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# Magnetic adsorbents for the treatment of water/wastewater—A review

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ABSTRACT

In recent years, adsorption has displayed promising and effective results as a treatment technology for water and wastewater by industries. In the process, a number of adsorbents have been synthesized and applied for the treatment of pollutants such as metals, dyes, pharmaceutical products in solutions. However, for adsorption to be unconditionally adopted by industries, a few obstacles such as high capital cost, difficult segregation of adsorbent from solution, and complex synthesis processes need to be addressed. The removal of suspend adsorbents in wastewater from a continuous flow system is a challenge which if addressed properly would enable us to recover the spent adsorbent efficiently. The spent adsorbents can then be regenerated and used again by the industries thereby leading to reduced capital investment. Therefore, studies have been carried out aiming at the incorporation of magnetism in such adsorbents to aid their removal from wastewater. This review aims to comprehensively list and discuss adsorbents which exhibit magnetic properties and their adsorption behaviour under diverse conditions. The literature survey presented in this paper renders evidence to the good potential of magnetic adsorbents to remove various pollutants from wastewater. However, the practical utility of such adsorbents needs to be explored before they can be commercially applied.



**Contents**



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## 1. Introduction

Water is an essential source for maintaining life on this planet. Even though it is available in abundance, the chemical composition varies across the strata, thus affecting its suitability for domestic as well as industrial purposes. Groundwater accounts for only 0.6 % of the total available water resources [1]. It is this 0.6% which caters to the global water needs. However, with the onset of rapid industrialization, the quality of drinking water has reduced significantly. Discharge of industrial effluent, solid waste from households and industries etc., are responsible for the increasing levels of groundwater pollution. Hence to treat water, several techniques such as membrane separation process [2–4], coagulation and flocculation [5–6], filtration [7–10], adsorption [11–16], chemical treatment [17–18] have been developed.

Adsorption is a surface boundary phenomenon of accumulation of species onto a liquid or solid phase from a bulk phase. It is a phenomenon which has been observed since ancient times. Current available literature dates it back to 1773 when Scheele carried out adsorption experiments of the uptake of gases by charcoal and clay [19]. Since then, the field of adsorption has witnessed a lot of research. Some significant contributions to this field were the development of isotherm models by Langmuir [20] and Freundlich [21] and the kinetic models developed by Lagregren [22] and Ho [23]. Today, adsorption plays an important role in the industrial processes. Higher efficiency and insensitivity to toxic substances compared to the other conventional methods of water purification has made it much more popular.

Some adsorbents which have been widely used for water purification are activated carbon [24–31], silica gel [32–36], zeolite [37–43], clay minerals [44–47]. However due to their high generation costs, researchers shifted their focus to the use of dead biomass and waste such as peanut shell [48], garden grass [49], ground coffee [50], saw dust [51–52], sunflower leaves [53], egg shells [54], almond shell [55] sugarcane bagasse [56], Anabaena sphaerica [57], Bacillus laterosporus [58], green algae [59], orange peel [60], pine cone [61], guava leaf [62] for the removal of dyes, metals and organic pollutants from wastewater. Agricultural waste as adsorbents presents us with an attractive option due to their low cost and high abundance. Numerous studies have been conducted to develop cheaper effective adsorbents containing natural biopolymers. Even though these adsorbents have proved to be very effective in the removal of pollutants from wastewater, they suffer one inherent disadvantage. It is difficult to separate them from wastewater in a continuous flow system. Hence, studies have been conducted to explore the use of magnetism as an effective means of separating these suspended adsorbents from water.

The use of magnetism for water purification is an age old concept. Available texts predate the use of magnetism for water treatment to as early as 1873 [63]. Since then magnetism has been employed in various water treatment methods such as anti scaling technique in boilers, pipelines in factories [64–67], coagulation [68], biological processes [69–70]. The use of magnetism in an adsorption process is a relatively newer concept; one which is gathering increasing attention from the researchers day by day. Magnetic adsorbents are a new class of adsorbents where a base adsorbent is embedded with magnetic particles which are oxides of metals such as Fe, Co, Ni and Cu [71]. On application of an external magnetic field, the magnetic adsorbent can be rapidly and easily separated from water due to the presence of the metal component in the adsorbent. Magnetic ion exchange resins (MIEX) were first used for the removal of natural organic matter in 1995 [72]. Since then magnetic particles modified with polymer [73–74], carbon nanotubes [75] etc., have been used commercially.

This review focuses on the use of various magnetic adsorbents for the removal of pollutants from wastewater. A summary of the data published pertinent to the topic is presented and the results of these findings have been discussed. At the end, the results (relating to pH, adsorption capacity, isotherms, and kinetics) have been compiled in the form of a table. For more information, the readers are advised to refer to the full articles that are listed in the References

## 2. Magnetic adsorbents

### 2.1. Sorption of Anions

#### 2.1.1. Arsenic

Arsenic is a toxic carcinogen present in drinking water predominantly as As (III) ($H_3AsO_3$, $H_2AsO_3^-$, and $HAsO_3^{2-}$) and As (V) ($H_3AsO_4$, $H_2AsO_4^-$, and $HAsO_3^{2-}$) [76]. These oxides are difficult to destroy and can be only transformed into insoluble compounds. Chronic exposure to arsenic contaminated water can cause serious medical complications such as loss of appetite, cancer of skin, lungs and bladder [77]. Hence in order to minimize the health risk, the World Health Organization (WHO) has set 10 $\mu$g/L as the maximum limit of arsenic that can be present in drinking water. Removal of arsenic from industrial wastewater has recently gained a lot of attention. Numerous investigations have been performed on the study of magnetically treated adsorbents and their capability to remove arsenic from water.

Shan and Tong [78] fabricated Mag–Fe–Mn containing 46.1% Fe and 9.2% Mn by weight .Batch experiments were carried out and the adsorption isotherms of Mag-Fe-Mn, Mag-Mn, Mag-Fe, Mag-core were examined and it was found that the four adsorbents followed freundlich model better which was possible due to the irreversible adsorption and heterogeneous nature of adsorbents. Langmuir adsorption capacity of Mag-Fe-Mn was nearly twice that of the other adsorbents. The authors studied the effect of pH on the removal efficiency of the adsorbent. Removal percentage of As(III) remained above 95% in the pH range of 4–8. At pH > 8, enhanced electrostatic repulsion due to deprotonation of arsenic species, negative zeta potential of Mag–Fe–Mn particles and the potential competition from the hydroxyl ion were responsible for the decreased removal of arsenic.

Kilianová et al. [79] used ultrafine $Fe_2O_3$ particles as an adsorbent for removal of arsenate ions from an aqueous solution. The authors found all As(V) was removed when the pH was in acidic range. This corresponded well with the zeta potential of the adsorbent which was equal to 7.6. 100% efficiency was achieved between pH of 5 and 7.6, and Fe/As ≈ 20/1. Arsenic removal at equilibrium was found to be 45 mg/g. Binary oxides of chitosan were synthesized by template method for removal of arsenite from water [80]. No effect of pH was observed in the range of 3–9 and reduced thereafter. The adsorption capacity obtained from the Langmuir model was 16.94 mg/g. Presence of $Ca^{2+}$ and $Mg^{2+}$ significantly affected the performance of the adsorbent. Field trials reduced the initial As(III) concentration from 983.71 $\mu$g/l to7.44 $\mu$g/l. Luo et al. [81] studied the interaction of arsenic ions with $Fe_3O_4$–RGO–$MnO_2$ nanoparticles where RGO is Reduced Graphite Oxide, over the entire pH range; with initial arsenic concentration ranging from