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Some Polyaniline Based Adsorbent materials for the Removal of dyes and Heavy Metals from Solution: a Review

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Abstract: The dye contaminant and Heavy metals represent one of the most important kinds of pollutants, causing serious damage to the ecological balance. Thus, their removal from aqueous solution is a major environmental concern worldwide. The process of adsorption being very simple, economical, and effective is widely applied for the decontamination of wastewaters from heavy metals and dye contaminants. In this process, the adsorbent is the key factor affecting the performance; for this reason, significant efforts have been made to develop highly efficient and selective adsorbents with outstanding properties. This research article presents a brief review of some selected paper on different methods for synthesis of polyaniline based adsorbent materials for the removal of dyes contaminants and heavy metals from solutions along with the influence of the synthesis method on their size, morphology, and properties. In addition, the study evaluates the adsorption efficiency of various developed materials and nanocomposites for the adsorption of heavy metals and dyes from aqueous solution.

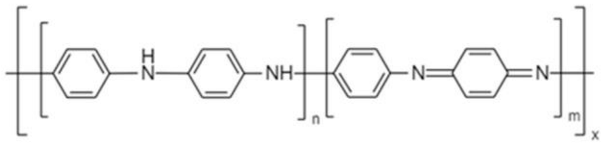
Keywords: Adsorbent, PANI, Dyes, Heavy Metals, nanocomposites.

1. Intruduction:

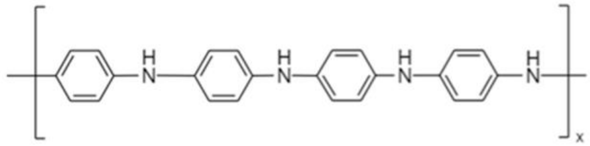
In last few decades tremendous and uncontrollably has increased the use of organic synthetic dyes. different types of dyes are frequently employed in plastics, paper, cosmetics, leather, and textile industries for coloring purposes[1-2] In the same manner anthropogenic sources that are related to a variety of industries, i.e., mining, metal corrosion inhibition, electroplating, batteries, tanneries, plastics, fertilizers, microelectronics, food companies, cosmetics petrochemicals, and metallurgy are responsible for contamination of Surface water and ground water by various organic and inorganic pollutant among them, are dyes and heavy metals.[1-3] Textile is one of the important sector which produces excessive color waste water. The major users of dyes in India are textiles, paper, plastics, printing inks and food stuff. Dying effluents are characterized by their fluctuating pH, with large load of suspended solids, High oxygen demands, resistance to biodegradability and stability to heat light and oxidizing agents. Color increases COD and BOD levels of water resources .consumption of dye polluted water cause allergy reactions, dermatitis, skin irritations, cancer and mutation both in babies and grownups. Most of the dyes are highly soluble in water and are resistant to light and moderate oxidative agents and cannot be completely removed. Industrial dyes are highly toxic, carcinogenic and mutagenic, even at relatively low concentrations, causing serious environmental hazards and severe damage to humans. Exposure to heavy metals has proven to be a serious threat. There are several related health risks, including neurodegenerative diseases (Alzheimer's and Parkinson's diseases), oxidative stress and subsequent tissue damage cardiovascular diseases, liver cancer, kidney damage, and renal cancer[4-6] Aggressive research on the effective treatment of heavy metals and colored compounds has resulted in several technologies, including ion exchange, precipitation, electro coagulation, flocculation, reverse osmosis, biological treatment and membrane separation.[7] In spite of being efficient, these methods suffer from some drawbacks, such as high capital demands, high energy requirements and operational costs, being time-consuming, low removal efficiency, having regeneration problem and the disposal problem of residual metal sludge. Consequently, it remains challenging to develop an efficient, economical, and sustainable technology. However, adsorption is the most frequently used technique to remove dyes from water, because this technique, in addition to easiness and low cost, causes low generation of residues and the adsorbent used may be regenerated and reused. Due to this in this review article author has theoretically reviewed some selective articles which discussed novel adsorbent and its application in waste water treatment especially for removal of dye effluents and metal contaminants using Polyaniline based adsorbents. We focus on the adsorption efficiency and regeneration capacity of the developed materials to provide a background for future research. This article is structured in such a way that information on polyaniline based adsorbent and its varied applications are described.

2. Polyaniline Polymer

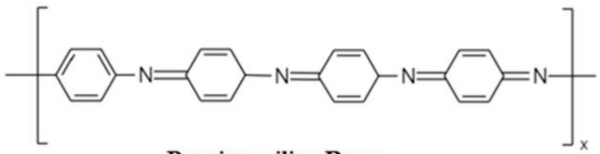
Polyaniline commonly abbreviated as PANI or Pani—also known as aniline black— was discovered for the first time by Ferdinand Runge in 1834 from the initial oxidation of aniline. Later, in 1862, Henry Lether by achieved its first electrochemical polymerization. Since then, it has been applied in a variety of colored materials and dyes. Recently, PANI has gained much attention of the scientific community due to the rediscovery of its conductive properties in the 1980s. Its structure consists of a succession of aromatic rings of the benzene diamine and/or quinone di-imine types, bridged by a nitrogen heteroatom. PANI has three oxidation states that are represented in Figure fully reduced leucoemeraldine base (LB), fully oxidized pernigraniline base (PB), and half-oxidized emeraldine base (EB)—which is converted to emeraldine salt via protonation with organic and inorganic acids.



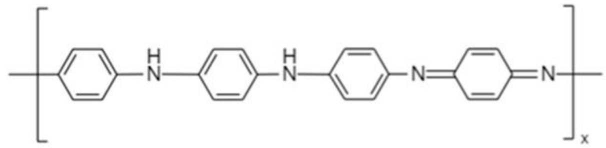
Basic structure of Polyaniline



Leucomeraldine Base



Pernigraniline Base



Emeraldine Base

Among the conducting polymer, Polyaniline (PANI) is one such polymer whose synthesis does not require any special equipment or precautions.

3. Polyaniline based adsorbent Synthesis and adsorption properties for dyes.

3.1 **polyaniline-modified rice bran adsorbent:**

To remove the possible contamination from the purchased rice bran, 100 g of rice bran was washed with 0.1 M nitric acid solution three times. Afterwards, it was again washed with distilled water a few times so that the pH of the solution under the filter paper was adjusted with the pH of distilled water. Then, 10 g of the prepared rice bran and 4 g of aniline were poured into a container. Afterwards, 250 mL of 1.0 M HCl as the polar solvent was added to the mixture, and then, the mixture was stirred for at least 30 minutes using a stirrer. In another container, 15 g of ammonium persulfate was added to 250 mL of 1.0 M HCl. Once the content of the first container was stirred for at least 30 minutes, the contents of the second container were poured into the first container, and the container was put on the stirrer for another 2 hours until the completion of the reaction. Afterwards, the stirred final solution was poured onto a filter paper and washed with distilled water until the pH of the solution in the container under the filter paper was equalized with the pH of distilled water. Ultimately, the resulting paste was put close to a dehumidifier in desiccators for 24 hours until it was completely dried [8]. During the research they prepared adsorbent from rice bran and aniline, and then studied effect of different factors like pH, dye concentration, adsorption dosages, contact time etc. and also studied adsorption kinetics. He concluded in his paper that the polyaniline-modified rice bran could be used as an excellent adsorbent for the removal of Acid orange 7dye from aqueous solutions. The maximum dye removal efficiency for AO7 was obtained at pH = 3. Also, it was revealed that AO7 dye removal follows the pseudo-second-order kinetic model and it is a spontaneous process [8]. It is clear that Polyaniline-modified rice bran can be a perfect adsorbent for removal of dye from aqueous solutions.

3.2 Polyaniline coated sawdust as an adsorbent:

The sawdust was first washed with distilled water in order to remove impurities and finally dried at 333K for 2hours. In order to prepare polyaniline coated sawdust, 5.0g of sawdust immersed in 50 ml of 0.20M freshly distilled aniline in 1M HCl solution for 6 hours before polymerization. The excess of the monomer solution was removed by simple decantation. Then 50 ml of 0.5M $(NH4)_2\ S_2\ O_8$ as an oxidant solution was added into the mixture gradually and the reaction were allowed to continue for 4 hours at room temperature. The poly-aniline coated sawdust (PAn/SD) was filtered, washed with distilled water, dried in an oven at about 60 ºC and sieved before use [9]. Polyaniline coated sawdust (PAn/SD) as a novel adsorbent material synthesized, did characterization, further *Batch* mode adsorption study was performed to investigate the effects of the main parameters such as contact time, pH, initial dye concentration and temperature for removing acidic (Acid Orange 7) and basic (Basic Red 29) dyes from aqueous solutions. Using the prepared adsorbent, various kinetic studies and isotherm studies were employed to analyze the feasibility and mechanism of adsorption of both the dyes. The kinetic study obeys pseudo second order and the isotherm study fits with Freundlich model for both acidic and basic dyes. After maintaining the factors like dye concentration, agitation time, pH and temperature. The maximum percentage removal was 83.90% for AO7 (Anionic dye) and 81.80% for BR 29 (Cationic dye) by PAn/SD with the initial dye concentration of 50 ppm at 300C. The waste fruit material obtained from the plant Cordia Sebestena in which its sawdust is coated with polyaniline called polyaniline coated sawdust (PAn/SD) adsorbent is very effective and economically viable for the removal of both anionic (AO7) and cationic (BR29) dyes [9].

3.3 Polyaniline Derived-Carbon as adsorbent:

PANI was firstly pyrolyzed at 550 °C for 2 h under nitrogen flow. The pyrolyzed product was mixed well with KOH (the weight of KOH was 2 times that of the pyrolyzed product) and carbonized again at 600–900 °C for 1 h under nitrogen flow.[10] As the material is prepared by pyrolysis The hydrophobicity, pore size and mesopore volume were found to increase monotonously with increasing pyrolysis temperature. In addition, the best PDC (KOH-900) was very effective in the adsorption of dyes, especially those of a large size [10].

3.4 Polyaniline/Magnetite (Fe3O4) Composites as Adsorbent:

Chemical oxidation method was used to synthesize PANI/Fe3O4 composites. First, 0.2 g Fe3O4 was mixed with 1.818 mL of aniline suspended in double distilled water (50 mL) and DBSA (0.5 mL). The mixture was stirred for about 30 min and followed by addition of 0.15 M FeCl3·6H2O prepared in 40 mL double distilled water as oxidizing agent. Initially the reaction mixture was milky white due to DBSA but turned reddish brown after addition of Fe_3O_4 particles. When oxidant was added a light green color appeared within 20 min, which changed into dark black after about 2 h. After 8 h continuous stirring, the synthesized product was washed with acetone and plenty of double distilled water. Finally, the clean precipitate was dried in an oven at 60^0 C for 24h.[11]. PANI/ Fe_3O_4 composites, whose syntheses were confirmed through various spectroscopic techniques, such as SEM, FTIR, EDX, UV, and XRD, can effectively be utilized as adsorbents for removal of BB_3 (cationic dye) from aqueous solution. It was envisaged that the synergy between PANI and magnetite would impart promising properties onto the composite material, as a high amount of dye (78.13 mg/g) was adsorbed on PANI/ Fe_3O_4composites in comparison to that adsorbed for Fe_3O_4 (7.474 mg/g) and PANI (47.977). The enhanced adsorption capability of the composites is attributed to the increase in surface area and pore volume of the hybrid materials [11].

4. Polyaniline based adsorbent Synthesis and adsorption properties for Heavy metals.

4.1 Adsorbent materials based on polyaniline and agriculture waste:

Clean Rice raw and Peanut Shell were dried before grinded and sieved (0.27 mm). Their powder grains were ultrasonically washed by acetone, then filtrated and dried at 50oC for 1 day. The soaking method for preparing materials was done following as 2 g of RR or PS powder grain soaked into 20ml of formic acid PANi solution (5 g L-1) under stirring of 3 h and then still of the night. The product was dried under *vacuum* condition at 70^{o}C in 8 h[12]. Composites based on polyaniline (PANi) and agriculture waste (peanut shell (PS), rice raw (RR) prepared by soaking method. After Characterizing the material by different method such as SEM, Infrared, XRD and by studying different adsorption models it is cleared that The maximum adsorption capacities of Pb2+ (185.1852mg/g) and Cd2+ (131.5789mg/g) ions onto PANi-PS were higher than those onto PANi-RR (158.7302mg/g and 93.4579mg/g for Pb^{2+} and Cd^{2+} ions, respectively. Composites based on PANi and agriculture waste such as RR and PS can be used as inexpensive adsorbents for removing Pb^{2+} and Cd^{2+} ions from solution by adsorption among them PANi-PS composite is more effective one than PANi-RR. The adsorption process of both metal ions fitted into Langmuir isotherm model better than Freundlich and Temkin isotherm models. [12].

4.2 Polyaniline synthesis at different condition and its effect on removal of Chromium from solution:

Absorptive characteristics of polyaniline synthesized in different solvents were studied. Water and mixture of water with other solvents were implemented for polyaniline synthesis. Synthesized polyanilines in powder shape is used as an adsorbent to remove toxic hexavalent chromium from aqueous solutions. Experiments were conducted in batch mode. Removal mechanism involving polyaniline is the combination of surface adsorption and reduction. The kind of solvent used at synthesizing stage can affect the capacity of produced polyanilines for removal of heavy metals including chromium. Synthesized polyaniline in water had the maximum chromium removal efficiency. The morphology study of polyanilines show that the type of solvent used for polymer synthesis affect the morphology of polyaniline [13]. Synthesized polyaniline in water has steady surface pores and has the best total and hexavalent chromium removal efficiency. Synthesized polyanilines in mixture of water and other solvents have a scale like surface. These results indicate all polyanilines can be used as good adsorbents for removal of chromium in solutions.

4.3 Polyaniline and its Composites for Adsorption/Recovery of Chromium (VI) from Aqueous Solutions:

In order to make polyaniline soluble in formic acid for coating and composite formation, the polymer was treated with 0.5 M NaOH solution for 2 hours. Then it was washed with distilled water and dried in an oven at 60^{o}C. 0.50g of base treated PAn, emeraldine base (EB) was dissolved in 50 mL of formic acid. The polymer solution was filtered in order to remove any non-dissolvable solids. For preparation of polyaniline coated sawdust (SD/PAn), 5 g sawdust were mixed with 50 mL of EB in formic acid (1% w/v) in a beaker (100 cm3) and stirred for two hours at room temperature and left for another 2 hours without stirring. The excess of the solvent was evaporated by heating the SD/PAn at 60^{o}C in an oven [14]. SD/PAn adsorbent is cheap and simple to prepare and can be used successfully for removal of Cr(VI) ion from aqueous solutions.

Sorption capacity of polyaniline toward Cr(VI) is greatly affected by pH of the treated solution. It was found that SD/PAn column was a useful sorbent for Cr(VI) elimination at relatively low acidic solutions (pH=1-2). Adsorption was negligible at pH values higher than 4. The rate of adsorption decreased severely under alkaline conditions (pH > 6). As a result, adsorption/desorption of Cr(VI) by SD/PAn column can be achieved by simple pH control. Adsorption of Cr(VI) by PAn is supposed to be based on anion exchange properties of acid doped polyaniline (replacement of Cl^- by $HCrO_4$- or $Cr_2O_7$2-) and some chemical reactions such as complex formation or redox reactions. Formic acid is a suitable solvent of choice for processing of polyaniline using cast method for coating or preparation of polyaniline composites with conventional polymers. It is cheap, available, and volatile compared to other solvents for polyaniline (e.g. NMP)[14]. However it is very odorous and should be handled carefully.

5. Conclusions:

This review article presents different polyaniline-based nanomaterials/adsorbents for the removal of dyes and heavy metals from aqueous solution, using the adsorption process as one of the most simple, effective, and economical methods for water treatment. From the selected published paper reviewed here, it can be observed that the preparation methods and synthesis conditions such as pH, temperature, and the presence of dopants are of great importance, as they influence the morphology and adsorption properties of the resulting adsorbent materials.

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