

Comparison between Nanokaolin and Nanocopper Oxide for removal of Direct Blue 3B from Water, in vitro

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Abstract: Increasing concentrations of azo-dyes such as direct blue 3B in surface and groundwater are a chief environmental distress in current years. In this study, nanokaolin and nanocopper oxide were used as a trial for removal of direct blue 3B residue from watery solution. Methods, nanoKaolin and nanocopper oxide were characterized by X Ray Diffraction (XRD), surface area and Transmission Electronic Microscope (TEM) methods. Impact of different factors like, adsorbent dosage, interaction time, and preliminary level of direct blue 3B and temperature on adsorption of direct blue 3B on nanokaolin and nanocopper oxide was investigated. The results investigated that the greatest state for elimination of direct blue 3B was revealed at 90 min contact time and 1g/L adsorbent dosage. The elimination of direct blue 3B diminished with the rise of initial level. Langmuir and Freundlich isotherm models were used for the equilibrium data. Kinetic study applied pseudo first and second direction. Results pointed to the possible role of nanokaolin and nanocopper oxide for elimination of direct blue 3B from aqueous solutions.

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1. Introduction

Stains or dyes are complex organic composites which are used for many purposes in different industries to stain the formed products. These dyes are expelled from several industrial sources like cosmetic, textile, rubber, leather, paper, and printing activities. Waste water emissions comprise stains or dyes which may represent probable health or environmental hazards. Many adverse effects are arisen due to some dyes such as toxicity, carcinogenicity and can lead to eye and skin inflammation. So, several investigators have been searching for a tool or methods for elimination of these stains or dyes from aqueous solutions by using various separating techniques. The various techniques used for elimination of dyes from wastewater include, coagulation/flocculation, adsorption, unconventional oxidation technologies, ozonation, and membrane-filtration, aerobic and anaerobic degradation. There are some obstacles that limit the applications of such techniques for removal of dyes such as total cost, operation efficiency and the design [1].

The environmental topics related with remaining colour in textile discharges have pretended a main task to environmental experts in addition to the textile staining processors. The necessities to eradicate colour from textile discharge on site preceding to release to drain have been increasingly stiffened due to enlarged public criticisms about coloured water passages. Most stains or dyes are resistant to degradation as its molecules are highly stable and not affected by

chemicals, biological, light and it is difficult to treat the resultant pollution by either exposure or treatment. Several authors in the past few decades tried to make and develop proficient and cost effective technologies to eliminate colour from textile discharge. [2].

There are many means for taxonomy of stains or dyes. Each class of stain or dye has a very distinctive properties, chemical structure, and special way of attachment. Whereas some stains or dyes can chemically react with the substrates to establishing strong bonds in the procedure, other dyes can be conjugated by physical forces.

Some of known ways of taxonomy is shown below [3] depending on:

- The nuclear structure.
- The source of materials.
- Industrial classification of the Dyes.
- The nature of their respective chromophores.

Classification based on the source of materials

Another classification of stains or dyes depending on its source either natural or synthetic dyes.

Natural pigments (dyes)

Thousands of years ago the human beings coloring several of their materials to accept them the good appearance, desired color or for the purposes of protection, such as clothes, Leather, pottery, food, and homes or buildings. Two methods were used in the past for giving different colors either a painting (cover with stains) or dyeing (cover the whole surface) [4]. The natural dyes are driven from plant or animal

sources and are stable in colour not contain any chemical additives or having chemical formula but carry a numbers specific for each degree of colors.

Synthetic pigments (Dyes)

These pigments or dyes composed from organic or inorganic components so it called synthetic or semi-synthetic compounds such as Acid, Basic, Mordant, Reactive, Vat, Metal complex, Disperse dye, Sulphur, etc [5].

The main goal of scientist to discoloring or removing of dyes residues from colored discharges by simple not costly methods, in order to reduce the environmental pollution. The methods applied nowadays for removing of pigments or stains or dyes from wastewaters effluents are not completely effective and costly and cannot applied to treat all kinds of pigments in the wastewaters. The present study give an importance for using of native materials such as grinded rice hull in the adsorption purpose or as adsorbent agent. Methylene blue dissolved in water was used with different levels (5-25 mg/l), then were mixed and shaken with definite quantities of adsorbents material (rice hulls) for calculation of the capacity of adsorption. In this experiment the treated and non-treated grinded rice hulls were tested for adsorption of methylene blue dye.

Many parameters in the current work were estimate their influence of degree of removal of MB dye from the mixture, these parameters comprise, concentration of adsorbents, concentration of methylene blue (MB), pH of the mixture and the interaction time between the dye and adsorbents. In this experiment, the concentrated dye was impounded from the mixture in a time ranged from 60-90 min post initiation of each trial. The impact of the pH of the solution affected on the capacity of adsorption, where, when the pH increased from (3 to 10) the capacity of adsorption was also increased from 72 to 94%. Moreover, addition of citric acid to the grinded rice hulls not enhanced the adsorption capacity or effect on degree of removal of dye from the solution [6].

As mentioned before by many scientists, pigments or dyes are organic or non organic in composition derived from plant or animal sources that are applied to accept the desired colour to several materials such as fur, hair, paper, leather, cosmetics, drugs, greases, waxes, textile materials and plastics. Industrial pigments discharge in the wastewater represents a major source of environmental pollution. Therefore, the investigators searching for suitable methods for removal of dyes from industrial wastewater, via applying of different methods and techniques for this purpose. One of these techniques for removal of pigments is the method of adsorption. In spite of many techniques were applied for removal of pigments from industrial effluents, but the method

of adsorption is still used due to it is relatively non-expensive and can be used for most types of pollutants either from the water or wastewater. Another technique used for removal of stains from wastewater is the batch reactor where it characterized by its practicability and easiness in application beside it considered economically non-costly. Another area of research dealing with the use of colarane blue BGFS Anthraquinone dye and Fe_2O_3 as an agent for removing of the dye from the solution of real wastewater. The results revealed that the optimum removal of dye by using 0.3 gm Fe_2O_3 (initial conc. 125 ppm) from the solution was obtained at pH 2. [7].

Most of goods and food products add different coloring agents such as pigments or dyes either natural or synthetic dyes to give a good appearance and acceptability of the consumers. The occurrence of these visible coloring agents in the water is not acceptable. Therefore, the current work was performed in the laboratory scale for estimation of the ability of orange peel as adsorbent for removal of dyes or stains from wastewater and to set up it as a standard for treatment of wastewater procedure for compound bind industry. These materials were treated to withdrawn the color from the solution by using different concentrations of adsorbent and also to determine the efficacy of different pH and interaction time on the removal potency from the wastewater. The obtained data revealed that the degree of removal of dye at pH 7 was averaged 60-70% and the interaction time was 120 minutes, while the maximum amount of adsorbent was equal 1.5g/25mL. The balanced adsorption performance was estimated by using Langmuir adsorption isotherm mode [8].

Fresh water plays an important role in the life of societies, without water no life. There are a shortage of the water in most countries in the world particularly in north of Africa not sufficient to cover the requirements of cultivation and modern extensions in the desert. With respect to textile industries that consumed a large quantities of water and in the same time release a thousands of meters of polluted water annually, where about 17 - 20% of freshwater pollution is caused by textile discharge, which raised a dangerous environmental attention. [9].

Many industrial products in different sectors such as textile products, food sector, printing and pharmaceuticals used synthetic organic stains (e.g., azo dyes). The widely used of these stains are intractable, accordingly they can convey colour on various crude substances. The end products of biotransformation processes of dye compound resulting in production of definite dyes, dye precursors and some aromatic amine metabolites which possess a carcinogenic effect. Generally, the discharge of colouring agents (dyes/ pigments/stains) into water

either with small or large quantities will lead to changes in the colour and taste of water and consider one of the main pollutants in the environment, consequently reflected on the health of human and animal directly (via consuming of pollutant water) or indirectly (via eating of animal products or plants by products, drink or irrigated from polluted wastewater, respectively). Therefore, several trials was and still paid to withdrawn dyes or pigments from wastewater; till nowadays, there is no suitable or appropriate treatment can be used for treatment of waste water possessing enough efficiency and not costly for removal of dyes in the water discharged from textile industries. [10].

The technique of adsorption of stains/pigments is considered a recent technology applied for management of waste water holding various kinds of colouring agents. About 23 direct red dyes from dyes released in wastewater can be removed by using the technique of adsorption through using of rice husk as adsorbent substrate either in treated or non-treated formula. The procedure of adsorption includes: cleaning of rice husk by washing, then rice husk is dried at 105°C, then citric acid (0.6 Mole) is added to the dried rice husk for 2 hours and dried at 120 °C. To obtain a rice husk suitable for removal of 23 direct red dyes, this processes is repeated several times by using treated and untreated rice husk. Different concentrations of dissolved dyes were left to interact with definite concentration of adsorbent to determine the efficiency of adsorbent to remove the color and the suitable time required for contact, in addition to pH of the solution [11].

Developing pollutants revealed lately in the water streams are in the form of synthetic chemicals due to the interference in the natural environment and increased in the activities of human and industrial discharges. Most of these activities not subjected for safety roles of environment, even most of them not subjected for regular observation from the official authorities, and can possibly cause harmful impacts

in human, animal aquatic life due to increase in the liberated toxicants in the surroundings. May trials were done by the researchers to cultivate some types of plants (wastewater treatment plants, WWTPs) capable of trapping or absorb some pollutants from wastewater, which are not completely effective in removal of different kinds of such pollutants from wastewater, and accordingly the necessity for treatment of the this water are urgent [12].

The remnants of pigments/dyes in the wastewater considered one of the hot topics that require more of efforts to find a suitable treatment technique to reduce the degree of pollution in the environment. This study was depends on an information collected from different sources dealing with methods used for purification of wastewater from colouring agents (dyes/pigments) which carried out during the period from 2008 to 2010. Remarkable methods for the control of dye waste comprise catalytic oxidation, biological treatment, sorption process, filtration, and combined treatments [13].

Therefore, the main aim of of the current study is to eradicate from Direct Blue 3B (azo-dye) from industrial effluents in wastewater via using photodegradation technique and nano-materials and determination the efficiency of both two methods in the percentage of withdrawn from water.

2. Experimental

Chemical and Reagents

All chemicals used in experiment were of analytical grade. Preparation of direct blue 3B was at 0.5×10^{-3} g/L concentration. Kaolin and nanocopper oxide are used at 0.1g/100ml.

Apparatus:

- TEM spectra were recorded by JSM-6380LA scanning electron.
- X-ray diffraction spectra were recorded by microscope (Jeol) Altima 4 X-Ray diffraction (Rigaco).

Table.1 Design of Experiment (2 Folds)

Fold 1 (Optimum Removal %)					
Volume of dye	100 ml				
Conc. Of dye (g/l)	1×10^{-3}	0.5×10^{-3}	0.25×10^{-3}	0.12×10^{-3}	0.06×10^{-3}
Conc. Of nano material	0.1 g/100ml				
Temp.	25 °C				
Stirring	200 rpm				
Time	120 mins.				
Fold 2 (Different Conditions)					
Effect of Time	5-120 mins				
Effect of Dose	0.1-0.4 g/100 ml				
Effect of pH	1-8				
Effect of Stirring	100-500 rpm				
Effect of Temp.	25-75 °C				

Nanomaterials

Different materials in the nano-scale (copper oxide and kaolin) were prepared and used. The crude materials were prepared in laboratory as follows:

Characterization of kaolin: (TEM, XRD and FTR) for kaolin.

Kaolin Nanoparticles

Preparation of Kaolin Nanoparticles

Nanokaolin is a product of kaolin, also known as white clay. Kaolin was established as supplementary cementitious material in concrete. The inclusion of kaolin in concrete enhances strength and durability and prolongs concrete life span. Nanokaolin can be developed by using sol gel technique which involves high energy milling [650-750 °C]. The process of milling been influenced by time of milling, ball and jar type. Ceramic type Zirconia has been used as jar and ball type in this process. Time of milling was set from 4 hours to 24 hours. Sample was analyzed by using particle size analyzer to determine the particle size and surface area of kaolin. From the results it has been shown that the optimum milling period for nanoKaolin is 24 hours base on particle size compared to 4 hours. Furthermore, one day milling produces a massive increment of surface area compare to others. In conclusion, 24 hours could be considered as the optimum cycle time in the production of nanokaolin [14].

Copper oxide Nanoparticles

Preparation of Copper Oxide

CuO nano powder was prepared by Sol-Gel method. An aqueous solution of $\text{CuCl}_2 \cdot 6\text{H}_2\text{O}$ (0.2 M) was prepared in cleaned round bottom flask. 1 ml of glacial acetic acid was added to the above aqueous solution and heated to 100 °C with constant stirring. 8 M NaOH was added to above heated solution till pH reaches to 7. The color of the solution turned from blue to black immediately and a large amount of black precipitate was formed immediately. It was centrifuged and washed 3-4 times with deionized water. The obtained precipitate was dried in air for 24 h [15].

The powder was characterized by several techniques. The crystalline phases of CuO nano particles were determined by X-Ray diffractometer (XRD, BrukerD8 Advance, Germany) using Cu $K\alpha$ as radiation source (40 kv, Step Size 0.020, scan rate 0.50 min⁻¹, 200≤700). The Nano particle size and zeta potential is estimated by particle size analyzer (SZ-100 Nanoparticle, Horiba, Germany) data. The morphology of the prepared nanoparticles were calculated by transmission electron microscope (TEM, Hitachi VP-SEM S-3400N, Germany), FTIR are present functional group at wave number (3446, 3359, 3317, 2361, 988,922, 831,598 cm⁻¹).

Batch experiments

The batch experiments were carried out in 250 ml Erlenmeyer containing 100 ml of aqueous solution. The suspension was shaken at (25 C⁰) shaker at 250 rpm. The residual concentration of direct blue 3B in supernatant was analyzed by HACH UV-spectrophotometer. Effects of adsorbent dosage (0.2-0.4 g/L), contact time (10-90 min), initial direct blue 3B in concentration (0.031 to 1*10⁻³ g/L) and temperature (25 C⁰-65 C⁰) on photodegradation of d by nanokaolin and nanocopper oxide were investigated. Direct blue 3B The adsorption capacity q_e (mg/g) of the adsorbent was calculated from the following equations:

$$(1) q_e = (C_i - C_e)V / W$$

$$(2) R\% = (C_i - C_e) 100 / C_i$$

Where C_i is initial direct blue 3B, C_e is the residual concentration reached at equilibrium state, V is the volume of solution (L) and W is the weight of adsorbent (g).

3. Results and Discussion

Characterization of Kaolin Nanoparticles

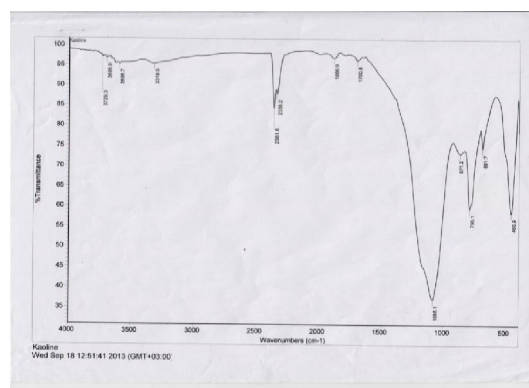


Fig. (1): FTIR for Kaolin nanoparticles

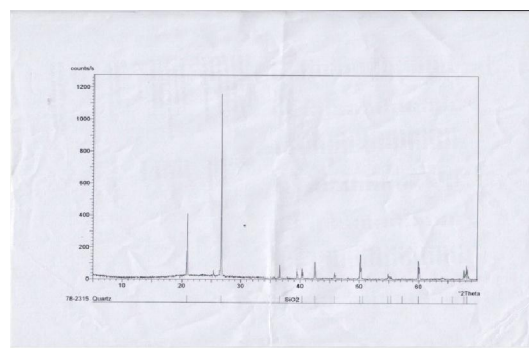


Fig. (2): XRD for Kaolin nanoparticles

A systematic characterization on kaolin has been performed by FT-IR, XRD and TEM. The FT-IR spectrum of nanokaolin is shown in **Fig. (1)**. The two

absorption peaks at wavelength of 1085 cm^{-1} and 460 cm^{-1} indicates the formation of nanoparticles. **Fig. (2)** shows the powder XRD pattern of nanokaolin samples under ambient condition. The broad peak reveals the existence of an amorphous phase Kaolin. The characteristic broad peak at 12θ to 68θ indicates that nanoKaolin is predominately present in the sample. **Fig. (3)** shows the TEM image of fresh synthesized Kaolin of nanoparticles. It could be observed that the kaolin is in the form nanospheres, which exists in a diameter of 31- 60 nm.

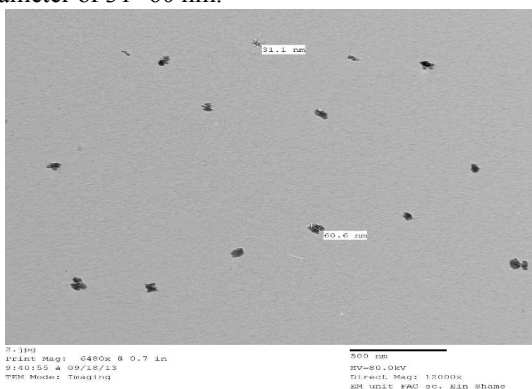


Fig. (3): TEM for Kaolin nanoparticles

Characterization of Copper Oxide Nanoparticles

The XRD shape of prepared CuO nanoparticles is shown in fig (4). Entirely the peaks in diffraction pattern demonstrates monoclinic structure of CuO, and compared with the peaks of JCPDF card no. [89-5895] and miller indices are recognized. The lattice structures were calculated from XRD result is as follows: The average grain size is approximately 18.09nm by using Debye-Scherrer formula. Lattice parameters from XRD counted, $a=0.46\text{nm}$, $b=0.34\text{nm}$, $c=0.50\text{nm}$. Formula for the measuring of grain size $D=0.9\lambda/\beta\cos\theta$ Where β is full width half maxima of the peak. Morphology index was calculated from XRD full width half maxima and it says that positive correlation between the size of the particle and the morphology index, when the first is increased the second also increased.

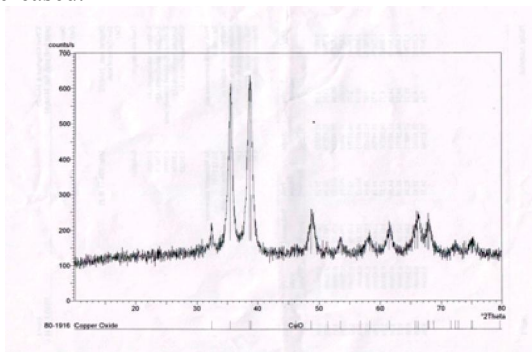


Fig. (4): XRD pattern of CuO nanoparticles.

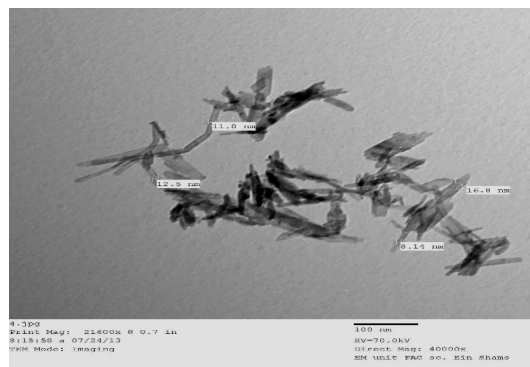


Fig. (5): TEM for CuO nanoparticles

TEM micrograph of CuO nanoparticles are shown in fig. (5). The real size of nanoparticles is determined from TEM micrograph. Utmost of the nanoparticles have size around fewer than 50nm and is in association with the particle size analyzer records. The TEM graph is too demonstrated that the CuO Nanoparticles is approximately uniform in size and diverged in shape.

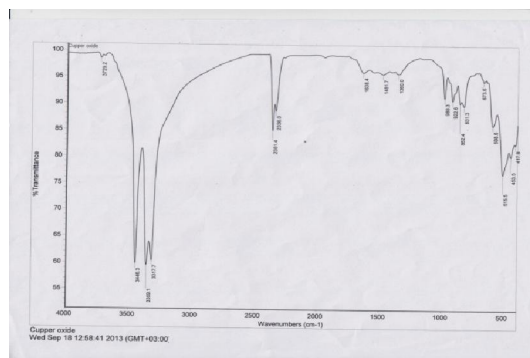


Fig. (6): FTIR for CuO nanoparticles

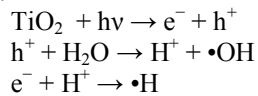
Effect of contact time for direct blue3B in presence of UV:

In the current work, photon absorption during direct photolysis, produced compounds in excited electronic states that are predisposed to chemical transformation. Direct photolysis by UV, the impurity to be damaged can absorb the episode radiation and goes through degradation initial from its excited state [16]. UV irradiation can destroy and decompose some organic molecules via bond cleavage and emission of free radicals, but generally at very slow degrees [17].

In the presence of UV radiation, the rate of dye removal is high in the beginning indicating that degradation for dye is fast during the first period. The removal reached its medium value after about 60 min for direct blue 3B (68%).

The mechanism of nanoTiO₂ photo catalysis is determined as follows: TiO₂ absorbs UV light to generate electron (e⁻) and hole (h⁺). The holes combine with H₂O on the surface of TiO₂ to form H⁺

and $\cdot\text{OH}$ free radicals. H^+ and electron react to give $\cdot\text{H}$. The $\cdot\text{H}$ and $\cdot\text{OH}$ free radicals outbreak the organic molecule, and then produce some intermediate products. The mechanism of photo catalytic degradation under UV light irradiation is described by [18]:



$\cdot\text{OH}$ ($\cdot\text{H}$) \rightarrow dye \rightarrow oxidative products \rightarrow end product

Shown in Fig (7).

Effect of contact time for direct blue 3B in presence of kaolin, nanocupper oxide and UV lamp

When kaolin nanoparticles were used as photo catalyst in present UV lamp, the percent of Db3B removal was high and reach to (93%) at 15 min with nanokaolin and Db3B (65%) at 75 min. When used nanocupper oxide. The experiments were performed

until 75 min for reach maxim removal 70%. The rate of removal was increase in the beginning due to a large surface area of the adsorbent that available. The relation between removal percent for dye under consideration and contact time is shown in Fig.8.

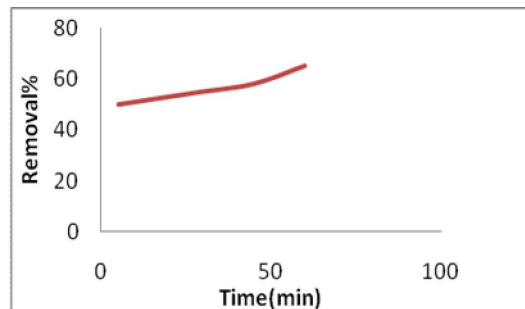


Fig. (7): Effect of contact time for in present of UV only

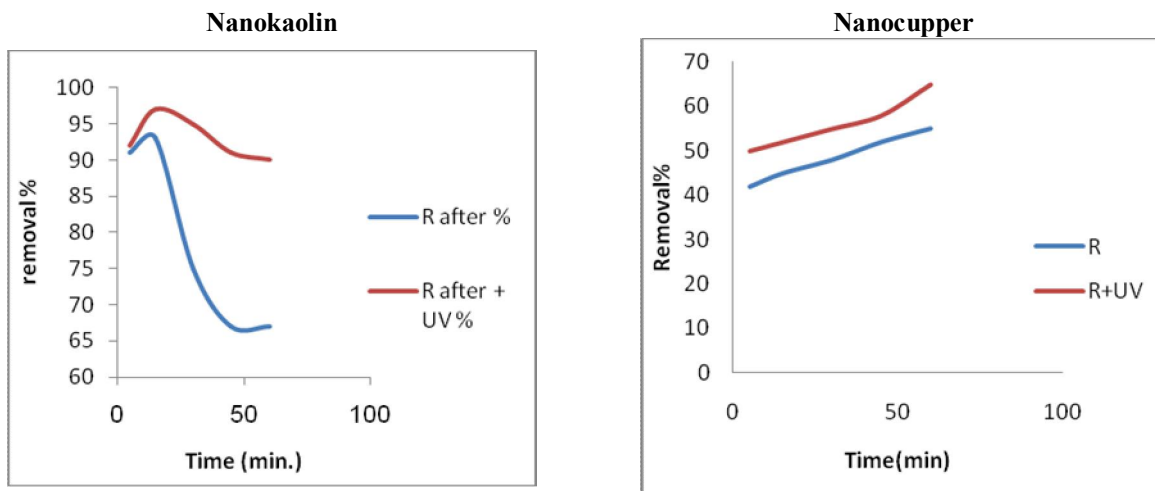


Fig. (8): Effect of contact time for direct blue 3B in presence of nanokaolin & nanocupper and UV lamp

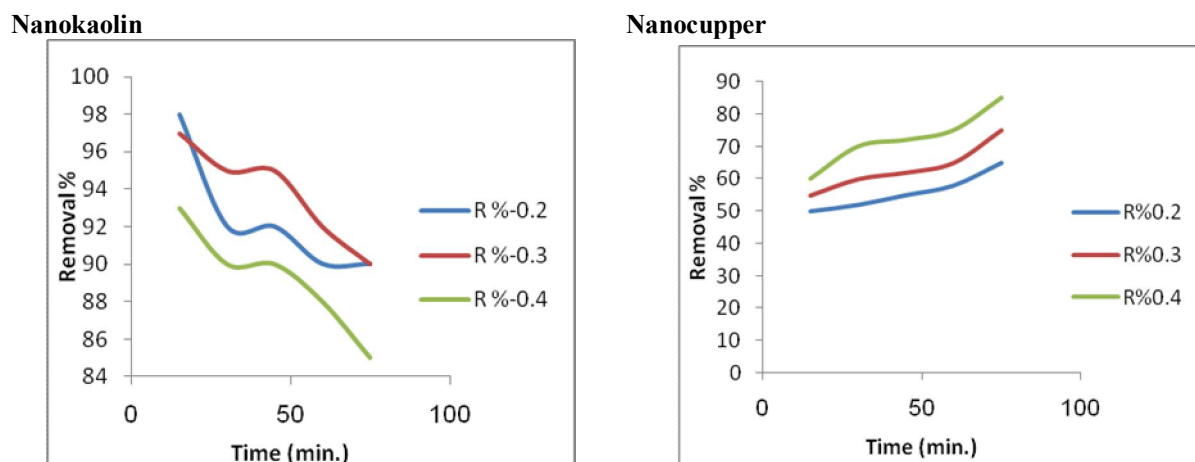


Fig. (9): Effect of different dose of nanokaolin & nanocupper on direct blue 3B

Effect of different doses for nanokaolin and nanocupper oxide on direct blue 3B

Fig.9. illustrates the effect of different amounts of nanokaolin and nanocupper oxide (0.2 to 0.4 g / 100 ml). When used 0.2g of nanokaolin the removal of Db3B. It is observed that the efficiency of removal decreased from 98% at 15 min to 90% at 75 min for Db3B. Efficiency of removal decrease from 97% at 15 min to 90% at 75 min at 0.3g of nano kaolin. Another state when using 0.4 g of nanokaolin the removal % of Db3B reached 93% at 15 min but when reach to equilibrium removal% become 85% at 75 min. Another case when using 0.2 g of nanocupper oxide removal% reached 50% at 15 min and 65% at equilibrium state for Db3B at using 0.2g of nanocupper oxide. Another state when using 0.3 g of nanocupper oxide Db3B reached 55% at 10 min but 74% at 75 min. Another case when using 0.4 g of nanocupper oxide Db3B reached to 60% at 10 min and 85 % at 75 min at equilibrium state.

Effect of Initial Direct blue 3B Concentration on nano cupper oxide and nanokaolin Uptake

The mechanism of removal of dye is dependent mainly on the initial dye level, where at low levels, dyes are adsorbed by specific sites, whereas with increasing dyes levels from (0.25×10^{-3} to 1×10^{-3}) the specific locations are saturated and the interchange locations are occupied. It is observed that with increasing initial concentrations, the adsorption capacity increases while the percent dyes removal decreases. However an upsurge in dye uptake was noticed, the reduce in rate of adsorption may be returned to lack of enough surface area to attract much more dyes existing in the aqueous solution. While in case of low levels of dyes in the solution, the dye found in solution could intermingle with the binding locations and accordingly the rate of adsorption was increased [19]. The general shapes of the isotherms are similar for different biomasses. However, the adsorption capacities and affinities are significantly different.

In the same time, some investigations demonstrated that adsorption is independent on the level of pollutant, and in some instances, the rate of adsorption is diminished with elevated initial level of contaminant [20]. In such case various clarifications were anticipated, all of which depend on the adsorption of pollutant molecules on the solid surface. Only one elucidation presumed that at high pollutant level, the pollutant molecules may compete with the adsorbed intermediates and suppress the process of decomposition [21].

Effect of direct blue 3B concentrations removal by nanokaolin and nanocupper oxide in present UV lamp

The impact of original concentration of dye on the rate of dye accumulation into nanokaolin and nanocupper oxide was done by applying batch agitation in 250 ml beakers containing dye solutions of starting levels ranging from 1×10^{-3} to 0.031 mg L^{-1} , agitated at 250 rpm and at room temperature ($25 \pm 1^\circ\text{C}$) without any change in the initial pH of the test solution. The equilibrium concentration was evaluated after 75 min of contact time. The photodegradation for dye data presented in **Fig (7)** indicates that the percentage removal of direct blue 3B decreases with increase in initial direct blue 3B concentration. Explain the effect of UV lamp making photodegradation for direct blue 3B to reach maximum removal% reach to 70% for direct blue 3B for dye 0.5×10^{-3} .

Effect of pH in photodegradation of direct blue 3B in present UV lamp

Effect of pH on photodegradation of direct blue 3B on surface of nanokaolin and nanocupper oxide are variable, but give maximum degradation at natural pH =3 for direct blue 3B. Reach removal 95% at pH =4 with nanokaolin. Removal% reach to 85% with nanocupper oxide.

Effect of stirring in photodegradation of direct blue 3B in present UV lamp

Effect of stirring on photodegradation of direct blue 3B on surface of nanokaolin and nanocupper oxide are variable, but give maximum degradation at stirring 500 rpm for direct blue 3B reach removal 95% with nanokaolin and 85% with nanocupper oxide in **Fig. (9)**.

Effect of temperature for removal of direct blue 3B in presence of UV lamp

The mechanism of action of nanoparticles for efficient removal of contaminant is dependent mainly on the temperature of the medium. The cause of this effect is believed to be the truth that temperature is a significant factor influencing the adsorption and photocatalysis. In such case of photocatalytic procedure, the photocatalytic decomposition rate decreases with rising in temperature. In other words, another explanation, the higher in a temperature affords increase in electron transfers in valance bond to higher energy levels and hereafter simplifying the electron-hole production that could be employed in starting reduction and oxidation reactions [22]. The types of photon-generated holes, and hydroxyl radicals ($\bullet\text{OH}$) and electrons can therefore decompose organic contaminant to intermediates, and subsequently are additional defragmented to CO_2 and H_2O .

Generally, the activated energy liberated by photo catalytic reaction is to some extent influenced by the degree of temperature, but sequential redox reaction may be greatly affected by the degrees of temperature which influences both degree of adsorption and collision frequency of molecules [23].

Accordingly the general impact on the photo catalytic performance will be governed by the relative significance of these phenomena. direct blue 3B removal% decrease from 75% at 35°C to 70% at 65°C but in using nanocopper oxide removal% increase from 60% at 25°C to 85% at 75°C.

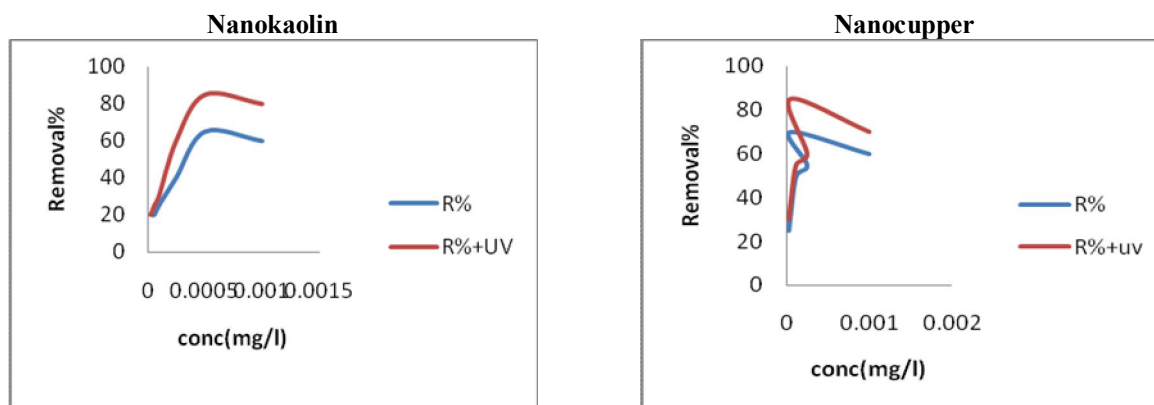


Fig. (10): Effect of direct blue 3B concentration removal by nanokaolin and nanocopper oxide in present UV lamp

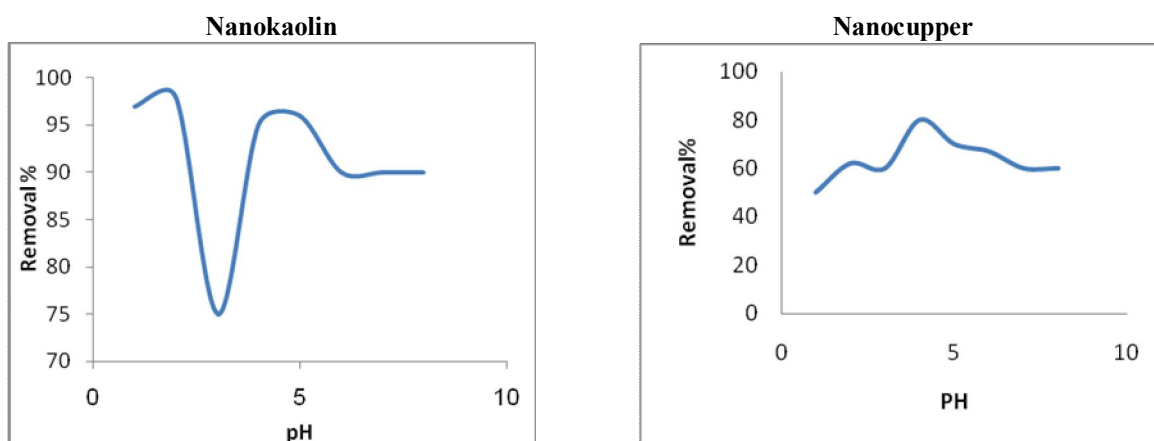


Fig. (11): Effect of pH in photodegradation of direct blue 3B in presence of UV lamp

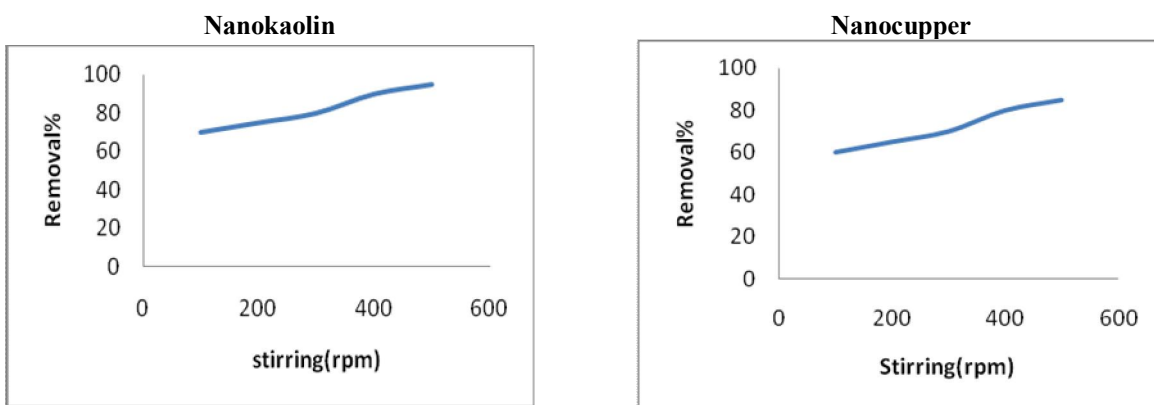


Fig. (12): Effect of stirring in photodegradation of direct blue 3B in presence of UV lamp

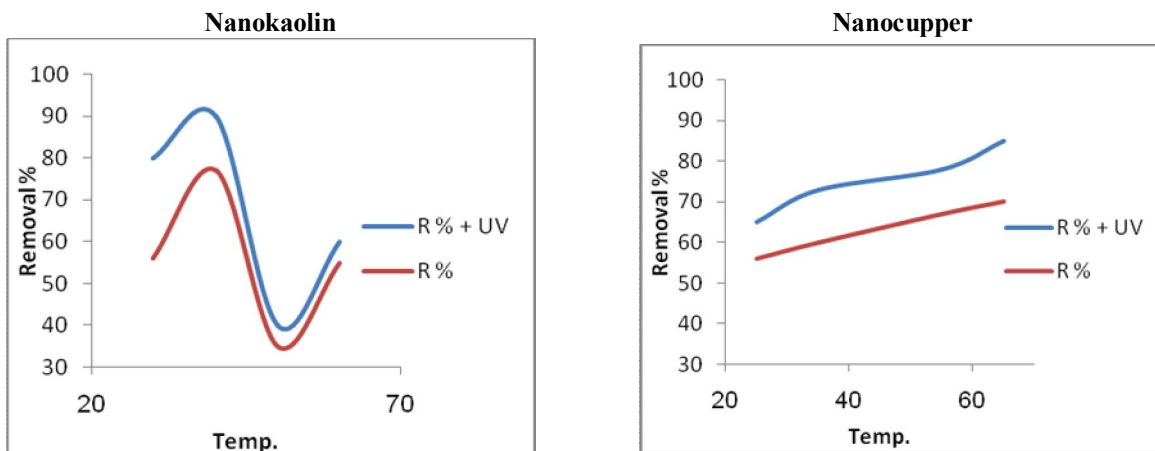


Fig. (13): Effect of temperature for removal direct blue 3B in presence of UV lamp

In order to appraise the thermodynamic viability of the withdrawal process and to approve the nature of the adsorption process, thermodynamic parameters (ΔG° , ΔH° and ΔS°) were counted from the following equations [5,6]:

$$K_D = \frac{C_{Ad}}{C_e} \quad (4)$$

$$\Delta G = -RT \ln K_D \quad (5)$$

$$\ln K_D = -\left(\frac{\Delta H}{RT}\right) + \frac{\Delta S}{R} \quad (6)$$

where K_D is the equilibrium constant, C_{Ad} (mg/L) is the level of the dye adsorbed on solid at equilibrium, C_e (mg/L) is the equilibrium level of dye in the solution, R is the universal gas constant, $8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}$, T is the absolute temperature in K , and the value of K_D in can be obtained from the adsorption percent at equilibrium. The values of ΔH and ΔS can be obtained from the slope and intercept of a van't Hoff plot of $\ln K_D$ versus $1/T$ as seen in Fig 10. and the thermodynamic parameters for adsorption of direct blue 3B on kaolin are listed in Tables 2, 3. and Tables 4, 5 with nanocupper oxide.

Table 2: Effect of temperature on removal for direct blue 3B

T	1/T	Removal %	K_D	$\ln K_D$	R^2
303	3.30×10^{-3}	70	35	3.55	0.995
313	3.195×10^{-3}	74	25	3.22	intercept = -4.77 slope = 2500
323	3.096×10^{-3}	72	20	2.99	
333	3.003×10^{-3}	71	15	2.77	

Table 3: Thermodynamic parameters for direct blue

ΔH kJ/mol	ΔS J/mol	ΔG kJ/mol			
		303 k	313 k	323 k	333 k
-20790.9	-39.3956	-8942.95	-8379.35	-7805.68	-7461.65

Table 4: Effect of temperature on removal for direct blue 3B on nanocupper oxide

T	1/T	Removal %	KD	$\ln KD$	R^2
303	3.30×10^{-3}	65	40	3.66	0.904
313	3.195×10^{-3}	73	30	3.4	Intercept= 18.4 Slope = -605
323	3.096×10^{-3}	78	25	3.21	
333	3.003×10^{-3}	85	15	2.77	

Table 5: Thermodynamic parameters for direct blue 3B on nanocupper oxide

ΔH kJ/mol	ΔS J/mol	ΔG kJ/mol			
		303 k	313 k	323 k	333 k
50532.42	153.2268	4610.03	1795.575	1122.556	-398.673

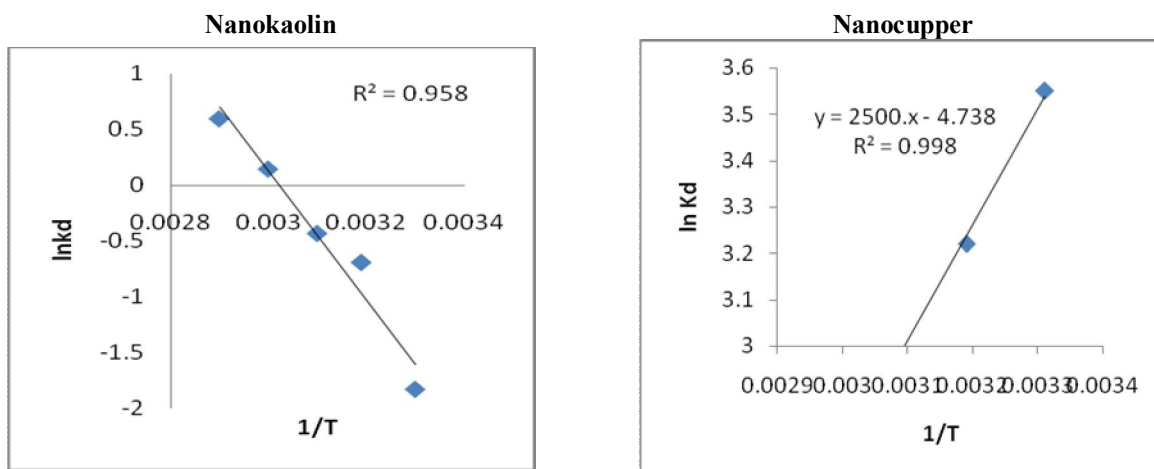


Fig. (14): Relationship between $\ln kd$ and $1/T$

Adsorption Isotherms

The adsorption isotherm shows by what means the adsorption molecules disperse among the liquid and the solid phases when the adsorption manner arrived an equilibrium state. The analysis of the isotherm results by fitting them to diverse isotherm models is an essential procedure to bargain the appropriate model that can be applied for design purpose. The isotherm informations were formfitting to the Langmuir and Freundlich isotherms.

The Langmuir Model

The Langmuir adsorption isotherm has been effectively practical to many contaminant adsorption steps and has been the utmost extensively applied sorption isotherm for the sorption of a solute from a liquid solution [24]. The saturated monolayer isotherm can be symbolized as:

$$q_e = \frac{Q_0 b C_e}{1 + b C_e}$$

The above equation can be reordered to the general linear form:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0}$$

Where C_e is the equilibrium concentration (mg/L); q_e is the amount of dye adsorbed per unit mass of adsorbent (mg/g); Q_0 is q_e for a complete monolayer (mg/g), a constant connected to sorption capacity; and b is a constant related to the affinity of the binding locations and energy of adsorption (L/mg). A high b value pointed to a high affinity. The values of Q_0 and b were for all adsorbents estimated respectively from intercept and slopes of the linear plots of C_e/q_e vs. C_e .

The critical characteristics of Langmuir isotherm can be stated by a dimensionless constant called equilibrium parameter R_L , defined by [25]:

$$R_L = \ln K_F + \frac{1}{n} \ln C_e$$

The value of R_L indicates the type of the isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

Langmuir Adsorption Isotherm for nanokaolin

The different adsorption parameters for adsorption of direct blue 3B are collected in **Table 5**. These parameters are C_0 , C_e , $\ln C_e$, q_e , $\ln q_e$ and C_e/q_e . The plot of C_e vs. C_e/q_e gave straight lines for all dye **Fig. (15)**, from their slopes and intercepts, the values of Q_0 and b could be evaluated, respectively.

Table 6: Adsorption parameters for direct blue3B on nanokaolin

Azo-Dye	C_0	C_e	$\ln C_e$	q_e	$\ln q_e$	C_e/q_e
Direct blue 3B	0.001	0.0001	-9.21	0.00036	7.9	0.28
	0.005	0.0005	-5.23	0.0018	6.3	0.27
	0.0001	0.002	-8.2	1	1	0.002
	0.00006	0.00001	-12.5	0.000036	-1	0.28
	0.00003	0.00001	-13.3	0.000018	-2	0.56

Table 6: Adsorption parameters for direct blue 3B on nanocupper oxide.

Azo-Dye	C_0	C_e	$\ln C_e$	q_e	$\ln q_e$	C_e/q_e
Direct blue 3B	0.001	0.00074	-7.2	0.00015	-8.80	4.93
	0.005	0.0025	-5.8	0.0005	-7.60	5
	0.002	0.0021	-6.1	0.0006	-7.41	3.5
	0.0001	0.25	-1.3	0.062	-2.78	4.03
	0.00006	0.15	-1.8	0.066	-5.2	2.27

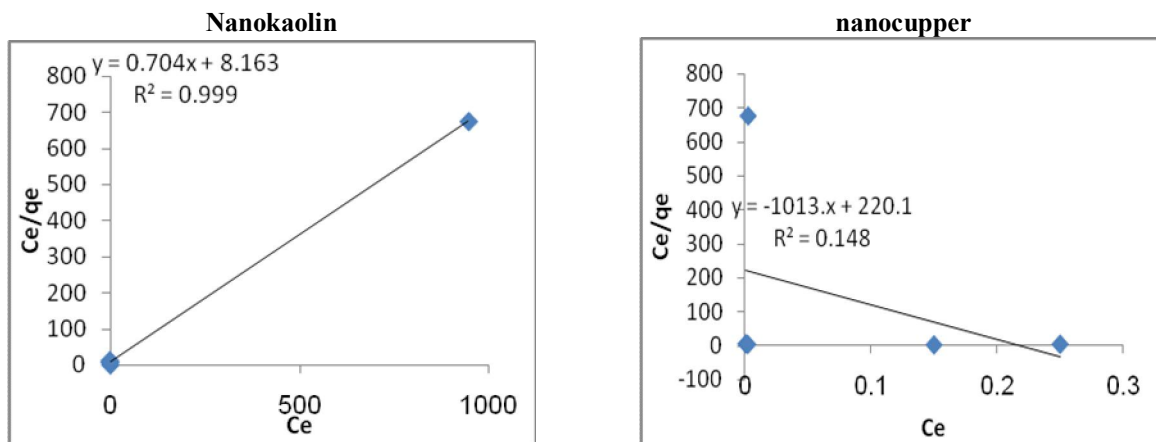


Fig. (15): Langmuir isotherm for direct blue 3B with nanokaolin and nanocupper oxide.

The data obtained for slope, intercept, Q_0 and b are shown in **Table 8**. The applicability of the model was examined by evaluating the correlation coefficient (R). The higher the values of R , the more applicable the model for the dye examined.

The Freundlich Model

On the other hand, the Freundlich isotherm accepts that the adsorption befalls on heterogeneous surface at locations with various energy of adsorption and with non-identical adsorption places that are not constantly accessible. Mathematically it is characterized by the heterogeneity factor ' $1/n$ '[26]. Freundlich model can be represented by the linear form as follows:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$$

Where K_F is the Freundlich constant $(\text{mg/g})/(\text{L/mg})^n$ and n is the heterogeneity factor. The K_F value is related to the adsorption capacity; while $1/n$ value is related to the adsorption intensity. A plot

of $\ln q_e$ versus $\ln C_e$, gives a straight line with K_F and $1/n$ determined from the intercept and the slope, respectively.

Freundlich Adsorption Isotherm for nanokaolin and nanocupper oxide on direct blue 3B

The adsorption isotherm was applied for adsorption of dye on nanokaolin and nanocupper oxide by drawing the relation between $\ln C_e$ and $\ln q_e$ Fig. (16) The slope of the resulting straight line is equals to $1/n$, while the intercept equals to $\ln K_F$. The data obtained for Freundlich isotherm model for direct blue 3B are collected in **Tables 6 and 7**. As shown in table 9, the counted Freundlich isotherm constants and the conforming coefficient of correlation values are tabulated. The coefficient of correlation was high (R^2 values are 0.990 and 0.951) indicating a good linearity. The results show that the values of n are greater than unity (n) indicating that dye is favorably adsorbed on direct blue3B of Freundlich constants indicate easy uptake of dyes from aqueous solution.

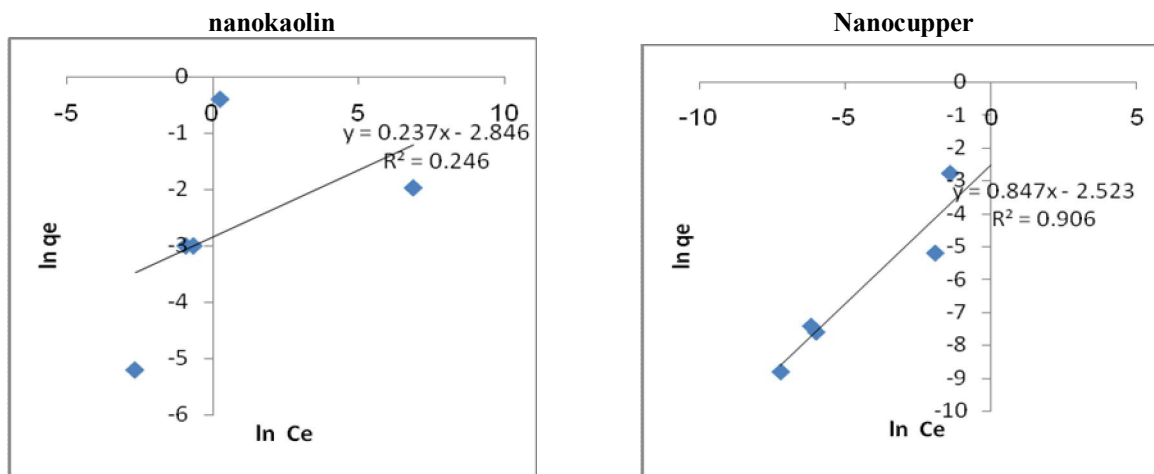


Fig. (16): Freundlich isotherm direct blue 3B on nanokaolin and nanocupper oxide

Table 8: Langmuir equation parameters for nanokaolin and nanocupper oxide on direct blue 3B

Azo-Dye	Slope	Intercept	Q ₀	b	R ²
Db3B/kaolin	0.704	8.16	1.42	11.58	0.999
Db3B/cupper oxide	1013	220.1	0.0009	0.217	0.148

Table 9: Freundlich equation parameters for nano kaolin and nanocupper oxide

Azo-Dye	Slope	Intercept	K _F	n	R ²
Db3B/kaolin	0.235	-2.48	0.0580	0.521	0.95
Db3B/cupper	0.841	-2.51	0.087	0.001	0.901

Kinetic Studies

The pseudo-first order equation is generally expressed as follows [27]:

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right)t$$

As q_e and q_t are the sorption capacities at equilibrium and at time t , respectively (mg g^{-1}) and k_1 (min^{-1}) is the rate constant. The equation pertinent to experimental data usually fluctuates from a true first order equation in two ways: (i) the parameter $\log(q_e - q_t)$ does not symbolize the number of accessible places and (ii) the parameter $\log(q_e)$ is an adaptable parameter and frequently it is found not equal to the intercept of a plot of $\log(q_e - q_t)$ against t , while in a true first order $\log(q_e)$ should be equal to the intercept of a plot of $\log(q_e - q_t)$ against t . So as to fit the pseudo-first order equation to experimental results, the equilibrium capacity, q_e must be known.

On the other hand, if the rate of degradation is a second-order mechanism, the pseudo-second order kinetic rate equation is expressed as:

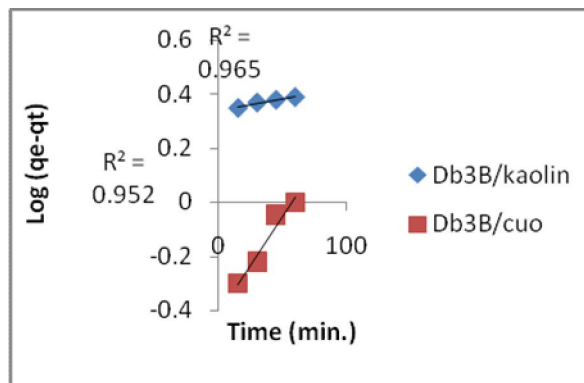
$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$

Where q_e and q_t are the sorption capacities at equilibrium and at time t , respectively (mg g^{-1}) and k is the rate constant of pseudo-second order reaction ($\text{g mg}^{-1} \text{min}^{-1}$).

If pseudo-second-order kinetics are applicable, the plot of t/q_t against t should give a linear association, from which q_e and k_2 can be calculated from the slope and intercept of the plot.

Table 10: Photodegradation parameters of direct blue 3B on nanokaolin and nanocupper oxide

Dyes	Log (q _e -q _t)	T (min)
Db3B/kaolin	0.35	15
	0.37	30
	0.38	45
	0.39	60
Db3B/cupper	-0.301	15
	-0.221	30
	-0.045	45
	0	60

**Fig. (17):** The pseudo-first order for direct blue 3B on nanokaolin and nanocupper oxide

Conclusion

Heterogeneous photocatalysis using kaolin nanoparticles as photocatalyst was confirmed to be an efficient tool for the decomposition of direct blue 3B in its aqueous solution. The obtained data established that increasing the substrate level, short exposure period, and kaolin and nanocupper oxide dosage in a suitable range donated to the photocatalytic decomposition of direct blue 3B. The removal of the dye by adsorption on kaolin and cupper oxide nanoparticles was found to follow Freundlich isotherm model. The rate of photodegradation follows pseudo first order with a rate constant 2.94 and 25 min^{-1} for direct blue 3B with nanokaolin.

Recommendations

- The presence of azo-dyes compounds is a real challenge that has to be faced, it is recommended to eliminate those compounds using nanokaolin in wastewater treatment plants especially that are receiving industrial wastewater.

- Further studies can be done in the field of nano-size particles that can be used for elimination of similar industrial wastes.

- The idea of using natural products (cheap, available and non-toxic) in removal of pollutants from

water bodies has to be studied to reach what can be called a "green approach".

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