treated properly it can cause severe health hazards. Using composite of different metals that are magnetically active, wastewater could be treated by the process of adsorption and after treatment these composites can be removed easily with the help of simple magnet. Zeolites with iron oxides are used in removal of both organic and inorganic contaminants. Carbon nanotubes (CNTs) is used for various metal ions and organic pollutants such as Cu(II) from water, Sr(II), cationic dyes and Pb(II). MWCNT/nano-iron oxide is used for removal of chromium ions. Magnetic sorbent HNT–Fe_3O_4 is used for neutral red (NR), methyl orange (MO) and methylene blue (MB), metal ions or residual dyes from wastewaters. Activated carbons are helpful in removing phenols, chloro phenols and pesticides, several gases, heavy metal cationic contaminants. MnO–Fe_2O_3 and graphene are used for removal of azo-dye acid red B (ARB) and decolouration of methylene blue (MB) respectively. Magnetic cellulose/activated carbon, iron with glucose and Fe_3O_4@graphene composites (FGC) are used for removal of azo dyes, organic dyes or other pollutant and cationic and anionic dyes in water solution respectively. Ni/Mo_2C is used for removal of nitrogen compounds and sulfur from liquid fuels and model dyes such as indigo carmine and methylene blue. Al_2O_3/Ni composite has both magnetic and superior mechanical properties. Cupper based composites have applications in power engineering, spintronics, instrument making, microelectronics, etc. Zinc ferrite is efficient and fast magnetic for purification of dyes, zinc/iron oxide composite have strong antibacterial activity and ZnO/Ag used as photocatalytic degradation of methylene blue dye. While manganese mono-boride have outstanding mechanical and ferromagnetic properties, Zirconium-chitosan hybrid used for oil recovery from oil-in-water emulsion and Fe_3O_4/CeO_2 composite used in wastewater treatment and automotive exhaust treatment.

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