

Removal of Dyes from the Environment by Adsorption Process

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Abstract Organic dyes are considered as serious water pollutants. There are several ways for removal of these compounds from environment, which are mainly based on biological, chemical, and physical methods. In this paper, we first classify the common organic dyes which are in use in today's industry; then, methods of their elimination from environmental water and wastewater will be discussed very briefly, with an emphasize on adsorption techniques. At the end, some modern advanced adsorbents are presented.

Keywords Organic Dyes, Removal, Adsorption

1. Introduction

The coloring industry is a large-scale and one of the most important industries across the world. However, its wastewater in the environmental is considered as a harmful source of pollution for creatures due to variety of dyes present in it. Mutagenic and carcinogenic of some dyes have been proved [1,2]. Dysfunction of kidney, liver, brain, reproductive system and central nervous system are some effects of dyes on human being [3]. Therefore removal of dyes from environmental is of important consideration. Researchers are looking for low-cost methods to remove these dyes from the aquatic environment. It is estimated that textile industries release approximately 100 tons of dyes and pigments to the water streams annually [4-6]. Lethal dose of some dyes are collected in Table 1.

Table 1. Toxicity of some dyes

Name	LD ⁵⁰ (mg/Kg rat)	Source
1 Malachite green	275	[7]
2 Acid orange 165	60	[8]
3 Basic Blue 7	100	[8]
4 Basic Blue 81	205	[8]
5 Basic Violet 16	90	[8]
6 Basic Yellow 21	171	[8]
7 Direct Orange 62	150	[8]

Commercial dyes can be classified according to their structure, their color and their application. Their assortment in terms of their chemical nature is presented in Table 2 [9].

Table 2. Classification of dyes based on their nature

Class	Application	Examples
1 Acid dyes	Nylon, wool, silk, modified acrylics, paper, leather, food, inkjet printing and cosmetics.	Acid red 88, Acid red 18
2 Cationic (Basic) Dyes	Poly acrylonitrile, paper, modified polyesters, modified nylons, cation dye able polyethylene terephthalate, wool, silk, tannin mordanted cotton and medicine.	Crystal Violet, Methylene Blue, Safranin, Basic fuschin
3 Disperse Dyes	Nylon, polyester, cellulose, acrylic fibers and cellulose acetate.	Disperse Red 1, Disperse Orange 37
4 Direct Dyes	Rayon and cotton, leather, paper and nylon.	Congo Red, Brilliant Blue, copper blue 2R
5 Reactive Dyes	Wool, nylon, cotton and other cellulosic.	Reactive Black 5, Reactive Orange 16
6 Solvent Dyes	Gasoline, plastics, oils, lubricants and waxes.	Solvent Red 1, Solvent Red 49, Solvent Red 24, Solvent Red 111
7 Sulfur Dyes	Cotton and rayon, paper, leather, silk and wood.	Sulfur Brilliant Green, Sulfur black 1
8 Vat Dyes	Cotton, rayon and wool.	Vat red 10, vat violet 13 and vat orange 1.

There are a wide variety of methods to remove pollutants from environmental waters or sewage. Most of them can be classified as biological, chemical, and physical purification processes (Fig. 1) [10,11]. Of these techniques, adsorption is considered to be the most well-known process. The accumulation of adsorbates at gas-solid or liquid-solid interface is called adsorption phenomena [12]. In most cases, adsorption is reversible because of weak Van der

Waals bonds between adsorbent and adsorbate [13]. Isotherm models are fundamental concepts that deal with adsorption science. They explain how adsorbate and adsorbent interact to each other; and also by these models, the adsorption capacity can be calculated [14,15]. While chemical treatments produce foul odor and byproducts, and are expensive; adsorption phenomena is of interest for dyes removal because of its low cost and flexibility in design and also because this process does not produce any harmful substances after removal of the target compounds. The most important disadvantage for biological treatment methods is that many of these processes are very time consuming. For example, mix bacteria decolorization needs up to 30 hours to be completed. On the other hand, some dyes cannot be removed by physical methods such as ion exchange; and for electrokinetic coagulation, high volume of sludge is produced. Conversely, adsorption is economical, easy to use, and can eliminate almost all type of contaminants. That's why this process is widely in use for removal of not only dyes and pigments, but also for other contaminants such as heavy metal impurities from waste water or sewage [16-22].

The first attempts for using adsorption process for removal of an unwanted compound was started in 1550 BC by Egyptians who used charcoal to adsorb odorous vapors from wounds and intestine. Phoenicians observed the application of charcoals filters in 460 BC purify water [12, 23]. The first article about the removal of dyes by adsorption process was published by Chapman and Siebold in 1912. In this paper, they described separation of dye molecules from water [24]. Concepts which were added in 20 century to this type of adsorbing dyes were isotherm models of adsorption, mainly by Hebert Freundlich and Irving Langmuir [25]. Also by invention of transmission electron microscopy and scanning electron microscope which were invented in 1935 we are now able to monitor the quality of adsorption [26, 27]. Nowadays a wide range of theories describe adsorption phenomena and there are a lot of practical examples, including industrial and environmental tasks that were carried out by this phenomenon. In all of them, molecular modeling plays a significant role which researchers can conjugate it with experimental techniques to achieve highest adsorption capacity.

Since adsorption deals with a lot of crucial domains such as membrane separation, chromatography and ion exchange, every development in these areas will affect tremendously on the development of new adsorption techniques.

It is obvious that the adsorption characteristics and structural adsorbents play a crucial role in using of them in various applications. Characteristics that can effect on removal of contaminations are adsorption capacity, specific surface area, pore volume, grain size and pore size distribution. They are so important because if they change, the efficiency of removal change too [28].

For the removal of dyes a wide variety of adsorbents has been used, of them, the most common are discussed below.

Zeolites are selective adsorbents which can be found in the environment and can be also synthesized in laboratory. Zeolites are highly porous and their charges are negative. Application of 3A zeolite to remove Rhodamine B is common and this adsorbent can remove ~90% of this contaminant from industrial wastewater [16].

Alumina is an especial crystalline gel which is synthesized in various sizes and its appearance is granule with surface area of $200-300 \text{ m}^2\text{g}^{-1}$. Alumina is a great adsorbent for removal of disperse dyes from water [29].

Silica gel is a porous, non-crystalline granule. The surface area of it booms expeditiously rather than alumina and reaches to $900 \text{ m}^2\text{g}^{-1}$. Silica gel is prepared by the coagulation of colloidal silicic acid. A maximum adsorption capacity of 11.1 mg/g for modified silica gel was reported for removal of sulfur dyes from aqueous solutions [30].

Activated carbon is the oldest well-known adsorbent and it usually is prepared from coconut shell, lignite, wood, coal, and so on. Since commercial activated carbon for dye removal is expensive, some adsorbents which special features like eco-friendly and environmental friendly have been used. There are numerous articles about removing of dyes and other pollutants by activated carbon. Furthermore, surface area in activated carbon is quite high (near $200 \text{ m}^2\text{g}^{-1}$) [31, 32]. Despite that this adsorbent is very effective, it is not selective.

It is ideal for all of the adsorbents to be regenerated after being used and became saturated. Various techniques such as electrochemical, thermal, chemical methods and ultrasonic were reported for this purpose [33].

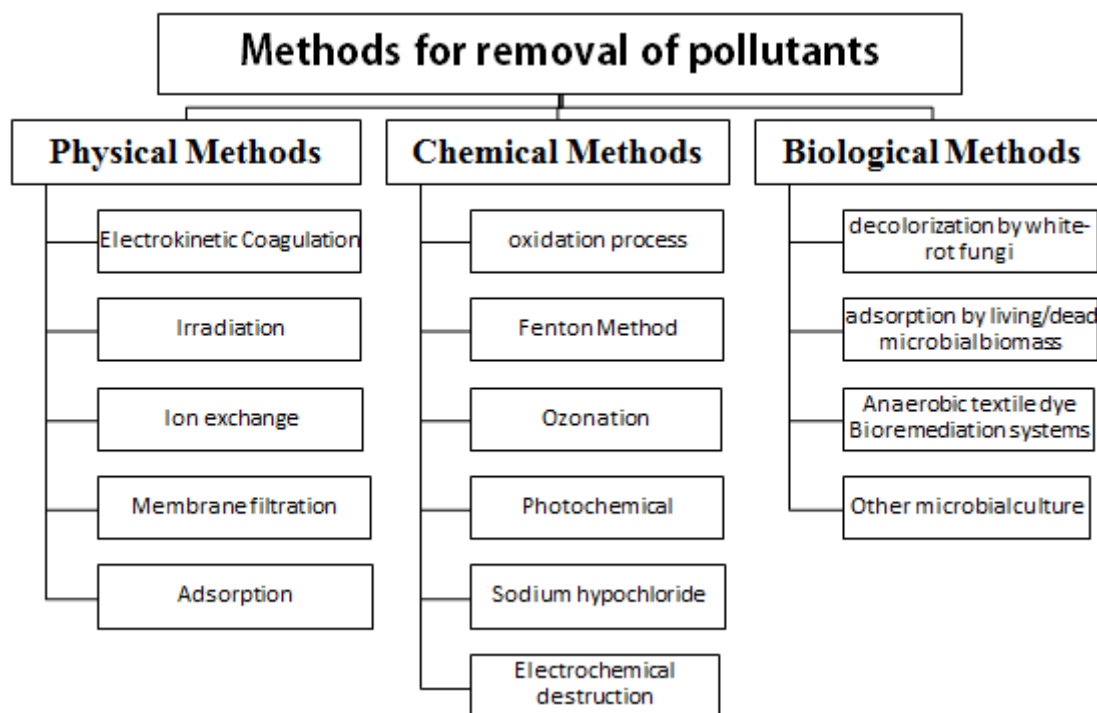


Figure 1. Methods generally in use for removal of pollutants

Occasionally, some adsorbents are disposed after using because they cannot be regenerated and consequently they became secondary pollutants. Researchers try to make some new adsorbents with high surface area to solve this problem. Recently, many papers have been published that show there is a tendency to synthesize high surface area materials such as modified silica and zeolites; ZnO and TiO₂ on clay; metal-organic frameworks; carbon nanocages; graphene; nanotubes; porous polymers and functional 3D boron nitride nanostructures to remove dyestuffs from water [34-40]. Not only the most of these adsorbents can be reused, but they are very efficient and fast, thanks to their high surface area.

It is anticipated that over the next 10 years the developing and investigating of new adsorbents with super adsorption capacity will be more rapid and novel adsorbents will be tested to solve pollution problem to some extent. Just as an example, super adsorbents polymers (SAPs), which are the 3 dimensional networks of polymers, can adsorb more than 100 times of liquid of their own weight. Since SAPs possess ionic groups in 3 demonstrate networks, they adsorb oppositely charged materials [41]. Form these characteristic, researchers can provide and achieve selective super adsorbents.

2. Conclusions

Urbanization has left some negative effects on environment such as releasing dyes to water streams. Since organic dyes are carcinogenic and mutagenic, researchers are trying to find some methods to remove this pollution

from water/wastewater. Adsorption is an economical and simple method for this purpose. We reviewed some common adsorption techniques in this manuscript. Some modern adsorbents which are expected to be in use in the future are also presented. They have the ability to be re-generated and possess extremely high surface area.

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