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Synthesis and characterization of CuO nanoparticles and CuO/PVA-PVP nanocomposites: adsorption activity for malachite green (MG) dye and antibacterial property in wastewater treatment

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Abstract

Contaminated waterways, particularly effluent from the dye industry, are one of the major issues today. Among various methods adsorption being the most straight forward, low-cost, effective, and successful to treat such effluents. For this purpose, Copper oxide nanoparticles (CuO) and Copper oxide nanoparticles embedded within Polyvinyl alcohol (PVA) and Polyvinyl

pyrrolidone (PVP) mixed polymer (CuO/PVA-PVP) were synthesized using precipitation methods and different analytical techniques such as dynamic light scattering (DLS), powdered X-ray diffraction (XRD), fourier-transform infrared (FTIR) spectroscopy and transmission electron microscopy (TEM) were used to characterize morphology and size. Synthesized nanomaterials were used for the adsorption of malachite green (MG) dye in aqueous solution by the batch adsorption method. Various experimental conditions e.g., contact time, concentrations, pH, were optimized to obtain best adsorption outcome. Adsorption kinetics and isotherm suggested that it follows Pseudo-second-order-kinetic and Freundlich isotherm. The *invitro* antibacterial activity was investigated using disk diffusion and minimum inhibitory concentration (MIC) test against *Staphylococcus aureus* (S.aureus), a gram positive and *Escherichia coli* (E.coli), a gram negative bacteria, where both the synthesized nanoparticles showed a decent antibacterial activity against both the bacterial strain.

Keywords: CuO nanoparticles, CuO/PVA-PVP nanocomposites, Dye adsorption, Malachite green, Wastewater treatment, Antimicrobial.

1. Introduction

Nanotechnology is one of the most important and useful innovations of contemporary science, and has gained an enormous attention during the last three decades because of vast range of applications[1]. Nanotechnology is a branch of study which deals with extremely small particles. In the realm of material science, where tiny size plays a key role in defining fundamental characteristics, amazing evolutions have occurred during recent time. As the subject of study expands, commercial exploration evolves day by day[2]. The nanoparticle having smaller surface

area and greater activity in interacting with metallic species outperforms the larger particles in the adsorption phenomenon.

Pollution of potable water resources has become one of the main headaches for the scientific society. Researchers are trying to develop applications to reduce pollution, which is a tragic problem in the recent situation and especially in the case of water. Water pollution has become one of the most severe issues nowadays due to being polluted by various toxic materials, such as agricultural practices, household waste, especially industrial pollution. Among which textile dye is one of the most polluting aspects of the global fashion industry. Though the progress of the textile and dye industries is a profitable venture, the drawback is the creation of dangerous organic wastes, which eventually pollute the water and disturb the ecosystem. Dyes are mainly contained with complex mixture of dye bases, salts, acid, compounds, organ chlorinated, auxiliary chemicals, and heavy metals which are water soluble so it is very difficult to remove them with the conventional methods. Coloring dye is the first contaminant detected in water, and it must be removed from wastewater before it may be discharged into bodies of water. Which can obstruct light penetration, slows photosynthetic activity and biota growth, and has a proclivity for chelating metal ions, resulting in micro-toxicity in fish and other species and reduction in dissolved oxygen level[3–7]. Among many harmful dyes, malachite green (MG) is one of them, which is cationic in nature and used as a coloring agent in silk, leather, paper industries also used as a tropical anti-protozoal agent, fungicide, and antiseptic in the aquaculture industry to control disease and fish parasites. However, MG is highly cytotoxic and also can be a liver tumor enhancing agent. The toxicity of MG dye increases with exposure time, temperature, and concentration. There are many conventional procedures to remove dyes from water, such as electro coagulation[8], potentiometric[9], degradation using visible light[8,10], adsorption[11] and bio-gradation[12,13].

Among the different dye removal techniques adsorption process is an extensively used process with various advantages. Because of its great efficiency in removing harmful contaminants, ease of operation and low cost, liquid phase adsorption offers a significant advantage over other approaches[14]. Due to small size and high adsorption effectiveness, nanoscale metal oxides possibly provide a more cost-effective water treatment and remediation technique[15]. Many metal oxides (Zn, Sn, Fe, Co, Ni, Cu, etc.) are used to remove toxic dyes from waste water[16,17]. Among them, Copper oxide (CuO) nanoparticles have been discovered to be a good adsorbent for heavy metals and dyes[18–20]. CuO nanoparticles also act as a photo catalyst under sunlight irradiation. It has gained a tremendous role in science and technology due to its unique features such as high specific surface area, chemical stability, electrochemical activity, high electron communication features, fungicide, optical switch, metallurgy reagent, gas sensor, pigment, field emission (FE) emitter, magnetic storage media and so on. In addition, also one of the valuable antimicrobial agents due to being cheap and easily mixed with water and polymers[21,22]. The goal of this study is to make CuO nanoparticles that are coated with a PVA and PVP blend matrix in a simple and straightforward way. Both amorphous polymers are highly water soluble, synthetic, and biocompatible. When two polymers are mixed their aqueous blending form inter chain hydrogen bonds with in PVA and PVP develop potential applications that are more similar to those of the homopolymer. The stability and performance of nanoparticle in their application field become better with coated with these blend matrices[23–26]. Our present work is to determine the effect of the morphology of the prepared nanoparticles and compare the MG dye adsorption efficiency as well as antibacterial activity between CuO nanoparticles (NPs) and CuO/PVA-PVP nanocomposites (NCs).

2. Experimental

2.1 Materials

Copper (II) acetate monohydrate $[\text{Cu}(\text{COOH})_2 \cdot \text{H}_2\text{O}]$, Glacial Acetic acid (CH_3COOH), Sodium hydroxide (NaOH), Polyvinyl alcohol (PVA), Polyvinyl pyrrolidone (PVP), Malachite Green 1% (w/v) solution, Hydrochloric acid (HCl) were of analytical grade and were purchased from Sigma-Aldrich. All the solutions were prepared using Milli-Q water (MQ water).

2.2 Synthesis of Copper oxide (CuO) nanoparticles

CuO nanoparticles were synthesized by aqueous precipitation method[27]. 200 mL of 7% CH_3COOH solution was prepared and 4gm of copper (II) acetate mixed with it, then the mixture was stirred for a few minutes until the solution turned green. A 0.9 (M) sodium hydroxide solution was mixed with it in a dropwise manner, maintaining its pH~12, which is followed by heating at 100°C . The mixture was cooled at room temperature and a black precipitate was obtained and separated by centrifugal force (4000 rpm) and washed several times with distilled water and ethanol. The resulting product was dried at 80°C in a hot air oven for 8 h to obtain the dry powder of CuO nanoparticles.

2.3 Synthesis of CuO/PVA-PVP blend nanocomposite

Equal amount (1 gm of each polymer mixed with double distilled water) of PVA and PVP solution was dissolved in 120 ml water under magnetic stirring at 100°C [23]. After the dissolution of polymer composites, CuO nanoparticles (pre prepared in section 2.2) were mixed with the polymer solution and sonicated for 1 h until homogenous solution was obtained. The mixture was stirred for next 1 h, and further ultrasonication was done for complete dispersal of CuO in PVA-PVP solution. It was then spread out on a clean, level glass plate and dried in a hot air oven for 24

hours at 60 °C. The dried films were taken from the glass plate and cut into little pieces for later usage.

2.4 Characterizations

The hydrodynamical size distribution of particles were measured by Litesizer 500 (Anton paar, Austria), at a scattering angle of 90° at 28°C. For the optical characteristics of the samples UV/Vis spectroscopy had been applied by using a UV/Vis spectrophotometer (Thermo Scientific Evolution 201, U.S) within a wavelength range of 200–800 nm, using a 1cm path length quartz cuvette. Fourier-transform infrared spectroscopy (FTIR, alphaT, Bruker, Germany) was adopted to analysis the functional groups on the surface, the scanning was executed in the range of 3500–500 cm^{-1} . The crystal structures were characterized using an X-ray diffraction (XRD, Explorer, GNR Italy) with Cu K α radiation. For the size and morphology transmission electron microscopy (TEM) was performed on a JEM-2100 (JEOL, Japan) operating at an accelerating voltage of 200 KV, equipped with energy dispersive X-ray spectroscopy (EDS) for the element composition and selected area electron diffraction (SAED) for the crystalline phase identification. For the centrifugation force a centrifuge (Remi R-4C) was used. And the pH of the solutions was adjusted using a pH meter (Fisher Scientific, Accumet)

2.5 Adsorption studies

The adsorption experiment of CuO NPs and CuO/PVA-PVP NCs were performed by batch method at room temperature. Known amount of malachite green and nanoparticles were taken in conical flask, and then the mixture was shaken thoroughly for 150 min. The dye absorbances were measured at the maximum absorption wavelength, and the samples were collected at predetermined intervals i.e., 618 nm for MG using a 1 cm path length cuvette in UV-vis

spectrophotometer Various parameters like contact time (30-150 min), dye concentration in solution (1.0-5.0 mg/L) and nanomaterial concentration (2-10 mg), pH (2-10) were varied during the experiments, pH was adjusted using dilute NaOH and dilute HCl.

The acquired results were verified using adsorption isotherm models such as Langmuir and Freundlich, as well as pseudo-first-order and pseudo-second-order equations to simulate the kinetics of the experiments.

The amount of adsorption percentage (%) and adsorption capacity was evaluated by two equations (1) and (2), respectively.

$$\% \text{ adsorption} = \left[\frac{C_0 - C_e}{C_0} \right] \times 100 \dots \dots \dots (1)$$

$$Q_e = \frac{V(C_0 - C_e)}{M} \dots \dots \dots (2)$$

C_0 and C_e designate the colorant's initial and final concentrations (mg/L), q_e the amount of colorant removed by the adsorbents (CuO and CuO/PVA-PVP) at the final phase of the reaction (mg/g), V is the volume (L), and M is the weight of adsorbents (CuO and CuO/PVA-PVP) (gm).

2.6 Antibacterial activity studies

2.6.1 Bacteria Culture Preparation

A gram negative bacteria *E.coli* (ATCC 25922) and a gram positive bacteria *S.aureus* (ATCC 29213) were cultured in Luria Broth (LB) for 24h at 37 °C and standardized to 0.5 McFarland standard.

2.6.2 Disk Diffusion Test

The antibacterial effect of CuO NPs and CuO/PVA-PVP NCs were performed against *E.coli* and *S.aureus* by disk diffusion method. 100 μ L of each bacteria cell suspension (0.5 McFarland Standard) was spread over the LB-Agar plate and allowed to dry for 5 minutes. Then sterile paper disk (5 mm) was placed on the plate and 10 μ L of solution (concentration of 1 mg/mL) of respective compounds were poured on each disk. The plates were then sealed with parafilm and incubated at 37°C for 24 hours, after which the diameter of each inhibitory zone was measured. Water was taken as negative control[28].

2.6.3 Minimum inhibitory concentration (MIC) determination

The minimum inhibitory concentration of the CuO NPs and CuO/PVA-PVP NCs were determined by broth dilution method. 50 μ L LB was dispensed in each well of column 1-10. 50 μ L of then 50 μ L serially diluted solution of tested compound was poured in column 1-10, concentration sequence from 4 mg/mL to 0.0078 mg/mL followed by addition of standardized bacteria inoculum (1×10^5 cfu/ml). Column 11 was for positive control (only bacteria) and column 12 contain 100 μ L LB (for sterility). And the micro plates were incubated at 37°C for 24 h. And the lowest concentration of compound with no visible growth of bacteria was determined as MIC[29,30].

3. Results and discussion

3.1 DLS experiment

CuO NPs and CuO/PVA-PVP NCs were characterized by dynamic light scattering (DLS) measurements from which the hydrodynamical size distribution was investigated. Both CuO NPs and CuO/PVA-PVP NCs showed single peak having hydrodynamic diameter of 421 nm and 512 nm and polydispersity index 28.5% and 11.3% respectively. These results reveals that both samples were monodispersed i.e., all particles were in the similar size range (Fig.S1).

3.2 UV-Vis analysis

The UV-Vis spectra of both nanoparticles CuO NPs and CuO/PVA-PVP NCs are shown in the Fig. 1 which range was in between 300-400 nm with confirm their good formation and appeared due to surface plasmon resonance (SPR) of metal oxide [31]. This UV-Vis characterization mainly observes for the confirmation of nanoparticle by knowing their absorption peak.

Fig. 1: UV-Vis of CuO nanoparticle and CuO/PVA-PVP nanocomposite.

3.3 FTIR analysis

The Fourier Transform Infra-Red (FTIR) spectrum of CuO NPs and CuO/PVA-PVP NCs are shown in the Fig.2(a) and Fig.2(b) respectively. In Fig.2(a) the band at 597.87 cm^{-1} was attributed to the Cu-O stretching vibration [32]. The appearance of the peak 1408.01 cm^{-1} is due to the adsorption of CO_2 molecules and the peak 1548.35 cm^{-1} is responsible for surface bound hydroxyl groups. The peak at 1648.58 cm^{-1} indicates the stretching vibration of the C = C bond and the peak 2363.79 cm^{-1} is due to O=C=O the stretching vibration. The band 2923.94 cm^{-1} and 3221.69 cm^{-1} belong to symmetric and asymmetric stretching vibration of O-H bond, respectively [33], whereas for CuO/PVA-PVP NCs in Fig.2(b) the peak at 586.23 cm^{-1} and 837.85

cm^{-1} indicated Cu-O stretching vibration[31] and C-C stretching vibration 1090.17 cm^{-1} is responsible for stretching C = O and bending of -OH, 1245.67 cm^{-1} is for C-N stretching vibration[34]. 1368.65 cm^{-1} , 1425.90 cm^{-1} appeared due to -CH₂ bending and C-N stretching. Another strong band at 1647.83 cm^{-1} and 1713.56 cm^{-1} is responsible for C-N stretching and stretching vibration of C=O bond. A weak band 2943.38 cm^{-1} is assigned to -CH₂ asymmetric stretching and a wide, strong band at 3293.31 cm^{-1} is due to -OH stretching vibration of the sample[35].

Fig. 2: FTIR image of (a) CuO nanoparticles and (b) CuO/PVA-PVP nanocomposites.

3.4 Powder XRD analysis

The CuO nanoparticle XRD pattern in Fig.3(a) shows a series of diffraction peaks at $2\theta = 32.57^\circ, 35.51^\circ, 38.84^\circ, 46.48^\circ, 48.83^\circ, 53.54^\circ, 58.23^\circ, 61.76^\circ, 66.25^\circ, 68.22^\circ$ which corresponds to the crystal planes of copper oxide (110), (022), (200), (-112), (-202), (020), (202), (-113), (022), (220) and similarly the XRD pattern of CuO/PVA-PVP NCs in Fig.3(b) shows a diffraction peaks at $2\theta = 32.70^\circ, 35.62^\circ, 38.87^\circ, 48.94^\circ, 53.75^\circ, 58.23^\circ, 61.69^\circ, 66.39^\circ, 68.19^\circ$ corresponds to the crystal

planes (110),(022),(200),(-112),(-202),(020),(202),(-113),(022),(220) which are almost in good agreement with recent observations and indexed to monoclinic crystal structure of CuO (file no "pdf # 892531")Bragg's reflection pattern of copper nanocrystals[36]

Fig. 3: The X-ray diffraction pattern of (a) CuO nanoparticles and (b) CuO/PVA-PVP nanocomposites.

3.5 TEM and EDS analysis

Transmission electron microscopy (TEM) reveals the size and morphology of CuO NPs and CuO/PVA-PVP NCs shown in Fig.4 with a regular and rod-shaped narrow size distribution (Fig. S2). The average diameters of CuO NPs and CuO/PVA-PVP NCs are 16.04 and 14.55 nm with respectively. The bigger size of the CuO NPs compare to the CuO/PVA-PVP NCs may be due to the fact that uncoated nanoparticles might aggregated due to dipole-dipole interaction but in case of CuO/PVA-PVP NCs the interparticle distance is enhanced in the absence of interparticle aggregates, as the range of dipolar coupling connected to the space between particles and most of the particles discrete. Resulting, decrease in the size of CuO/PVA-PVP NCs[37]. The structure of

generated nanoparticles and nanocomposites was investigated using selected area electron diffraction (SAED). The SAED contrast images reveal a series of diffraction rings with bright spots, which could be due to the polycrystalline and amorphous nature of the nanomaterial. In addition, TEM-EDS (Fig. S3) was performed to determine the composition of the nanoparticles, which indicates the presence of Cu and O molecules, but the presence of carbon (C) in CuO NPs is due to copper grid and in case of CuO/PVA-PVP NCs, the presence of C confirmed the presence of PVA-PVP polymer.

(a)

(b)

(c)

(d)

Fig. 4: TEM images, SAED patterns of CuO nanoparticles (a,b) and CuO/PVA-PVP nanocomposites (c,d) respectively.

3.6 Effect of adsorbent dose

The adsorption experiences were performed by testing different CuO NPs and CuO/PVA-PVP NCs dosages varying from 2-10 mg in 10 mL of MG dye solution containing 2 mg/L as initial dye concentration at room temperature and natural pH. The results are presented in Fig.5 for CuO NPs and CuO/PVA-PVP NCs, respectively. The elimination of dyes increased from 25.71 to 64.33% and 53.60 to 92.40% for CuO NPs and CuO/PVA-PVP NCs as the dosage was increased from 2 to 10 mg. More adsorbent sites and surface area for the adsorbate were clearly provided by a greater adsorbent dosage. As the adsorbent dosage was increased, more surface area became accessible for adsorption, leading to an increase in active sites on the adsorbent, making adsorbate ion penetration to the sorption sites easier. From the graph it can be observed that as the sorbent dosage increases, the available site of adsorption also increases which causes highest percent of removal efficiency[38].

Fig. 5: Effect of dose on dye removal through (a) CuO nanoparticles and (b) CuO/PVA-PVP nanocomposites.

3.7 Dye adsorption isotherm study for MG dye

Adsorption isotherms are the most important parameters for exploring the interaction between adsorbate and adsorbent, and represent the result accurately. For this experiment using the batch method, 10 mL dye solution with different initial concentration (1-5 mg/L) and known amount of adsorbent i.e., CuO NPs and CuO/PVA-PVP NCs (10 mg) was taken in a borosilicate Erlenmeyer flask in room temperature (28°C) and natural pH and was shaken at constant rpm for 150 minutes.

To determine the adsorption isotherm, which basically established the equilibrium relationship of adsorption between dye and nanoparticles, two equilibrium models, the Langmuir and the Freundlich were interpreted and correlation coefficients were calculated to identify the best fit. Adsorption isotherms represent the adsorbate's interaction with the adsorbent and provide information on the material's adsorption capability. The correlation coefficients (R^2) and statistical characteristics were examined using the linear form of Langmuir and Freundlich models.

The linear form Langmuir isotherm equation is given below in equation (3) [28] .

$$\frac{C_e}{Q_e} = \frac{1}{(Q_m K_L)} + \frac{C_e}{Q_m} \dots \dots \dots (3)$$

Where Q_e is the amount of adsorbed dye on the adsorbent at equilibrium (mg/g), C_e is the equilibrium concentration of dye solution (mg/L), K_L is the Langmuir constant (L/mg) and the maximum adsorption capacity is Q_m . A slope of $1/Q_m$ is obtained from the plot $\frac{C_e}{Q_e}$ vs. C_e from

where the maximum adsorption capacity was determined [Fig. 6(a) and 6(c)]. The values of Q_m , K_L which were calculated from the isotherm are listed in table 1.

Another dimensionless constant which called equilibrium parameter is R_L to describe the essential characteristics of Langmuir isotherm using equation (4) below:

$$R_L = \frac{1}{(1+K_L C_0)} \dots \dots \dots (4)$$

Where C_0 (mg/g) is the initial adsorbate concentration, K_L is the Langmuir constant. The value of R_L is classified as $0 < R_L < 1$ the adsorption process is satisfactory and for $R_L \geq 1$ for unsatisfactory.

The Freundlich isotherm describes the heterogeneous surface adsorption. The linear form of this equation is given in equation (5).

$$\log Q_e = \log K_F + \left(\frac{1}{n}\right) \log C_e \dots \dots \dots (5)$$

Where K_F (L/g) and $\frac{1}{n}$ are the adsorption capacity and adsorption intensity or surface heterogeneity respectively, which are obtain by the plot of $\log Q_e$ vs. $\log C_e$ from equation (5). The $\frac{1}{n}$ is lower than 1 means that the adsorption is favorable.

Fig. 6: (a) Langmuir and (b) Freundlich models for CuO nanoparticles ;(c) Langmuir and (d) Freundlich models for CuO/PVA-PVP nanocomposites.

Adsorbent	Adsorbate	Langmuir isotherm				Freundlich isotherm		
		Q_m (mg/g)	K_L	R_L	R^2	K_F	$1/n$	R^2
CuO/PVA-PVP	MG dye	7.57	0.196	0.192-0.836	0.923	1.546	0.822	0.993
CuO		3.63	3.571	0.053-0.218	0.954	9.204	0.305	0.974

Table 1: Adsorption isotherm parameters for MG dye on CuO/PVA-PVP and CuO adsorbents.

Langmuir [Fig. 6(a) and 6(c)] and Freundlich plots (Fig. 6(b) and 6(d)) of CuO NPs and CuO/PVA-PVP NCs are shown in the fig 6 respectively. From Table 1, the R^2 value of both CuO/PVA-PVP NCs and CuO NPs reveals that the Freundlich isotherm model having R^2 close to 1 (R^2 - 0.993 and 0.974) is well fitted compare to that Langmuir isotherm (R^2 - 0.923 and 0.954) for both the cases.

The Freundlich model predicts a heterogeneous surface with a non-uniform distribution of adsorbate and multilayer adsorption of adsorbate on the adsorbent surface. Lower value of $\frac{1}{n}$ and R_L i.e., within 0 to 1, are indicating the adsorption is favorable for both the cases.

3.8 Dye adsorption kinetic study for MG dye

One of the key factors in determining adsorption efficiency is kinetic adsorption. The kinetic adsorption experiences were done by taking a fixed amount of CuO NPs and CuO/PVA-PVP NCs (10 mg) in 10 mL MG dye (2 mg/L) solution at room temperature and natural pH for 150 minutes and samples were collected at every 25 minutes interval and the absorbance was measured. The adsorption process, which included mass transfer and chemical reaction, were investigated using kinetics models and kinetic study was investigated using two models: Pseudo-first-order and pseudo-second-order models. The linear form equations of these models are given below:

$$\text{Pseudo-first-order kinetic model: } \log(Q_e - Q_t) = \log(Q_e) - \frac{K_1 t}{2.303} \dots \dots \dots (6)$$

$$\text{Pseudo-second-order kinetic model: } \frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{t}{Q_e} \dots \dots \dots (7)$$

Where Q_e and Q_t are the adsorption capacity of dye at equilibrium time and time t (mg/g). K_1 (1/min) and K_2 (g/mg min) are the equilibrium rate constant of Pseudo-first-order and Pseudo-second-order respectively All kinetic data for both models are represented in table 2.

(a)

(b)

(c)

(d)

Fig. 7: (a) Pseudo –first-order and (b) Pseudo-second-order kinetic model of CuO NPs. and (c) Pseudo-first-order and (d) Pseudo-second-order kinetic models of CuO/PVA-PVP NCs.

Adsorbent	Adsorbate	Q _e (expt) (mg/g)	Pseudo-first-order			Pseudo-second-order		
			Q _e (cal) (mg/g)	K ₁ (min ⁻¹)	R ²	Q _e (cal) (mg/g)	K ₂ (g/mg.min)	R ²

CuO/PVA-PVP	Malachite Green (MG)	1.866	1.782	0.020	0.956	2.309	0.435	0.996
CuO		1.660	0.954	0.013	0.993	1.754	0.028	0.996

Table 2: Adsorption kinetic parameters for MG dye onto CuO/PVA-PVP and CuO adsorbents.

In the above table 2 all kinetic parameters (K_1 and K_2) as well as the correlation coefficients (R^2) are listed. The correlation factor (R^2) value is used to determine the best fitted kinetic model (Fig. 7). According to Table 2, Pseudo-second-order-kinetic model with higher correlation co-efficient value (R^2) is higher than Pseudo-first-order-kinetic model for both nanoparticles, these results suggest that the Pseudo-second-order kinetics will be used in the adsorption of MG dye onto CuO NPs and CuO/PVA-PVP NCs. This shows chemical adsorption and lack of internal diffusion resistance. The adsorbate and adsorbent exchange or share electrons, resulting in valency forces.

3.9 Effect of pH

The most important variable impacting dye adsorption onto adsorbent has been discovered as the pH of the solution. The effect of pH on the removal efficiency of the MG dye was investigated by changing the pH from 2 to 10 keeping at room temperature, dye concentration (2 mg/L, 10 mL) and adsorbent amount (10 mg) fixed. Solution pH is one of important parameter during the adsorption process. In Fig. 8 it was found that the nanoparticle removal efficiency increases with increasing the pH value; the highest removal efficiency of the dye was at pH 10 for both nanoparticles. The percentage of removal efficiency is comparatively less in the acidic range of

pH[39]. Increasing pH leads to formation of negative charge on the adsorbent surface whereas at low pH the presence of excess H^+ ions, the surface of these nanoparticles was positively charged. The negative charge enables high removal efficiency due to the electrostatic attraction between the adsorbent and positive charged adsorbate (MG dye), but other hand at low pH due to the strong repulsive force of the two positive charged dye and adsorbents, the decolorization process decreases[40].

Fig. 8: Effect of pH through CuO nanoparticles and CuO/PVA-PVP nanocomposites.

3.10 Antibacterial activity of CuO NPs and CuO/PVA-PVP NCs

The antibacterial activity of CuO and CuO/PVA-PVP against both *E.coli* and *S.aureus* in terms of ZOI is shown in Fig. S4 and tabulated in table 3.

Compound	<i>E.coli</i>		<i>S.aureus</i>	
	ZOI (mm)	MIC(mg/mL)	ZOI (mm)	MIC (mg/mL)

CuO	6	0.5	6	0.5
CuO/PVA-PVP	8	0.25	9	0.5

Table 3: Results of antibacterial activity of CuO and CuO/PVA-PVP nanoparticles against both *E.coli* and *S.aureus*.

The CuO/PVA-PVP NCs showed a slightly better ZOI value than that of CuO NPs against both the bacteria (Fig. S4). Negative control did not show any zone of inhibition. The MIC value against *E.coli* and *S.aureus* was found to be 0.5 mg/mL for CuO, whereas CuO/PVA-PVP exhibited a value of 0.25 mg/mL and 0.5 mg/mL (Table 3). By which it is confirmed that both the synthesized nanoparticles has a reasonable and indistinguishable antibacterial property against *E.coli* and *S.aureus*.

4. Conclusions:

Copper oxide nanoparticle (CuO) and copper oxide nanoparticle embedded within PVA and PVP mixed polymer (CuO/PVA-PVP) had been prepared successfully by the chemical precipitation method. These two nanomaterials were examined for their ability to remove malachite green (MG) color. The results indicated that both nanoparticles fit well with the Freundlich isotherm and follow the pseudo-second-order kinetic model. The maximum adsorption capacity of CuO NPs and CuO/PVA-PVP NCs. were found 3.63 and 7.57 mg/g respectively which indicating that CuO/PVA-PVP NCs. had a higher adsorption capacity than CuO NPs. Besides, in case of antibacterial test against *E.coli* and *S.aureus* CuO/PVA-PVP NCs. showed a better result

than CuO NPs. This research found that CuO/PVA-PVP NCs might be worth more than CuO NPs and it would be an environmentally acceptable and efficient option for treating organic dyes and decent antibacterial agent in the sectors of water environment and resource management.

Declaration of Competence Interest

The authors declare no competing financial interest.

Author Statement

Conceptualization, N.G., S.S., G.B., P.K.H.; Investigation and formal analysis, N.G., S.S., and L.R.S.; Writing: Original draft preparation, N.G., S.S.; Writing: Review and editing, G.B., P.K.H.; Supervision, P.K.H; All authors have read and agreed to the published version of the manuscript.

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Supplementary data

Supplementary data from this article are available along with this submission.

References:

- [1] A. Boretti, L. Rosa, Reassessing the projections of the World Water Development Report, *Npj Clean Water*. 2 (2019) 15. <https://doi.org/10.1038/s41545-019-0039-9>.
- [2] G.A. Mansoori, Principles of nanotechnology: molecular-based study of condensed matter in small systems, World Scientific, Hackensack, N.J, 2005.
- [3] I. Anastopoulos, A. Hosseini-Bandegharai, J. Fu, A.C. Mitropoulos, G.Z. Kyzas, Use of nanoparticles for dye adsorption: Review, *J. Dispers. Sci. Technol.* 39 (2018) 836–847. <https://doi.org/10.1080/01932691.2017.1398661>.

- [4] M. Goyal, Activated Carbon Adsorption., CRC Press, 2005.
<http://public.ebookcentral.proquest.com/choice/publicfullrecord.aspx?p=262065> (accessed June 25, 2021).
- [5] R. Khlifi, A. Hamza-Chaffai, Head and neck cancer due to heavy metal exposure via tobacco smoking and professional exposure: A review, *Toxicol. Appl. Pharmacol.* 248 (2010) 71–88. <https://doi.org/10.1016/j.taap.2010.08.003>.
- [6] C.B. Ernhart, A critical review of low-level prenatal lead exposure in the human: 1. Effects on the fetus and newborn, *Reprod. Toxicol.* 6 (1992) 9–19. [https://doi.org/10.1016/0890-6238\(92\)90017-N](https://doi.org/10.1016/0890-6238(92)90017-N).
- [7] C. Das, S. Singh, S. Bhakta, P. Mishra, G. Biswas, Bio-modified magnetic nanoparticles with Terminalia arjuna bark extract for the removal of methylene blue and lead (II) from simulated wastewater, *Chemosphere.* (2021) 132673.
<https://doi.org/10.1016/j.chemosphere.2021.132673>.
- [8] R. Saravanan, S. Joicy, V.K. Gupta, V. Narayanan, A. Stephen, Visible light induced degradation of methylene blue using CeO₂/V₂O₅ and CeO₂/CuO catalysts, *Mater. Sci. Eng. C.* 33 (2013) 4725–4731. <https://doi.org/10.1016/j.msec.2013.07.034>.
- [9] H. Khani, M.K. Rofouei, P. Arab, V.K. Gupta, Z. Vafaei, Multi-walled carbon nanotubes-ionic liquid-carbon paste electrode as a super selectivity sensor: Application to potentiometric monitoring of mercury ion(II), *J. Hazard. Mater.* 183 (2010) 402–409.
<https://doi.org/10.1016/j.jhazmat.2010.07.039>.
- [10] R. Saravanan, V.K. Gupta, V. Narayanan, A. Stephen, Visible light degradation of textile effluent using novel catalyst ZnO/ γ -Mn₂O₃, *J. Taiwan Inst. Chem. Eng.* 45 (2014) 1910–1917. <https://doi.org/10.1016/j.jtice.2013.12.021>.
- [11] M.K. Dahri, M.R.R. Kooh, L.B.L. Lim, Water remediation using low cost adsorbent walnut shell for removal of malachite green: Equilibrium, kinetics, thermodynamic and regeneration studies, *J. Environ. Chem. Eng.* 2 (2014) 1434–1444.
<https://doi.org/10.1016/j.jece.2014.07.008>.
- [12] L. Ayed, K. Chaieb, A. Cheref, A. Bakhrouf, Biodegradation of triphenylmethane dye Malachite Green by *Sphingomonas paucimobilis*, *World J. Microbiol. Biotechnol.* 25 (2009) 705–711. <https://doi.org/10.1007/s11274-008-9941-x>.
- [13] V.K. Gupta, A. Nayak, S. Agarwal, Bioadsorbents for remediation of heavy metals: Current status and their future prospects, *Environ. Eng. Res.* 20 (2015) 1–18.
<https://doi.org/10.4491/eer.2015.018>.
- [14] R. Karthik, S. Meenakshi, Removal of Pb(II) and Cd(II) ions from aqueous solution using polyaniline grafted chitosan, *Chem. Eng. J.* 263 (2015) 168–177.
<https://doi.org/10.1016/j.cej.2014.11.015>.
- [15] W. Zhang, [No title found], *J. Nanoparticle Res.* 5 (2003) 323–332.
<https://doi.org/10.1023/A:1025520116015>.
- [16] M. Mohapatra, S. Anand, Studies on sorption of Cd(II) on Tata chromite mine overburden, *J. Hazard. Mater.* 148 (2007) 553–559. <https://doi.org/10.1016/j.jhazmat.2007.03.008>.
- [17] B.L. Martins, C.C.V. Cruz, A.S. Luna, C.A. Henriques, Sorption and desorption of Pb²⁺ ions by dead *Sargassum* sp. biomass, *Biochem. Eng. J.* 27 (2006) 310–314.
<https://doi.org/10.1016/j.bej.2005.08.007>.
- [18] M. Naghizade Asl, N.M. Mahmodi, P. Teymouri, B. Shahmoradi, R. Rezaee, A. Maleki, Adsorption of organic dyes using copper oxide nanoparticles: isotherm and kinetic studies,

- Desalination Water Treat. 57 (2016) 25278–25287.
<https://doi.org/10.1080/19443994.2016.1151832>.
- [19] R. Rajesh, S.S. Iyer, J. Ezhilan, S.S. Kumar, R. Venkatesan, Graphene oxide supported copper oxide nanoneedles: An efficient hybrid material for removal of toxic azo dyes, *Spectrochim. Acta. A. Mol. Biomol. Spectrosc.* 166 (2016) 49–55.
<https://doi.org/10.1016/j.saa.2016.05.002>.
- [20] A.M. Ghaedi, S. Karamipour, A. Vafaei, M.M. Baneshi, V. Kiarostami, Optimization and modeling of simultaneous ultrasound-assisted adsorption of ternary dyes using copper oxide nanoparticles immobilized on activated carbon using response surface methodology and artificial neural network, *Ultrason. Sonochem.* 51 (2019) 264–280.
<https://doi.org/10.1016/j.ultsonch.2018.10.007>.
- [21] M. Shahmiri, N.A. Ibrahim, F. Shayesteh, N. Asim, N. Motallebi, Preparation of PVP-coated copper oxide nanosheets as antibacterial and antifungal agents, *J. Mater. Res.* 28 (2013) 3109–3118. <https://doi.org/10.1557/jmr.2013.316>.
- [22] . S., P. Thakur, V. Kumar, Kinetics and thermodynamic studies for removal of methylene blue dye by biosynthesize copper oxide nanoparticles and its antibacterial activity, *J. Environ. Health Sci. Eng.* 17 (2019) 367–376. <https://doi.org/10.1007/s40201-019-00354-1>.
- [23] S. Mallakpour, A. Jarahiyan, Enhancement of Poly(Vinyl Alcohol)–Poly(Vinyl Pyrrolidone) Blend Properties using Modified Copper (II) Oxide and Ultrasonic Irradiation, *Polym.-Plast. Technol. Eng.* 56 (2017) 1059–1067.
<https://doi.org/10.1080/03602559.2016.1253733>.
- [24] A.B. Seabra, M.G. de Oliveira, Poly(vinyl alcohol) and poly(vinyl pyrrolidone) blended films for local nitric oxide release, *Biomaterials.* 25 (2004) 3773–3782.
<https://doi.org/10.1016/j.biomaterials.2003.10.035>.
- [25] R.M. LillebyHelberg, Z. Dai, L. Ansaloni, L. Deng, PVA/PVP blend polymer matrix for hosting carriers in facilitated transport membranes: Synergistic enhancement of CO₂ separation performance, *Green Energy Environ.* 5 (2020) 59–68.
<https://doi.org/10.1016/j.gee.2019.10.001>.
- [26] Physics Department, Faculty of Science, Damietta University. P.O.Box 34517, New Damietta, Egypt, H. M. Zidan, Structural and Electrical Properties of PVA/PVP Blend Doped with Methylene Blue Dye, *Int. J. Electrochem. Sci.* (2016) 9041–9056.
<https://doi.org/10.20964/2016.11.08>.
- [27] K.S. Venkataprasanna, J. Prakash, S. Vignesh, G. Bharath, M. Venkatesan, F. Banat, S. Sahabudeen, S. Ramachandran, G. DevanandVenkatasubbu, Fabrication of Chitosan/PVA/GO/CuO patch for potential wound healing application, *Int. J. Biol. Macromol.* 143 (2020) 744–762. <https://doi.org/10.1016/j.ijbiomac.2019.10.029>.
- [28] C. Das, S. Sen, T. Singh, T. Ghosh, S.S. Paul, T.W. Kim, S. Jeon, D.K. Maiti, J. Im, G. Biswas, Green Synthesis, Characterization and Application of Natural Product Coated Magnetite Nanoparticles for Wastewater Treatment, *Nanomaterials.* 10 (2020) 1615.
<https://doi.org/10.3390/nano10081615>.
- [29] M. Balouiri, M. Sadiki, S.K. Ibnsouda, Methods for in vitro evaluating antimicrobial activity: A review, *J. Pharm. Anal.* 6 (2016) 71–79.
<https://doi.org/10.1016/j.jpha.2015.11.005>.
- [30] R.W. Bussmann, G. Malca-García, A. Glenn, D. Sharon, G. Chait, D. Díaz, K. Pourmand, B. Jonat, S. Somogy, G. Guardado, C. Aguirre, R. Chan, K. Meyer, A. Kuhlman, A. Townesmith, J. Effio-Carbajal, F. Frías-Fernandez, M. Benito, Minimum inhibitory

- concentrations of medicinal plants used in Northern Peru as antibacterial remedies, *J. Ethnopharmacol.* 132 (2010) 101–108. <https://doi.org/10.1016/j.jep.2010.07.048>.
- [31] P. Mulvaney, Surface Plasmon Spectroscopy of Nanosized Metal Particles, *Langmuir*. 12 (1996) 788–800. <https://doi.org/10.1021/la9502711>.
- [32] M. D, K.M. Peddi, R. R, CuO NANOPARTICLES: SYNTHESIS, CHARACTERIZATION AND THEIR BACTERICIDAL EFFICACY, *Int. J. Appl. Pharm.* 9 (2017) 71. <https://doi.org/10.22159/ijap.2017v9i6.71757>.
- [33] M.P.C. Rao, K. Kulandaivelu, V.K. Ponnusamy, J.J. Wu, A. Sambandam, Surfactant-assisted synthesis of copper oxide nanorods for the enhanced photocatalytic degradation of Reactive Black 5 dye in wastewater, *Environ. Sci. Pollut. Res.* 27 (2020) 17438–17445. <https://doi.org/10.1007/s11356-019-05434-1>.
- [34] S. Uma Maheshwari, K. Govindan, M. Raja, A. Raja, M.B.S. Pravin, S. Vasanth Kumar, Preliminary studies of PVA/PVP blends incorporated with HAp and β -TCP bone ceramic as template for hard tissue engineering, *Biomed. Mater. Eng.* 28 (2017) 401–415. <https://doi.org/10.3233/BME-171682>.
- [35] I. Jipa, A. Stoica, M. Stroescu, L.-M. Dobre, T. Dobre, S. Jinga, C. Tardei, Potassium sorbate release from poly(vinyl alcohol)-bacterial cellulose films, *Chem. Pap.* 66 (2012). <https://doi.org/10.2478/s11696-011-0068-4>.
- [36] S. Suresh, S. Karthikeyan, K. Jayamoorthy, FTIR and multivariate analysis to study the effect of bulk and nano copper oxide on peanut plant leaves, *J. Sci. Adv. Mater. Devices*. 1 (2016) 343–350. <https://doi.org/10.1016/j.jsamd.2016.08.004>.
- [37] S.V. Jadhav, D.S. Nikam, V.M. Khot, S.S. Mali, C.K. Hong, S.H. Pawar, PVA and PEG functionalised LSMO nanoparticles for magnetic fluid hyperthermia application, *Mater. Charact.* 102 (2015) 209–220. <https://doi.org/10.1016/j.matchar.2015.03.001>.
- [38] S. Yadav, A. Asthana, A.K. Singh, R. Chakraborty, S.S. Vidya, Md.A.B.H. Susan, S.A.C. Carabineiro, Adsorption of cationic dyes, drugs and metal from aqueous solutions using a polymer composite of magnetic/ β -cyclodextrin/activated charcoal/Na alginate: Isotherm, kinetics and regeneration studies, *J. Hazard. Mater.* 409 (2021) 124840. <https://doi.org/10.1016/j.jhazmat.2020.124840>.
- [39] G.Y. Abate, A.N. Alene, A.T. Habte, Y.A. Addis, Adsorptive Removal of Basic Green Dye from Aqueous Solution Using Humic Acid Modified Magnetite Nanoparticles: Kinetics, Equilibrium and Thermodynamic Studies, *J. Polym. Environ.* 29 (2021) 967–984. <https://doi.org/10.1007/s10924-020-01932-3>.
- [40] I. Ali, C. Peng, T. Ye, I. Naz, Sorption of cationic malachite green dye on phytogetic magnetic nanoparticles functionalized by 3-mercaptopropanoic acid, *RSC Adv.* 8 (2018) 8878–8897. <https://doi.org/10.1039/C8RA00245B>.

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