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Review

Removal of Reactive Blue 21 (RB21) Phthalocyanine Dye from Aqueous Solution by Adsorption Process: a Review

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Abstract

Phthalocyanine dyes are one of the major categories of reactive dyes. They are water-soluble metal complexes, mainly containing copper, that are resistant to bacterial degradation under aerobic and anaerobic conditions. In this review article, the authors present the removal of RB21 phthalocyanine dye in aqueous solution by adsorption based on the literature. Therefore, an exhaustive list of various adsorbents has been compiled here. Additionally, the performance of several adsorbents under different physico-chemical process parameters and their comparative adsorption capacity towards the adsorption of RB21 dye was also presented. Affective adsorption factors for the dye such as solution pH, initial dye concentration, adsorbent dosage and temperature are also included.

Keywords: Reactive Blue 21, phthalocyanine dyes, decolorization, adsorption, dye removal

Introduction

The textile industry has created a big environmental problem because it is one of the most chemically intensive industries on the planet. Over 3600 individual textile dyes are nowadays manufactured by the industry [1]. Every year, approximately 200,000 tons of these dyes are lost in effluents during dyeing and finishing operations [2]. More than 8000 chemicals are used by the industry in various textile production processes. Table 1 lists some of these chemicals. Most of these chemicals are toxic and directly or indirectly harm human health. Large quantities of water are needed to treat textiles [3]. Dye, even in low concentrations, is visible and impacts both aquatic life and the food chain. The average concentration of dyes in textile wastewater is about 300 mg.L^{-1} [4]. Disposal of this highly colored effluent in natural watercourses hinders the penetration of light, perturbs biological processes in the aquatic environment and gives an unpleasant aesthetic appearance [5]. Azo, anthraquinone, triarylmethane and phthalocyanine dyes are the most important dye groups [6]. Phthalocyanines are a group of dyes produced by the reaction of dicyanobenzene in the presence of a metallic type of Cu, Ni, Co, Pt. Copper phthalocyanines are the main derivative of this dye class, due to their beautiful blue to green shades, high dyeing resistance, excellent chemical stability, light fastness and resistant to bacterial degradation under aerobic as well as anaerobic conditions [7-9]. However, the process wastewater from

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Table 1. Major chemicals and dyes used in synthetic textile mills [81].

Sr No.	Chemical	Quantity Kg/month
1	Acetic Acid	1611
2	Ammonium Sulphate	858
3	P V Acetate	954
4	Wetting Agent	125
5	Caustic Soda	6212
6	Softener	856
7	Organic Solvent	247
8	Organic Resin	5115
9	Formic Acid	1227
10	Soap	154
11	Hydrosulphites	6563
12	Hydrochloric Acid	309
13	Hydrogen Peroxide	1038
14	Leveling & Dispersing Agent	547
15	Solvent 1425	321
16	Oxalic Acid	471
17	Polyesthylene Emulsion	1174
18	Sulphuric Acid	678
19	Disperse Dyes (Polyester)	1500
20	Vat Dyes (Viscose)	900
21	Sulphur Dyes	300
22	Reactive Dyes	45

the copper phthalocyanine production plant contains a high COD (Chemical Oxygen Demand) content and a considerable amount of copper. The result of this type of contamination can cause the formation of a mixed effluent, containing heavy metal ions and organic matter indicating a toxicity measure [10]. Various methods have been developed for the elimination of copper phthalocyanine dyes from the wastewater in order to reduce their environmental impact [11-16]. Adsorption is one of the principle methods employed in wastewater for the removal of dyes, due to its universality, affordability and ease of use [17]. The objective of this review is the compilation of different adsorbents for the removal of the reactive blue 21 phthalocyanine dye in aqueous solution.

Adsorption

Many dye removal methods have been tested and proven, including adsorption (physical method), which has emerged as one of the preferred dye removal techniques because of its exceptional ability to remove almost all types of dyes [18–20]. The adsorption means the deposition of a substance at the interface between two phases (gas-solid or liquid-solid). The substance that accumulates at the interface is called an adsorbate and the solid on which adsorption occurs is an adsorbent [21]. There are two types of adsorption: chemical sorption and physical sorption. Chemical adsorption or chemisorption is illustrated by the formation of strong chemical bonds between the molecules or ions of the adsorbate on the surface of the adsorbent, which is usually due to the exchange of electrons and therefore chemical sorption is usually irreversible. Physical adsorption or physisorption is characterized by weak van der Waals intraparticle bonds between the adsorbate and the adsorbent and therefore reversible in most cases [22]. This process offers a good alternative for the treatment of polluted water, especially if the sorbent is economical and doesn't necessitate an additional pretreatment step prior to its application [21]. The handicap of this method was the high cost of adsorbents, but with the discovery of inexpensive adsorbents that were just as effective, this method has become an economical method of dye removal around the world [23-25]. Several adsorbents are successfully used for the removal of RB21 phthalocyanine dye.

Activated Carbon

Activated Carbon is a remarkable highly adsorbent material that has a wide range of applications in the remediation of groundwater contamination and industrial wastes such as colored effluents [26,27]. Activated carbons have a wide range of surfaces which generally vary between 500 and 1500 $m^2.g^{-1}$, even up to 3000 $m^2.g^{-1}$ [28]. they can be produced from any material having high percentages of carbon in its composition. Preferable characteristics of activated carbons are their affinity for various compounds, their large surface area and their ability to be regenerated [29]. Activated carbon is effective in removing all types of dyes and a variety of pollutants from wastewater [30]. The application of activated carbon for the treatment of RB21 dye has been reported by Shakoor et al. (2016). It is prepared according to the experimental protocol [31]. The batch adsorption process was affected by the agitation speed within the range of 130-300 rpm, sorbent dose ranging from 0.4 to 1.3 g, the dye concentration from 2 to 16 ppm and the pH value between 3 and 8. The best removal of RB21 dye was obtained with a stirring speed of 210 rpm, a sorbent dose of 1.0 g, a dye concentration of 6 ppm and a pH of 3. The maximum adsorption capacity calculated using Langmuir isotherm model was found to be 7.08 $mg.g^{-1}$ [31].

Clinoptilolite

Clinoptilolite represents the most abundant natural zeolite and is used extensively throughout the world. Its typical chemical formula is $(NaKCa)_4(Al_6Si_{30}O_{72})\cdot 24H_2O$, and it is one of the unique candidates for adsorption of organic pollutants because it has special properties such as suitable structure, high stability, high cation exchange potential, cost-effectiveness and abundant distribution [32-34]. It has a characteristic tabular morphology showing an open reticular structure of easy access, formed by open channels of 8 to 10 limb rings. It was demonstrated that clinoptilolite has a high selectivity for certain pollutants [35,36]. Sismanoglu et al. (2010) reported the application of clinoptilolite for the removal of RB21 dye. This adsorbent was used directly for adsorption experiments without any treatment. The adsorption of the reactive dye RB21 on the clinoptilolite was investigated in a batch model. The initial concentration of the dye is between 10 and 250 $mg.L^{-1}$ prepared with doubly distilled water, 0.1 g of clinoptilolite and 10 mL of solution were stirred with a water bath to control the temperature at 25ºC without any change in the initial pH (7.6). The equilibrium time of adsorption was found to be 90 min for the clinoptilolite. The adsorption isotherm of RB21 on the clinoptilolite was well described by the Langmuir adsorption equation. The clinoptilolite monolayer coverage capacity for the RB21 dye was determined to be 9.652 $mg.g^{-1}$ [37].

Polyurethane Foam

Polyurethane foams (PUF) are considered to be suitable adsorbents for the retention of chemical substances because they are cheap and can be used without any prior treatment. In addition, PUF have an excellent chemical and thermal resistance, a high adsorption efficiency, the possibility of reuse after desorption of the colorants and a popularization [38, 39]. Due to the presence of polar and non-polar groups in their structures, PUF are able to retain different classes of substances. They can be applied for the retention of free molecules with high polarizability such as aromatic compounds, metal dithizonates or iodine, and also large anions with high polarizability [40,41]. The use of PUF for the treatment of the RB21 dye by de Jesus da Silveira Neta et al. (2011) has been reported. This adsorbent was used after rinsing with distilled water and drying at room temperature for 24 hours. The batch study using the Langmuir model was conducted to estimate the maximum adsorption capacity of the dye RB21 by the PUF. 80 mg of adsorbent in 15 mL aqueous dye solution were used at concentrations of 10-60 $mg.L^{-1}$ with keeping the pH value at 2. The equilibration time of adsorption was 180 min for PUF. The maximum adsorption capacity of PUF for the RB21 dye was 8.31 $mg.g^{-1}$ [42].

Chitosan/Polyamidoamine

Chitosan is one of the most promising and applicable materials in adsorption applications. Besides its physical properties (macromolecular structure, low-cost, non-toxicity, biocompatibility, biodegradability, etc.) [43], and its applications in many fields (cosmetics, medicine, biotechnology, membranes, food industry, etc. [44-47], chitosan was given particular attention as a functional material because of its adsorption potential. The presence of amino and hydroxyl groups in its molecules contributes to many possible adsorption interactions between chitosan and pollutants (dyes, metals, ions, phenols, pharmaceuticals compounds, pesticides, herbicides, etc.) [48, 49]. As is well known, the major advantage of chitosan is the existence of modifiable positions in its chemical structure [50]. Several functional groups have been introduced to modify chitosan to increase their adsorption capacity and improve their adsorption selectivity [51-53]. Chitosan/ polyamidoamine (PAMAM) has been reported to be an effective modification of chitosan for the removal of heavy metals and dyes in aqueous solution [54, 55]. Recently, many studies have reported the removal of dyes and metal ions using magnetic chitosan composite (MCS) adsorbents. The application of MCS/PAMAM for the removal of RB21 dye from the aqueous solution has been reported by Wang et al. (2015). MCS/PAMAM is well prepared following the experimental protocol [54]. The batch adsorption experiments were influenced by the adsorbent dose ranging from 5 to 50 mg, the dye concentration from 40 to 100 $mg.L^{-1}$, and the pH value between 2 and 11. The equilibrium time of adsorption was found to be 720 min. Adsorption capacity decreased from 390.69 to 159.04 $mg.g^{-1}$ when the dose of MCS/PAMAM was increased from 5 to 50 mg. The adsorption capacity reached a maximum of 201.16 $mg.g^{-1}$ at pH 6. The amount of dye adsorbed increased from 97.27 to 221. 06 $mg.g^{-1}$ with an increase in the initial concentration from 40 to 100 $mg.L^{-1}$, The maximum adsorption capacity calculated using Langmuir isotherm model was found to be 200 $mg.g^{-1}$ [54].

Chitosan-Zirconium Phosphate

Zirconium bis-(monohydrogen orthophosphate) monohydrate ($Zr(HPO_4)_2H_2O$), also known as layered α-zirconium phosphate (ZrP), is attracting increasing attention because of its ability to act as an ion exchanger, catalyst and intercalation support due to its lamellar structure and abundant hydroxyl groups [56]. Nevertheless, the disadvantage of these materials for practical applications is their microcrystalline nature which limits adsorbent recovery in discontinuous systems and affects the hydrodynamic properties of fixed bed systems [57]. This can be circumvented by immobilizing, grafting or encapsulating these materials in polymers [58,59]. Chitosan has an inherent affinity with ZrP, it was felt that chitosan-layered ZrP (CZrP) could have dye adsorption potential. Bhatt et al. (2019) reported the application of *CZrP* for the removal of RB21 dye. CZrP is well prepared following the experimental protocol [57]. Batch adsorption experiments were conducted at 30ºC with stirring at 200 rpm, the adsorbent dose (CZrP) of 0.05 g was used with 25 mL of dye (100 ppm) at contact time = 210 min, with pH ranging from 1 to 10. The maximum adsorption capacity was observed in the pH range 3-5. The maximum adsorption capacity calculated using Langmuir isotherm model was found to be 457 $mg.g^{-1}$ occurred at acidic (pH 3).

The Modified Microcrystalline Cellulose

Microcrystalline cellulose (MCC) is a purified hydrolyzed crystalline form of cellulose that appears as a white, odorless, tasteless, and crystalline powder with porous structure [60]. MCC is a practical material with excellent properties for the pharmaceutical, cosmetic, food, polymer composite and other industries [61]. It offers advantages such as low cost, low density and low abrasion of process equipment [62]. Chemical modification of the surface of MCC increases its adsorption capacity by enhancing its chemical and physical properties. The chemical modification of MCC by aminopropyltriethoxysilane (APTES) and hydroxypropyldodecyldimethylammonium and its uses in the removal of RB21 dyes are reported by Ravindra et al. (2019) and Hu et al. (2016) respectively. The MCC modified by APTES was well prepared according to the experimental protocol [63]. The batch adsorption experiments were affected by the pH value between 2 and 12, the initial dye concentration of 40 to 120 $mg.L^{-1}$, the adsorbent dose (MMCC) ranging from 0.1 to 0.3 g, the temperature varying between 30 and 50ºC, and the contact time from 0 to 60 min. The sorption of the dye decreases with increasing pH value, pH values of 2 were considered optimal for the adsorption of the dye RB21. Adsorption capacity increased from 8 to 20 $mg.g^{-1}$ with an increase in initial dye concentration from 40 to 120 $mg.L^{-1}$. The equilibrium time of adsorption was found to be 50 min. The efficiency of dye removal increased from 70 to 94% with the increase of the adsorbent dosage. Further experiments with an adsorbent of more than 0.25 g showed that there was no change in the results. 0.25 g can be considered the optimal amount of adsorbent for discoloration. The adsorption capacity increased from 23 to 30 $mg.g^{-1}$ with increasing temperature. The Langmuir isothermal adsorption model demonstrates a good adjustment with the adsorption capacity of 30 $mg.g^{-1}$ at 50ºC [63]. The MCC modified by hydroxypropyldodecyldimethylammonium is well prepared following the experimental protocol [12]. The batch adsorption experiments were affected by the pH value between 2 and 10, the initial dye concentration of 70 to 120 $mg.L^{-1}$, and the contact time from 0 to 350 min. Adsorption capacity reached 200 $mg.g^{-1}$ at initial pH 2, at a loading of 400 $mg.L^{-1}$ and at an initial concentration of 80 $mg.L^{-1}$ for 180 min. the Langmuir model best describes the adsorption process of the RB21 dye on MMCC, suggesting a monolayer adsorption process with no interaction between the adsorbed dye molecules, the maximum dye adsorption capacity of the Langmuir isothermal model at 40ºC was 408.90 $mg.g^{-1}$ [12].

Sepiolite

Sepiolite is an abundant and cheap natural clay mineral. It is a hydrated magnesium silicate with a theoretical molecular formula of $Si_{12}O_{30}Mg_8(OH)_4(H_2O)_4.8H_2O$ [64,65]. Its structure is a needle-shaped crystalline structure that grows in the direction of the fiber, composed of two tetrahedral silica sheets and a central octahedral magnesium sheet [66]. Because of the discontinuous octahedral sheets, several porous channels develop in the sepiolite structure, allowing access to contaminants in the structure [67]; it has been successfully used for the adsorption of various contaminants such as heavy metals, dyes, oils, carbon dioxide, hydrogen and phosphorus [64, 67-71]. Sepiolite is a great adsorbent for organic species because it has a variety of attractive properties such as high specific surface area, high porosity, and high chemical and mechanical stability [72]. Demirbas and Nas (2009) reported the use of the sepiolite for the treatment of RB21 dye. This adsorbent was used directly for adsorption experiments without any treatment. The batch adsorption tests were controlled by experimental parameters such as initial dye concentration (100-750 $mg.L^{-1}$), pH (2-8), adsorbent dose (1-4 $g.L^{-1}$) and temperature (25-50 °C) during a contact time for a contact time of 16 h. As the initial concentration increased from 100 to 750 $mg.L^{-1}$, the amount of RB21 adsorbed increased from 20.2 to 54.3 $mg.g^{-1}$. The amount of RB21 adsorbed increased from 20.9 to 32.8 $mg.g^{-1}$ as the pH decreased from 8 to 2 and the optimum pH value was found to be 2. The quantity of adsorbed dye increased from 13.5 to 32.8 $mg.g^{-1}$ while reducing the adsorbent dosage from 4 to 1 $g.L^{-1}$. The maximum adsorption capacity of the dye increased from 48.1 to 60.8 $mg.g^{-1}$ as the temperature increased from 25 to 50ºC. The Langmuir isotherm provided the best correlation, the maximum dye adsorption capacity from the Langmuir isotherm model at 50ºC was 66.67 $mg.g^{-1}$ [73].

Fly Ash

Fly ash (FA) is a by-product of the combustion of coal in the power production process. Fly ash has been used effectively for construction materials, soil amendment and fill materials, but it is unlikely that these applications will result in the reuse of all fly ash produced. Therefore, great efforts are being taken to explore other applications prior to disposal [74]. The reuse of FA as an adsorbent for the removal of different types of pollutants in wastewater has attracted a lot of attention. It has been used to remove heavy metals, dyestuffs from water, it is considered an effective adsorbent due to its hollow sphere and activated surface [11]. The application of FA for the elimination of RB21 dye from the aqueous solution has been reported by Demirbas and Nas (2009). This adsorbent was used directly for adsorption experiments without any treatment. The batch adsorption tests were affected by the initial dye concentration (100-750 mg.L^{-1}), pH (2-8), adsorbent dose (1-4 g.L^{-1}) and temperature (25-50ºC) for a contact time of 16 hours. As the initial concentration increased from 100 to 750 mg.L^{-1}, the amount of RB21 adsorbed increased from 36.3 to 80.4 mg.g^{-1}. The amount of RB21 adsorbed decreased as the initial pH increased and the optimum pH value of the dye was found to be 2. The amount of RB21 adsorbed increased from 19.8 to 56.9 mg.g^{-1} when the pH changed from 8 to 2. The amount of adsorbed dye increased from 23.7 to 56.9 mg.g^{-1} while reducing the adsorbent dosage from 4 to 1 g.L^{-1}. The maximum adsorption capacity of the dye increased from 73.9 to 96.0 mg/g as the temperature increased from 25 to 50ºC. The Langmuir isotherm gave the best correlation, the maximum dye adsorption capacity of the Langmuir isothermal model at 50ºC was 106.71 mg.g^{-1} [73].

The Modified Carboxymethyl Cellulose/Fe_3O_4

Cellulose is among the world's most abundant natural polymers, providing excellent biodegradability and biocompatibility. Nevertheless, the compact and inactive molecular structure of cellulose demands that it be modified to enhance its hydrophilicity as an adsorbent for the removal of dyestuffs. The sodium carboxymethyl cellulose (CMC) is a derivative representative of cellulose with carboxymethyl groups (-CH_2COONa) attached to some of the hydroxyl groups in the cellulose backbone. The polar carboxyl groups make cellulose soluble, chemically reactive and highly chelated; therefore, the application of CMC in adsorption domains seems interesting and promising. Wang et al. (2016) reported the use of the magnetic CMC/Fe_3O_4 modified with hydrazine for the treatment of RB21 dye. CMC/Fe_3O_4 modified with hydrazine (MCMC/Fe_3O_4) is prepared in according to the experimental protocol [75]. The batch adsorption tests were impacted by initial pH (1.08-10), contact time (0-700 min), initial temperature (30-60ºC), adsorbent dose (20-80 mg.L^{-1}) and initial dye concentration (40-100 mg.L^{-1}). The elimination efficiency was found to decrease from 94.47% to 40.04% as the pH increased from 1.08 to 10.00. The adsorption capacity completely reached equilibrium after 240 min. Adsorption capacity was found to increase from 60.32 to 72.59 mg.g^{-1} with increasing temperature from 30 to 60ºC. The adsorption capacity decreased from 101.84 to 31.10 mg.g^{-1} as the adsorbent dose increased from 20 to 80 mg. The removal efficiency increased from 76.37% to 99.69% as the initial concentration increased from 40 to 100 mg.L^{-1}. The Langmuir isotherm gave the best correlation, the maximum dye adsorption capacity of the Langmuir isothermal model at 60ºC was 126.58 mg.g^{-1} [75].

Table 2. Maximum adsorption capacity of RB21 dye bye some adsorbents.

Adsorbent	Adsorption capacity (mg/g)	Reference
Activated carbon	7.08	[31]
Clinoptilolite	9.652	[37]
Polyurethane foam	8.31	[42]
Chitosan/polyamidoamine	666.67	[54]
CZrP	457	[57]
MCC/APTES	30	[63]
MCC/hydroxypropyldodecyld-imethylammonium	409.9	[12]
Sepiolite	66.67	[73]
Fly ash	106.71	[73]
The modified carboxymethyl cellulose/ Fe_3O_4	126.58	[75]
Sawdust biochar/Fe_3O_4	27.77778	[14]

Sawdust Biochar/Fe_3O_4

Biochar is largely studied for its role in carbon sequestration and as a soil conditioner. It is produced from carbon-rich biomass by thermal decomposition in oxygen limited environments [76]. It can serve as an effective adsorbent for organic and inorganic materials [25,77,78]. The adsorption capacity of biochar is strongly influenced by its surface characteristics, which depend on the type of raw material and production conditions [79]. Sawdust is a by-product of sawing wood in sawmills and is often disposed of as waste or simply burned for bioenergy production. The manufacture of biochar from sawdust and the use of biochar as an adsorbent to remove water pollutants have the double function of using waste and reducing pollution [80]. The application of the magnetic Sawdust biochar/Fe_3O_4 (SDB/Fe_3O_4) for the elimination of RB21 dye from the aqueous solution has been reported by Nadeem et al. (2019). This adsorbent was used after preparation following the experimental protocol [14]. Batch adsorption experiments were affected by contact time (15-105 min), adsorbent dose (0.1-0.35 g), pH (3-11), temperature (10-70ºC) and dye concentration (30-180 mg.L^{-1}). The elimination efficiency of RB21 increased with increasing contact time, but after 90 minutes there was no further improvement. The RB21 removal efficiency increased continuously with increasing adsorbent dose temperature. The neutral pH gives maximum adsorption of RB21. A decrease in removal efficiency was observed with the increase in the initial dye concentration. The maximum adsorption capacity calculated using Langmuir isotherm model was found to be 27.77778 $mg.g^{-1}$ [14].

Table 2 shows a comparison of the maximum adsorption capacities of various adsorbents for the RB21 dye. The maximum adsorption capacities for Chitosan/polyamidoamine and CZrP in this study were 666.67 $mg.g^{-1}$ and 457 $mg.g^{-1}$, respectively, representing higher values than most of the previous studies listed in Table 1. This indicates that the adsorbents were appropriate for the removal of RB21 phthalocyanine dye.

Conclusions

Many of the chemicals and dyes used in the textile industry have serious undesirable effects because their effects on the environment and on the public are not immediately apparent. Adsorption is one of the most effective advanced wastewater treatment processes used by industries to reduce dyes in the effluent. Locally available, efficient and inexpensive raw and processed materials could be used for the removal of dyes from its aqueous solution. Based on the literature reviewed here, the mechanism of adsorption of dyes on various adsorbents depends on the chemical nature of the materials and various physico-chemical parameters such as the pH of the solution, the initial concentration of the dye, the dosage of the adsorbent and the temperature of the system. Consequently, these factors must be taken into consideration when evaluating the adsorption capacity of different adsorbents.

Conflict of Interest

The authors declare no conflict of interest.

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