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Adsorption of Congo red and Rhodamine B dyes from their aqueous solutions using nanocomposites

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Abstract

The first part of the work was the preparation of (CuO) from plant extract (cumin), then preparation of copper oxide/multi-walled carbon nanotubes (CuO/MWCNTs) in a ratio (1:1) by loading multi-walled carbon nanotubes on copper oxide nanoparticles. The techniques for the characterization of CuO and (CuO/MWCNTs) are field emission scanning electron microscopy (FE-SEM), X-ray diffraction spectroscopy (XRD), Fourier transform infrared spectroscopy (FT-IR) and surface area analyzer (BET).

The nanocomposite (CuO/MWCNTs) was used for adsorption of two dyes (Congo red and Rhodamine B) from their aqueous solutions. The effect of contact time, amount of adsorbent, pH, concentration and temperature on the adsorption process were studied. The results obtained showed that the ideal adsorption time for each dyes on the surface of the nanocomposite (CuO/MWCNTs) was (50 min) for the Congo red and (70 min) for the Rhodamine B . The best weight for removing the two dye was 0.05 g. It was found that the best pH for removing Congo red dye was pH= 5 and Rhodamine B was pH= 9.

This study included application of three different isotherm (Langmuir, freundlich, tamkin), where the results of the study indicates that Freundlich isotherm was the best one which can describe removal of Rhodamine B and Temkin isotherm was the best one which can describe removal of Congo dye on CuO/MWCNTs.

Thermodynamic study of the adsorption was mentioned and show that the enthalpy change (ΔH) for the two dyes were positive values, which indicates that the adsorption process is endothermic. Negative values of the change in free energy (ΔG) indicate that the adsorption is spontaneous, and positive values of the entropy (ΔS) indicate that the adsorbed and interfering dyes are less organized on the surface.

Also included in the study the activation of the $CoMo/\gamma.Al_2O_3$ and diagnosed it using several techniques such as XRD, FT-IR, FE-SEM and BET.

Abstract

These nanocomposite was used to study the adsorption of Rhodamine B from their aqueous solutions. The effect of contact time, amount of adsorbent, pH, concentration and temperature on the adsorption process were studied, and the results showed that the best equilibrium time is (40 min). The best weight for dye removal is (0.25 g). The best pH to remove Rhodamine B is (pH = 2). The application of isotherm study Langmuir, Freundlich and Temkin on the experimental data of dye adsorption. Results gave linear relationships and good correlation coefficients, the best of which was Freundlich Isotherm. Thermodynamic of the adsorbent was mentioned as show that the enthalpy (ΔH) for the two dyes are positive values, which indicates that the adsorption process is endothermic. Negative values of the change in free energy (ΔG) indicate that the adsorption is spontaneous, and positive values of the entropy (ΔS) indicate that the adsorbed and interfering dye is less organized on the surface.

Chapter one
(General introduction & Literature Survey)

1.1. General introduction

Pollution can be defined simply as introduce of pollutants to the natural environment producing negative changes. While the pollutants are Strange materials that pollute the air, water and soil, pollutants vary according to chemical nature, resistance and concentration. There are various types of pollution includes air pollution, water pollutants, soil pollution, noise pollution, radioactive contamination, thermal pollution and pollution by heavy metals [1]. Millions of people dies from common diseases transmitted through water or human waste [2]. The biggest problem people face is insufficient access clean and safe water [3]. The principle pollutant types are: organic chemicals (phenol, phenol derivatives, polychlorinated biphenyls, oil, pesticides, dyes), inorganic chemicals (salts, nitrate, metals and their salts), organo metallic chemicals (methyl mercury, tri butyl tin, tetra ethyl lead), radio active elements (radon, radium, uranium) and biological (micro organisms , pollens) [4].

Rhodamine B (RhB) is among the toxic dyes due to the carcinogenic, neurotoxic effects and ability to cause several diseases for humans. [5]. The 108 tons of various dyes produced each year around the world, between 60 and 70 percent of them are azo dyes. Because azo dyes are used so often, a lot of wastewater is created that is azo dye-contaminated. The aromatic amine included in the diazo dye Congo Red is widely recognized to cause cancer. Azo dyes' aromatic characteristics make them resistant to oxidation. The long-term effects of dye on the environment have an effect on the flora and the wildlife [6,7].

The migration of pollutant (s) in aqueous media and subsequent development of containment measures have resulted in the use of adsorption among other techniques [8, 9]. A proper understanding and interpretation of adsorption isotherms is critical for the overall improvement of adsorption mechanism pathways and effective design of adsorption system [10].In recent times, linear regression analysis has been one of the most applied tools for defining the best fitting adsorption models because it quantifies the distribution of adsorbates, analyzes the adsorption system, and verifies the consistency of theoretical assumptions of adsorption isotherm model [11].

Nanoparticles are very good emerging materials adsorbents, catalysts, sensors as they have large specified surface area [12]. Nanoparticles differ in shape, size and structure. They can be spherical, cylindrical, tubular, conical, hollow, spiral, flat, etc. or irregular and vary in size from 1 nm to 100 nm. The surface can be homogeneous or irregular with surface differences. Some nanoparticles are crystalline or amorphous with single or polycrystalline solid materials that are either loose or lumpy [13]. As an emerging / enabling technology, nanotechnology is helping to improve, and even revolutionize, many traditional technologies and industrial areas, ranging from electronic encapsulation to energy conversion and storage [14]. Nanotechnology is widely used in a variety of disciplines, including medicine, commerce, agriculture, and chemistry [15] .

CuO nanomaterials have large specific surface area and exhibit useful size effects. There exists numerous methods to synthesize CuO of varying sizes in the nano regime and with different morphologies such as linear rod-shaped, two-dimensional nanosheets, and more complex three-dimensional sea urchin-like nanoflowers [16-20]. Many new CuO nanostructures are still being explored. Studies have shown that the properties of CuO are closely related to its morphology. To further improve electrochemical sensing electrode performance, mixing CuO with multi-walled carbon nanotubes (MWCNTs) has been proposed [21]. Carbon nanotubes (CNTs) are absolute hollow tubes that consist of rolled graphite sheet. In accordance with the number of layers of graphite sheet, the biosensors that are based on CNT are acknowledged to be the upcoming generation foundation for ultra-fast and ultra-sensitive bio-sensing systems. CNT has unique expeditious ability to analyze biological samples due to its high surface to volume ratio. CNTs possess numerous advantages which includes high sensitivity, fast response time, high stability and longer lifetime. CNTs provide a very fertile ground for research due to the specific mechanical, electrical, thermal, and chemical properties it holds [22]. Since its first discovery, MWCNTs have received much attention due to their remarkable physical properties and good chemical stability. The high conductivity of MWCNTs coupled with their nanometer sizes but high aspect ratios can increase the conductance of electrodes during the electrochemical detection process [23-25].

1.2.Literature Survey

- ***Panda, G. C., et al.(2009)*** Jute stick powder (JSP) has been found to be a promising material for adsorptive removal of congo red and rhodamine B from aqueous solutions. Physico-chemical parameters like dye concentration, solution pH, temperature and contact time have been varied to study the adsorption phenomenon. Favorable adsorption occurs at around pH 7.0 whereas temperature has no significant effect on adsorption of both the dyes. Kinetic results suggest the intra-particle diffusion of dyes as rate limiting step [26].
- ***Xiang, J. Y., et al (2010).*** CuO/MWCNT nanocomposite is prepared by a simple precipitation method. The MWCNTs are incorporated into the leaf-like CuO nanoplates and build up a network to connect the CuO nanoleaves. The as-prepared CuO/MWCNT exhibits superior reversible Li-ion storage, the capacity maintains 627 mAh g^{-1} at 60 mA g^{-1} even after 50 cycles. The improved capability is ascribed to the MWCNT network in the composite, which improves the electrical contact of CuO/CuO and CuO/current collector, facilitates the charge transfer on CuO/electrolyte interfaces, and compensates the volume change of CuO during cycling [27].
- ***Kareem, S. H., et al.(2012).*** Removal of Congo red, Rhodamine B, and Dispers Blue dyes from water solution have been achieved by using Flint Clay as an adsorbent. The adsorption was studied as a function of contact time, adsorbent dose, pH, and temperature under batch adsorption technique. The equilibrium data fit with Langmuir, Freundlich and Toth models of adsorption and the linear regression coefficient R2 was used to elucidate the best fitting isotherm model. [28].
- ***Alaei, M., et al.(2012).*** Tungsten trioxide nanoparticles with two different sizes (average particle sizes about 50 and 80 nm) were prepared by the

spray pyrolysis method. Photo degradation of Congo Red (azo dye) showed that photo catalytic property of the as-prepared WO 3 nanoparticles with average size about 80 nm is higher than the sample with average size about 50 nm. Photo degradation of Rhodamine B (cationic triarylmethane dye) showed that photo catalytic property of the as-prepared WO 3 nanoparticles with average size about 50 nm is higher than the sample with average size about 80 nm. The samples were characterized with X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), EDX analysis and UV-visible spectrum [29].

- ***Ilayaraja, M., et al.(2013).*** Investigate the removal of Rhodamine-B (RB) and Congo red (CR) dye from aqueous solutions by low cost bio-waste adsorbents, such as Maranta arundinacea activated carbon (MAC) under various experimental conditions. The effect of dye concentrations, contact time, temperature and adsorbent dose on the removal of dyes was studied. The kinetic experimental data were fitted to pseudo-firstand pseudo-second – order model. Results imply that adsorption of RB and CR on these adsorbents nicely followed the second order kinetics model and maximum adsorption capacity was found to be 88.4 mg/g for RB and 79.3 mg/g for CR, however it increase with increase in temperature for both dyes. The thermodynamics parameters of adsorption systems indicated spontaneous and exothermic process [30].
- ***Jiang, C., et al. (2016).*** A metal-organic frameworks materials, zeolitic imidazolate framework-8 (ZIF-8), was synthesized through hydrothermal reaction for the adsorptive removal of harmful Congo red (CR) from aqueous solution. Results showed that the maximum adsorption capacity of CR onto ZIF-8 was ultrahigh as 1250 mg g^{-1}. Adsorption behaviors can be successfully fitted by the pseudo-second order kinetic model and the Langmuir isotherm equation. Solution conditions (pH condition and the co-exist anions) may influent the adsorption behaviors. The

adsorption performance at various temperatures indicated the process was a spontaneous and endothermic adsorption reaction [31].

- ***Liu, X. W., et al (2016).*** Two non-enzymatic glucose sensors based on ordered self-assembly of flower-like CuO and CuO/MWCNTs modified graphite electrodes have been successfully fabricated by a facile and effective screen-printed way. The prepared flower-like CuO and CuO/MWCNTs were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray diffraction (XRD) [32].
- ***Omidi Khaniabadi, Y., et al. (2017).*** the sorption of Congo red (CR), as a toxic dye, from aqueous media was investigated using montmorillonite (MMT) as a low-cost adsorbent. The influence of several factors such as contact time, pH, adsorbent dosage, dye content, and ionic strength was investigated on the dye removal. MMT was characterized by Fourier transformed infrared (FTIR) spectroscopy and X-ray diffractometer (XRD). The optimum conditions for the sorption of CR were achieved over 40 min and at pH=2. According to the results ,MMT can be used as a low-cost, eco-friendly and effective option for the adsorption of CR from aqueous solutions [33].
- ***Ehsani, M., et al (2017).*** the colloidal CuO nanoparticles and CuO/MWCNT nanocomposite as the efficient nanocatalysts were introduced and compared for amplification of the luminol CLIA system. In the present work, we applied the antibody-nanomaterials conjugate without horseradish peroxidase (HRP) enzyme as the CLIA reaction catalyst. The CuO nanoparticles-antibody conjugates and CuO/MWCNT nanocomposite-antibody conjugates were prepared using the covalent binding. The results show that CuO nanoparticles and CuO/MWCNT nanocomposite enhance the luminol chemiluminescence intensity, significantly [34].

- ***Tu, N. T. et al.((2018).*** the Congo red dye (CGR) adsorption onto zeolitic imidazolate framework–67 (ZIF–67) is demonstrated. ZIF–67 was synthesized using the microwave method. The obtained ZIF–67 was characterized by means of X-ray diffraction (XRD), scanning electron microscope (SEM), thermal gravity analysis (TG), and X-ray photoelectron spectroscopy (XPS). ZIF–67 was employed to adsorb CGR from aqueous solutions. The first-order and second-order kinetic model, and Weber's intra-particle-diffusion and Boyd's film-diffusion model were utilized to study the adsorption kinetics [35].

- ***Yu, M. et al.(2019)*** Organo-vermiculites (OVTs) modified with 1,4-bis(dodecyldimethylammonio)-2-butane dibromide (12-A-12) and bis-*N*,*N*,*N*-dodecyldimethyl-*p*-phenylenediammonium dibromide (12-P-12) were prepared and mixed for adsorption of dyes and their structures were characterized by XRD, FT-IR, EA and TG. The improved spectrophotometric method to test each component concentration in mixed dyes has been ascertained. the simultaneous removal of rhodamine B (RB) and congo red (CR) by organo-vermiculites unprecedentedly, and verifies that the presence of RB promotes CR adsorption [36].
- ***Waheed, A., et al.(2019).*** A novel hyper cross-linked, 3,5-diacrylamidobenzoic acid based resin (APEADA) has been synthesized for the highly efficient removal of Congo red (CR) and Rhodamine B (RhB) from aqueous solution. The synthesized resin was extensively characterized by FT-IR, FESEM, PXRD, EDX, BET analysis, TGA and solid state 13C (CP-MAS) NMR. The thermodynamic analysis of the data revealed that the adsorption processes were exothermic and spontaneous. Moreover, APEADA showed efficient removal efficiency (80.13%) for

dyes in simulated effluents which warrants its utility and effectiveness in industrial waste water treatment [37].

- ***Sahar, J., et al. (2019).*** Graphene oxide was prepared by the modified Hummer's method for the effective removal of rhodamine B and Congo red from their aqueous solution. The synthesized graphene oxide was characterized by different techniques such as thermogravimetric/differential thermal analysis, scanning electron microscopy, Fourier transform infrared spectrometry and X-ray diffraction. It was found that among different models applied, the Langmuir isotherm model fitted the data very well for both the rhodamine B and Congo red dyes adsorption onto the graphene oxide. Moreover, Van't Hoff equation was used to calculate the various thermodynamic parameters such as, enthalpy (ΔH^o), entropy (ΔS^o) and Gibbs free energy (ΔG^o) for both the selected dyes. Further, this study depicts that the synthesized graphene oxide has a great potential to remove the dyes from waste water effectively [38].
- ***Hussain, M. M., et al (2020).*** Copper oxide decorated multi-walled carbon nanotube nanocomposites (CuO·MWCNT NCs) were prepared using a simple wet-chemical technique in basic medium. The CuO·MWCNT NCs were examined by using various analytical techniques, for example ultraviolet-visible spectroscopy (UV-visible), Fourier transform infrared spectroscopy (FTIR), X-ray powder diffraction (XRD), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS) [39].
- ***Kaya, N. (2021).*** Unmodified and acid/base-modified wood charcoal derived from oak wood has been utilized as an eco-friendly adsorbent for removal of anionic dye Congo Red (CR) and cationic dye Rhodamine B (RhB) from aqueous solution. The characterization of raw charcoal was

performed using FT-IR, BET and SEM/EDS analysis. As a result of this study, in which the effectiveness of modified and unmodified adsorbents was compared, it was determined that CR dye was removed at higher efficiency with HCl-modified charcoal. On the other hand, the RhB dye was better removed with NH3-modified charcoal [40].

- ***Vigneshwaran, S., et al. (2021).*** Herein, sulfur tethered adsorbent of Tapioca peel (S@TP) biochar was successfully fabricated and utilized for the removal of organic dyes such as Malachite Green (MG) and Rhodamine B (RhB) from water. The peel of tapioca was used as a precursor for the biochar preparation. The newly fabricated adsorbent could be as a capable adsorbent for the water/wastewater treatment process since the S@TP matrix possesses high removal and reusable efficiency towards dye molecules [41].

1.3.Aims of the study

1- Preparation of nanocomposite (CuO/MWCNTs) by the preparing (CuO) of using aqueous solution of (cumin) plant extract.

2- Use CuO/MWCNTs to Remove Rhodamine-B (RB) and Congo red (CR) dye) from their aqueous solutions. Then identify the optimal conditions for dyes adsorption , such as (contact time, quantity adsorbent, temperature, initial concentration and pH). Determine the appropriate adsorption isotherm and perform the thermodynamic study and of adsorption processes of the dyes.

3- Activation of the nanocomposite ($CoMo/\gamma.Al_2O_3$) and used it for adsorption Rhodamine-B (RB) from their aqueous solutions. Identify the optimal conditions for dye adsorption , such as (contact time, quantity adsorbent, temperature, initial concentration and pH) and determine the appropriate adsorption isotherm and study the thermodynamic of adsorption processes of dyes.

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