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Synthesis and Comparative Analysis of Metal-Doped TiO_2 Nanophotocatalysts for Textile Dye Removal from Wastewater

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ABSTRACT

The main cause of environmental pollution is industrial dye. The current study consists of the removal of Actacryl Green □-2□ dye by using batch study with photo catalyst and adsorption technology. The nanophotocatalysts were prepared by using sol gel method. At pH 10, Co/TiO2 and Cu/TiO2 maximum result in the removal of cationic dye. In contrast, Zn/TiO2 and TiO2 nanoparticles show maximum results at pH 6,8 respectively. The optimum dose for all kind of nanaophotocatalysts, Co/TiO2, Cu/TiO2, Zn/TiO2 and TiO2 was found to be 0.05g for the degradation of Actacryl Green □-2□ dye. The initial concentration of dye from 5 to 100 mL was recorded that higher absorption arise at 50 mL by all types of nanoparticles like TiO2 (23.892), Cu/TiO2 (21.213), Co/TiO2 (20.102), and Zn/TiO2 (22.654) respectively for the removal of Actacryl Green □-2□ dye. By varying temperature range from 35-65 °C higher absorption arises at 51 °C for the all type of nanophotocatalyst, TiO2 (23.998), Cu/TiO2 (21.765), Co/TiO2 (20.987), and Zn/TiO2 (22.867) correspondingly for the removal of cationic dye. The change in temperature was a physio-chemical process and endothermic process in which with raise in temperature the adsorption capability was increased. Pseudo-2nd order model fit having kinetic data, whereas the Langmuir model was best fit on equilibrium bio sorption data. Moreover, data show that removal of reactive green dye by adsorption with TiO2, Cu/TiO2, Co/TiO2, and Zn/TiO2 nanoparticles followed second-order kinetic (R^2 = 0.9518) and Langmuir model (0.9928). Fourier transform Infrared (FTIR) was used to characterized the nanophoto catalysts, that provide information about functional group of dye. So by using adsorption technology, the maximum degradation of dye from wastewater was detected, and TiO2 showed maximum percentage removal of cationic dye. Reactive green dye is effectively degraded in aqueous solution by catalysis with TiO2 though being exposed to sunlight.

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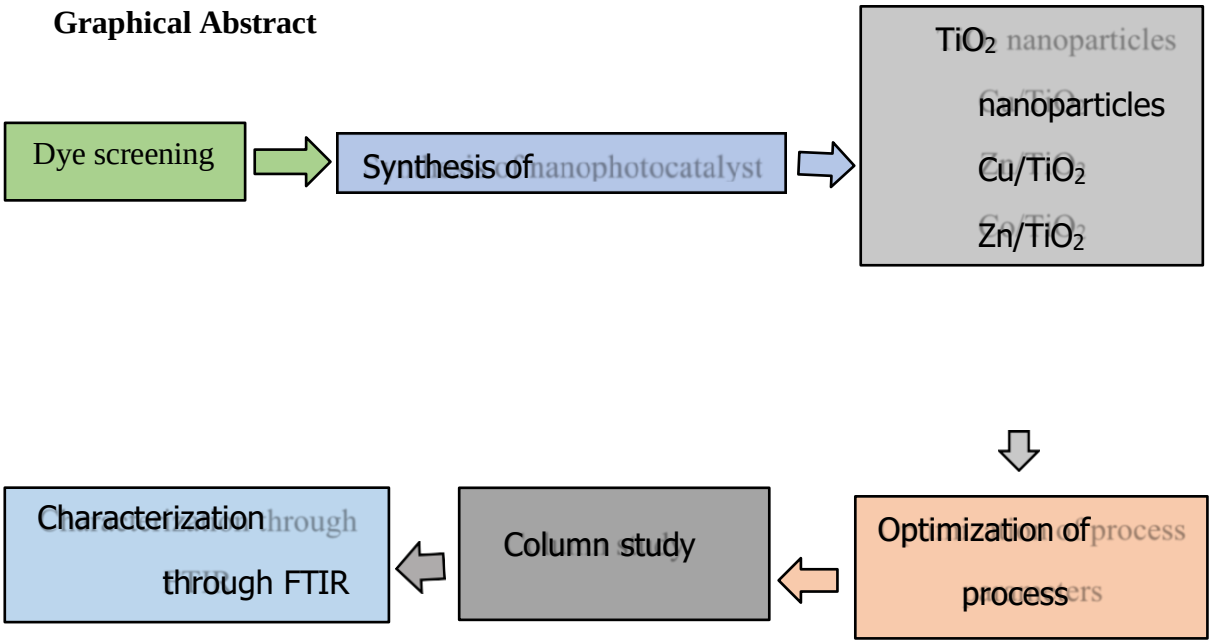
Graphical Abstract



Keywords: Nanophotocatalyst, catalysis, adsorption and desorption, Reactive Actacryl Green
□-2□ dye.

Introduction

One of the major issue is to control the environmental pollution almost for each country. There is various pollution of environment like noise, air, land, and waste water pollution but least one is more important. The burning of forest and vehicles mostly result from the openly smoke will be the air pollution while native sewage and waste of industries cause the wastewater contamination (Vidal, Ruiz et al. 2020).

Water is more necessary for the nature and is a universal solvent on earth. Entirely for the all life cycle it is chemically vital in the atmosphere. So the consequences of this for whole world and humanoid is specials. The human being hardly alive three days without drinking of water but can withstand by the short of foods in forty days. So due to these reason water is also called as "fluid of life". Water is used in many insistences like washing, irrigation, drinking and in industries for so many purposes (Rosenthal, Cao et al. 2020). Currently with fast growth of industries and society cause many problems of environment mainly water pollution has grown into one of the highest regarding issues in the whole world (Yosefi and Haghighi 2018). Development in world population the need of fresh water is increasing, and now a day's water recycle from civil waste treatment is feasible by both technical and economical point of view (Black, Adger et al. 2011). Water pollution is also increasing by the extensive use of the herbicides chemicals and entrance of that

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items into the animals and humans food chain causing severe health exposure, so water for drinking commonly challenging to assess (Anjaneyulu, Sreedhara Chary et al. 2005)

Dyes and toxic metal such as, chromium causing main water pollution due to the more use in leather, electroplating, paints industries. In broad, hexavalent usage of chromium is high effective hundred times as compared to chromium trivalent, and thus causing cancer in the lungs and digestive system and nausea. So there is need to remove these toxic material from the water by using some cheap reliable methods before discharging them into rivers and streams (Asahi, Morikawa et al. 2001). Many methods such as ion exchanger, reverse osmosis, chemical and electrochemical, adsorption and biological processes are used to remove the nitrate but due to their limitation less efficiency excellent cost their uses are restricted. Adsorption processes is costlier and widely used to remove of the contamination but due to their high rat some economical methods are demanding (Kiwaan, Atwee et al. 2019). About 700,000 tons of the 100,000 commercial dyes are effluents each year's so there needs several methods to degrade in the presence of sunlight (Huang, Mensi et al. 2019).

Nanotechnology having tremendous progress in the environmental and past decade. Nanomaterial due to their minor size, high surface area, good reactivity enables them able to use as reducing agent as well as adsorbent and as degradation for the removal of the dyes in the wastewater
treatment(Tiwari, Sellamuthu et al. 2017). Nano photo catalyst have benefit such as nano scale range (1-100 nm) lower is 1 nm and extreme value is 100 nm, energy band gap, physical stable, make them excellent to degrade the pollutants from the water (Nazir, Khan et al. 2020). Deferent semiconductor like TiO_2, Zn/TiO_2 and Fe/TiO_2 used to degrade wastewater treatment.TiO_2 has been relayed and considered extensively earlier it has been deliberated as one of best operative photo catalysts for the deprivation of carbon-based pollutants, due to its long exposure thermodynamic strength and comparative non toxicity (Bethi, Sonawane et al. 2016).

Degradation of dyes or organic pollutants is mostly performed by the TiO_2 instead of ZnO because of 3.0-3.2 eV of band gap. Although the price of ZnO is not high and upper photo catalytic competence than TiO_2 but due to temperature/environmental resistance make their application in degradation of organic pollutants are restricted. Binary of TiO_2/ZnO catalyst have advantageous that increase the value to degrade chemicals (Ghanbari, Salavati- Niasari et al. 2014). However, TiO_2 can be agitated merely by UV through a wavelength subordinate than 387.5 nm, that accounts for lower 7% than that of solar light and has a giant bandgap greater than
3.2 eV (Dlamini, Dlamini et al. 2022). TiO_2 as heterogeneous nano photo catalyst having many qualities that make them more superior abilities than the other materials, (a) high proficiency, (b) non-toxicity, (c) lower cost all of these properties smart it for the degradation of the dyes that is organic pollutant in wastewater treatment. Doping of TiO_2 with metal as well as nonmetal modified it
for efficient photo degradation. Merits of doping with metal are of following:

Decrease the band gap
Generate potentials trap for electron hole pairs

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Response of light expand, of TiO_2.

Due to all of these point doping has advantage than non-doping. TiO_2 as visible light to pledge catalysis (Tatarenko, Tatarenko et al. 2018). Under UV radiation, in an electrochemical cell for dissociation of water the electrode of titanium dioxide is widely offering for its huge application . TiO_2, is the most efficient photoactive material due to effective cost, high chemical stability and oxidizing ability (Sharma, Devi et al. 2023).

Table 2 Optimization of experimental process parameters

Types of materials/Nano photo catalyst	Techniques	Types of waste water	Optimizing parameter	References
B-ZnO/TiO2	Degradation	DR16	pH 3, 100% efficiency rate100%	(Habeeb, Zinatizadeh et al. 2023)
ZnO-Ce	Degradation	Reactive red 198	Temperature 40 C, concentration 3.18g/l, dose 0.16g/L, PH 6.5.	(Moslehnejad, Jahangiri et al. 2022)
ZnO/CuO	photodegradation	RhB	Contact time 60 mint, degradation efficiency 98%	(Siddiqui, Ansari et al. 2021)
MgO	Degradation	Alizarin red S	Time 20 mint, efficiency 80%,	(Kaur, Sharma et al. 2020)
ZnO/CuO/CNT	Degradation	Rhodamine 6 G	Concentration of initial dye 2.0 mg/L, Less than 9 pH 80 time	(Saravanakkumar, Abou Oualid et al. 2019)
ZnO	Degradation	AY23 (Acid Yellow 23)	Concentration 20 mg/L, pH 3, Ag doped, 30 time	(Aghdasi and Shokri 2016)
TiO2 and ZnO	Photo degradation	Acridine orange (AO)	10 mg /L concentration, pH 5 > 7, time 15 mints, 91.8 % removal of dye	(Chang, Huang et al. 2015)
Ce co-doped Ag–ZnO	Degradation	commercial azo NBB dye	2 _10^{-4} mol L_1 concentration, pH 9, Ce and Ag doping, 10 and 20 mints, 98.4% removal	(Spadavecchia 2013)
AgBr–ZnO	Degradation	Black Acid 1	2–5 _ 10_4 M dye	(Liu, Xie et al.

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			concentration, pH = 12	2011)
			Silver doped, 80 mints contact time, 94.9elemination power	
Titanium dioxide	Degradation	Removal of pathogen, E. coli in drinking water	0.05mg/g, time 120, 89 degradaion efficiency	(Mak, Lee et al. 2010)
(polymer coated nanoscale zerovalent iron) PNZVI	Degradation	trichloroethylene (TCE)	Concentration 5mg/L, pH= 3**,** time 60, 90 % degradation efficiency.	(Motornov, Roiter et al. 2010)
zinc sulfide	Degradation	safranin	5.0 mg/L concentration**,** alkaline pH = 11**,** doped with Nickel, 87–95 and 85 to 93	(Karamanoli 2009)
TiO2	Degradation	volatile organic molecules (VOCs)	Concentration 0.04 mg/g, pH < 8, contact time76	(Yu and Yu 2008)
Ag doped TiO2	Degradation	Direct Red 23	1 to 8 × 10^{-4} mol/L initial dye concentration, pH from 4 to 6**,** doped by Silver, 120 mints Excellent removal efficency	(Sobana, Selvam et al. 2008)
Nitrogen-doped TiO2	Degradation	rhodamine B	Concentration 0.02 g/L, pH >9, doping with Nitrogen 45 time, 92.3 degradation percentage	(Cong, Zhang et al. 2007)

Materials and Methods

Preparation of nanophotocatalyst

Materials

All the reagents and chemicals were of analytical grades used in current study and mostly obtained from the laboratory and chemical store superbright materials and nano technology
department of chemistry, university of agriculture

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Faisalabad. There have been different chemicals that used in the synthesis of dopant titanium dioxide such as titanium tetraisopropoxide, CTAB (cetyl trimethylammonium bromide), NH_4OH, $[Zn(NO_3)_2.6H_2O]$, and $[Cu(NO_3)_2.3H_2O]$, $[Co(NO_3).6H_2O]$ and Actacryl green □-2□ dye. Distilled Water Apply Through-Out Experiment. Washing and cleaning of all the necessary tools was initial step of this process.

Synthesis of Titanium Dioxide Nanoparticles

The synthesis of titanium dioxide nanoparticles can be done by sol gel method by using different chemical and reagents. 16 mL of titanium isopropoxide in 100 mL of measuring cylinder and then transferred into 250 mL neat and clean beaker. Then measured 30 mL of distilled water and transferred into the beaker that containing the required titanium isopropoxide in beaker. This content was stirred on magnetic stirrer for 30 mint until the mixture was cleared. The cetyl trimethyl ammonium bromide of 3 g measured on weighing balance and tranfrerd into an other hygienic beaker of 500 mL and added 20 mL of distilled water and then finely stirred on stirrer for 10 min till the solution was perfect clear. The liquefied CTAB and titanium isopropoxide solution was mixed together in a beaker. Then added few drops of ammonium hydroxide with the help of burette into the beaker contain both solutions of the required quantity. After the addition of NH_4OH the contents again stirred for 2 hours on magnetic stirrer. As the time completed for stirring of approximately 2 h the solution of CTAB and titanium isopropoxide was filtered on watsman filter paper. The liquid was obtained below the flask bottomed and residue obtained on the funnel. The precipitates that were obtained on the watsman paper was washed with distill water for just about in 15 to 20 mins. Afterwards sufficent washing the precipetate were dried in hot air oven for 5 h at temperature of 90 _C. Then the reqiured product was calcinated in furnace at 400_C for 3 hours.

The nanoparticles of pure titanium dioxide was obtained after the process of the calcination.

Doping of titanium dioxide with Zinc

The doping of titanium dioxide nanoparticle was done by adding 1 wt percent of zinc nitrate hexahydrate $[Zn(NO_3)_2.6H_2O]$. First weighed 3 g and 1 g of CTAB ($C_{19}H_{42}BrN$) and $[Zn(NO_3)_2.6H_2O]$ and dissolved in 20 and 100 mL of distill water. The former solution was stirred on magnetic stirrer for 10 to 15 mints. similarly, the solution of titanium tetraisopropxide was made in separate 500 mL clean beaker and stirrer for 30 min till contents were clear. Then by mixing both of solutions, the solution of zinc was added into above mixtures added then the required quantity of ammonium hydroxide [NH_4OH] drops wise with the help of dropper add it. As all mix then again stirrer for 2 h and filter, dry in oven at hot air for 5 hours and finally calcined residues in furnace. The doped Zn/TiO_2 was resulted in powder form.

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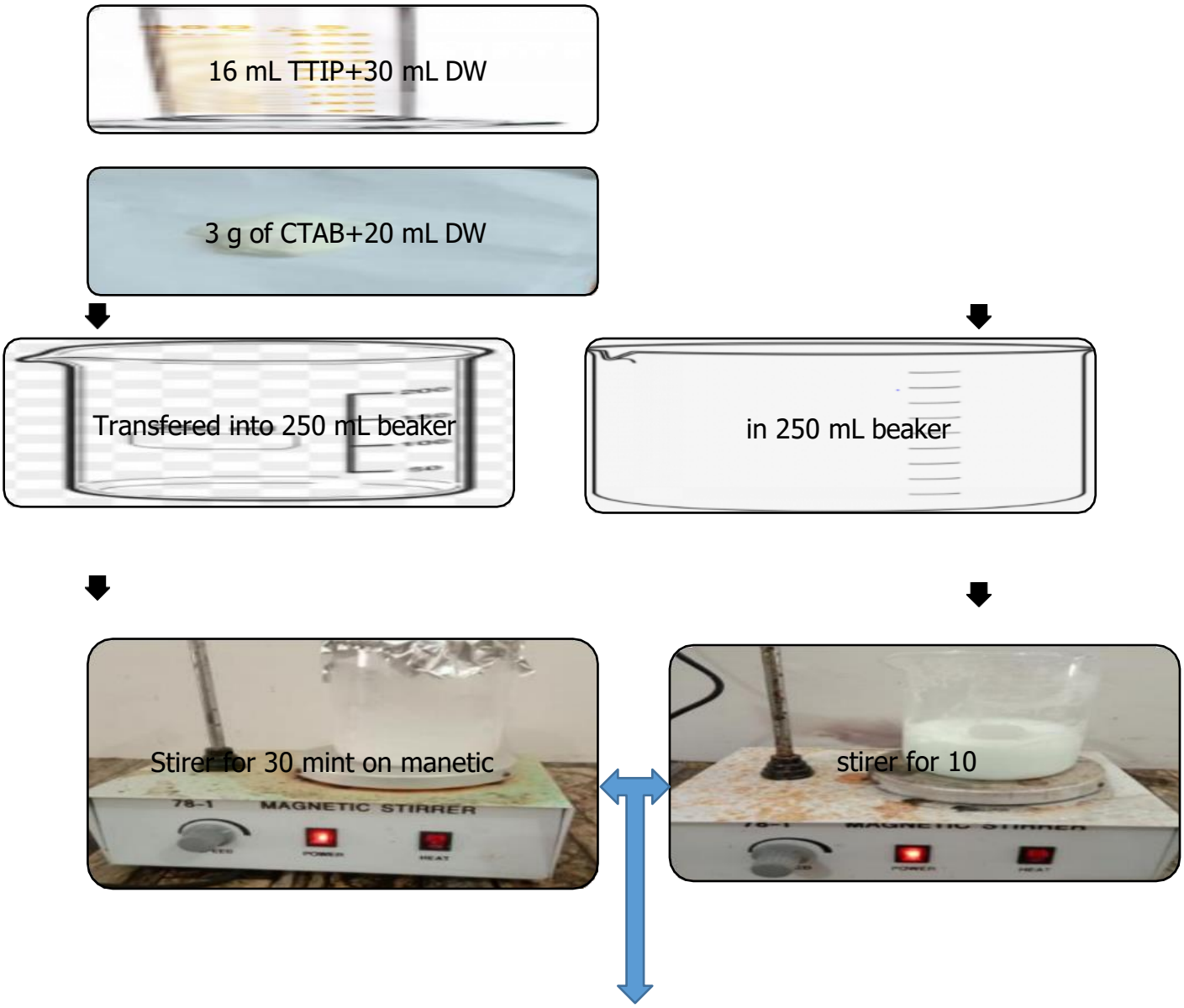
Doping of titanium dioxide with Cu and Co and their preparation

The 1 g of each copper nitrate trihydrate [$Cu(NO_3).3H_2O$] and cobalt nitrate hexahydrate [$Co(NO_3)_2.6H_2O$] was dissolved in 100 mL of distills H_2O and prepared the solution of 1 wt % of copper and cobalt. The procedures were same as used for the preparation of dopant Zn/TiO_2.The same stirred, drying, and calcination done as above case so after the calcination in furnace the doped Cu/TiO_2 and Co/TiO_2 was prepared by this method.



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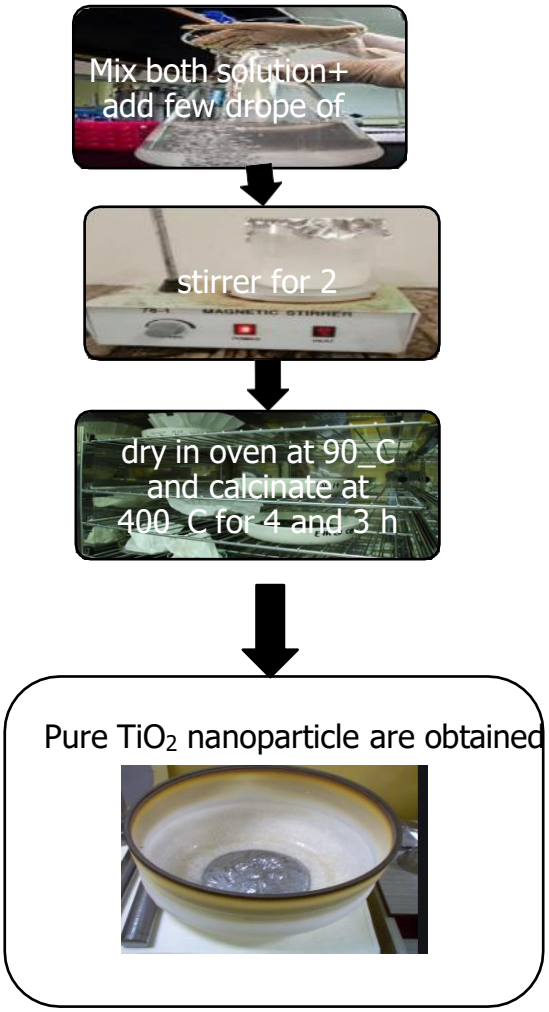

Result and Discussion

Effect of pH

The activity of nanophotocatalyst to exclude dye from wastewater is checked by the pH parameter so its importance is excellent. The pH can define as acidity or basicity measured in aqueous media. pH alternates have a great influence on ionic form and external property and of numerous nanophotoatalyst in solution of dyes. The pH solution affect not only on solubility of dye although on surface of sorbent (Bae, Kim et al. 2017). The nanophotocatalyst activity and as well as rate greatly influenced by pH. The pH varied from 2 to 12 of (cationic dyes) in present tentative study. The color change lightly at basic pH. The effect of pH on the titanium dioxide (TiO_2) and their doping with (Cu/TiO_2, Co/TiO_2, Zn/TiO_2) were synthesized by different chemicals via sol gel method and was examined to operate under experimental environment likes nano photo catalyst dosage 0.05mg/50ml, 25mg/50ml of the dye solution initially at 30-degree temperature, while shaking speed was 120 rpm and the contact time was 90 min. The 0.1 M NaOH and 0.1 M HCl was used to maintain the pH of solution. The results were given in the fig 3.1.

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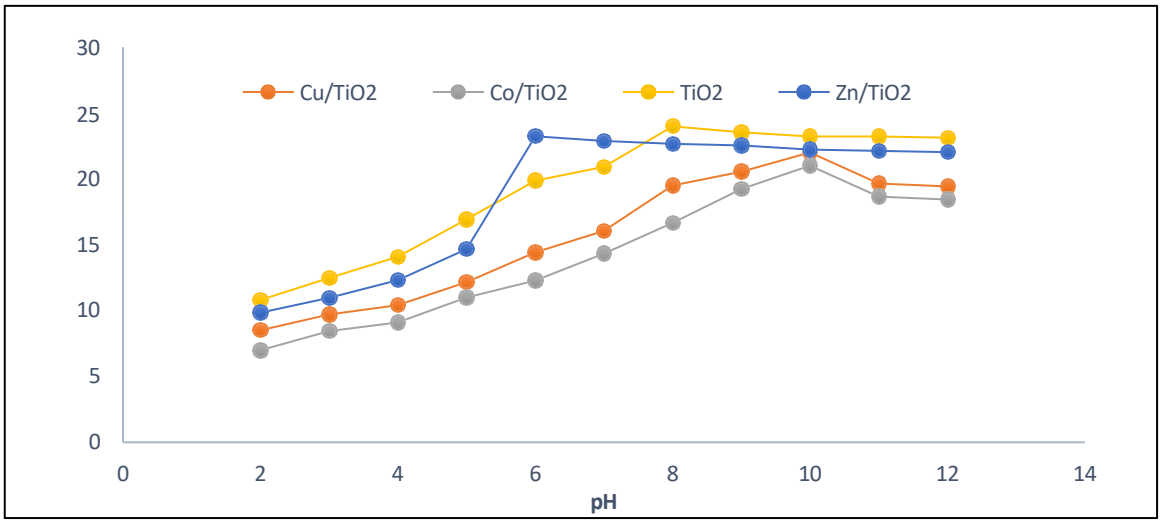

Figure 1 Effects of pH by different dopant nanophotocatalyst

Conditions: Catalyst dose 0.05g/50 mL, 30°C temperature, shaking speed 120 rpm and contact time 90 mins The above result showed that variation ability of biosorption of different dopant nanophotocatalyst for Acatcryl Green dye in solution aqua with alter the pH range from 2-12 by operating at constant condition (0.05g/25 mL catalyst dosage), 120 rpm and 30 °C shaking speed and temperature for 90 min. The cationic dye removal was obtained in basic and slightly acidic environment in (6, 8 and 10) for different catalyst that is optimum pH. To obtain maximum absorption capacity the optimum pH for Co/TiO_2, Cu/TiO_2, Zn/TiO_2 and TiO_2 were found to be 10(21.003), 10(22.01), 6(23.231), 8(23.987) respectively. At pH 10, Co/TiO_2 and Cu/TiO_2 were shows maximum result in the removal of reactive cationic dye At the same time Zn/TiO_2 shows maximum removal at pH 6 while TiO_2 maximum adsorption of dye result at pH 8. The major reason to produce more charge +Ve o to the surface of biosorbant because the deprotonation functionally group in basic media that show more attraction with dye molecules (Haghighi, Rahmani et al. 2016). The lower absorption capacity at for catalyst under acidic environment was due to the protonation of binding surface functional groups and that signify electrostatic force of attraction with cation dye (Aslam, Ismail et al. 2014).

The effect of the photo degradation for cationic (MG and CV) and anionic (phenol and MXR) dyes were observed in both acidic as well as basic media. The titanium act as positive and negative charge surface in acid and basic media (Wang, Yi et al. 2012). As at higher pH range the surface of titanium dioxide become negative and as result repel the anionic dye while in case of the lower range of pH its surface showed positive charge and result in strong electrostatic force of attraction among the catalyst and anionic dye. The TiO_2 surface at basic values show more degradation for malachit green as a catioinic dye due to attraction between both was stronger (Singh, Jabbour et al. 2012).

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Effect of catalyst dose

The dose of nanophotocatalyst plays an important role in degradation of dye. This factor is also significant because it decides the capacity of photo catalyst under operating suitable conditions (Sadaf, Bhatti et al. 2014). The dose of catalyst varied from 0.05, 0.1, and 0.2 to onward 0.7 g/25 mL of different nanocatlyst to exclude dye under optimum working condition pH, 6, 10, 8, 25 mg/250mL, time 90 min, temperature 30 ^{o}C, 120 rpm shaking speed. The result is given in the figure 3.2.

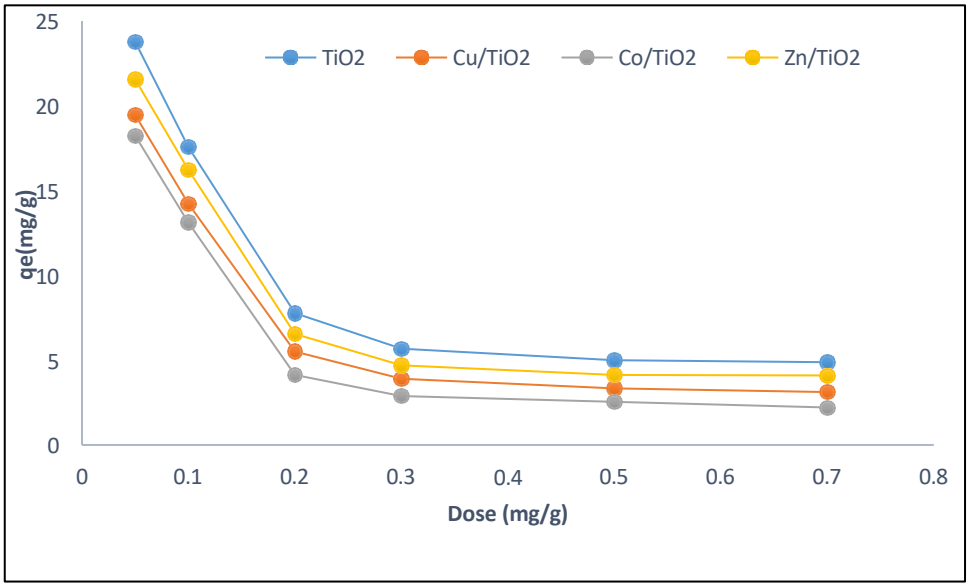

Figure 2. Dosage effect on catiomic dye at various conditions

Conditions: Optimum pH different, 120 rpm shaking speed, contact time 90 min, Temperature 25°C

The above results show actions of the sorption capacity of the dopant and pure titanium dioxide nanophotocatalyst under varying concentration of catalyst dosge from 0.05 to 0.7 g in keeping other parameters constant. The given results that come after the experiment showed that higher absorption arise at

initial concentration by the all type of nanophotocatalyst as well as their dopant agents like TiO_2 (23.76), Cu/TiO_2 (19.45), Co/TiO_2 (18.23), and Zn/TiO_2 (21.55). So the optimum dose for each nanocatalyst was 0.05g (Cavalcante, Dantas et al. 2016) . The capacity of sorption decrease gradually from 0.05 to 0.2 further decline was slow and then next become constant as no increase more with increase in dose amount. The reason for such behavior was due to the binding surface present at extreme initially for the molecule of the dye to attach and additional reach at value of constant. This one is obviously showed that dye removal did not reliant on increasing the catalyst

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dose but although on the functional group and surface area accessibility (Castro, Cavalcante et al. 2016). The degradation rate also increased by increasing the arability of the catalytic site. The lower sorption of the nanoparticle for the dye was also seen by one more factor as the dose increased it would overlap on the surface of cationic dye and shortened solute uptake so not degrade the dye efficiently (Siahpoosh and Soleimani 2017).

The maximum removal of Malachite Green by using TiO_2, 1% S-doped TiO_2 was observed at around 50 mg of optimum dose, as the dose increased above from this value catalytic efficiency decreased because of the more possibility of agglomeration no enter of solar light for effective photo catalytic proficiency (Schreiber Jr, Russell et al. 2006)

Effect of time

The time needed for the degradation of dyes is defined as the contact time by the help of nanophotocatalyst. This time of contact be measured by the percentage of dye removal verses contact time. This is very important for the application and calculating point of for degradation system as it time dependent parameter (Haider, Bukhari et al. 2012). The contact time was 90 min, the nano catalyst examined by performance of the batch experimentation for degradation process.

On the way to explore the influence of interaction time of diverse nanophotocatalyst (TiO_2, Zn/TiO_2, Co/TiO_2, Cu/TiO_2,) on degradation of cationic dye in best surroundings of pH, 6, 8, 10 dose of 0.05g, quivering 120 rpm speed, 25 mg/L solution of dye concentration, temperature 30°C

in performance parameter contact period variable as of 4-120 minutes. Results are shown in fig 3.3.

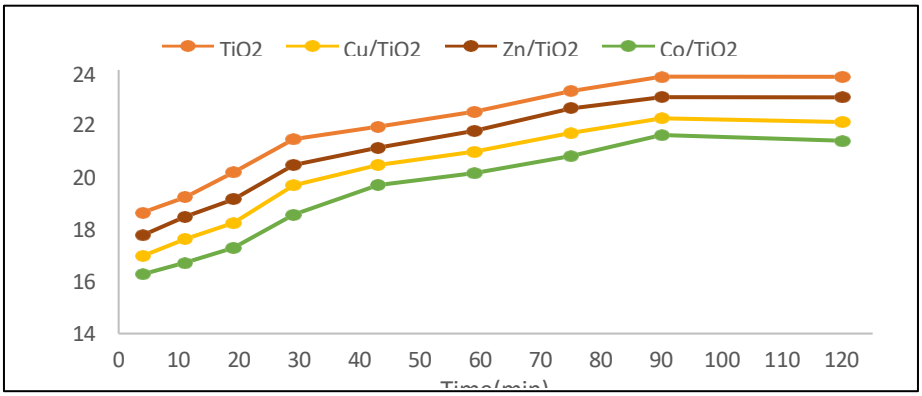

Figure 3. Effect of time on Actacryl green □-2□ dye using different nanophotocatalyst

Conditions: Optimum pH different, shaking speed 120 rpm, Temperature 30 °C and 0.05 g catalyst dose The above results shown that degradation of catatonic dye through different nanophotocatalyst were very rapid in first 50 to 90 min and then slow down and attain equilibrium in 120 min. The maximum absorption ability for pure and

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dopant nanophotocatalyst TiO_2 (23.64), Cu/TiO_2 (21.431), Co/TiO_2 (20.543), and Zn/TiO_2 (22.561) correspondingly attained and then achieved equilibrium. At 90 min time maximum dye adsorption capacity was observed and this time was taken as a contact time. One of the major reason for the no increase in the removal of dye by the raise in contact time may be due to the no availability of the more active binding functional site and slow uptake of the sorbate as result it attain equilibrium after 90 min (Wazir 2015).

The effect of time on the exclusion of MO (methyl orange) was also checked by using powder of seeds pumpkin. The adsorption was high in 1 h and as shaking persist for long time equilibrium achieved after 120 min. As the equilibria attained no more adsorption result as there was no availability of collision among sorbent and sorbate to interact more.

(Aliabadi and Mahmoodi 2018) noted the contact time effect for Azo dye removal using polyaniline or polypyrrole nanoparticles was increased till 5 min and then equilibrium achieved. No further change in adsorption capacity was observed after equilibrium achievement. The adsorption rate was faster at the initial stage of reaction and then slows down after about 15 min to attain equilibrium. The maximum adsorption rate was detected due to big surface area which provides more active sites for attachment of dye molecules. The rate of adsorption was decreased at high contact time, this reduction in adsorption capacity was due to less surface area which reduces the active binding sites availability at saturation point and after that equilibrium achieved.

Effect of temperature

Textile industries frequently release their wastes at properly higher temperatures hence temperature can show a significant part in the biosorption procedures of dyes and it is also a significant parameter in making of sorption system for its appliances for real wastes. The effect of various course temperatures in the series of 35-65 ºC on the biosorption capability of various chosen biosorbents for the exclusion of cationic dye from industrial waste water was investigated on fixed experimental operating circumstances.

On the way to explore the influence of interaction temperature of diverse nanophotocatalyst (TiO_2, Zn/TiO_2, Co/TiO_2, Cu/TiO_2,) on degradation of cationic dye in best surroundings of pH, 6, 8, 10, dose of 0.05g/25ml, quivering 120 rpm speed, 25 mg/L solution of dye concentration, time 90 min. Results are shown in fig 3.4.

qe(mg/g)

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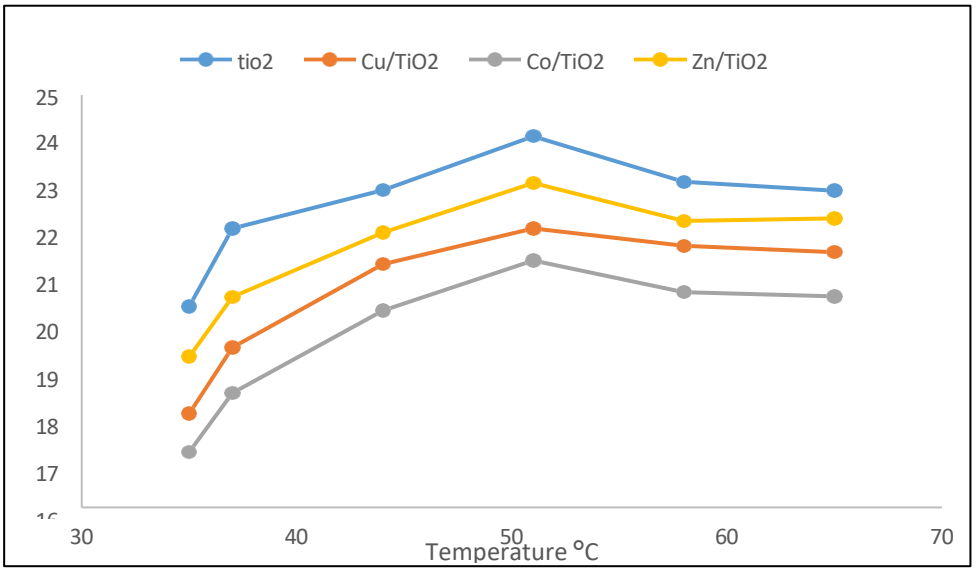

Figure 4. Effect of temperature on Actacryl green □-2□ dye using different nanophotocatalyst

Conditions: Optimum pH, 0.05g biosorbent dose, 120 rpm shaking speed, equilibrium time, 90 mint, 25 mg/L initial dye concentration

The above results show actions of the sorption capacity of the dopant and pure titanium dioxide nanophotocatalyst under varying temperature range from 35-65 °C in keeping other parameters constant. The given results that come after the experiment showed that higher absorption arise at 51 °C by the all type of nanophotocatalyst as well as their dopant agents like TiO_2 (23.998), Cu/TiO_2 (21.765), Co/TiO_2 (20.987), and Zn/TiO_2 (22.867) respectively for the removal of Actacryl Green □-2□ dye. The above graphs showing the result of change in temperature on the biosorption ability of adsorbent. It is clear from graphs as the temperature is increased the removal of dye increased which shows that the process of degradation of dye is endothermic. Maximum sorption capacity for all type of catalyst was observed at 51 °C. The change in

temperature was a physio-chemical process and endothermic process in which with raise in temperature the adsorption capability was increased. The raise in temperature raises the mobility of molecules of dye and more chances to adsorb on catalyst active sites. Whereas an increase in temperature decreases the adsorption capacity which shows that adsorption reaction was an exothermic process. As a result, adsorptive forces between active sites and dye molecules/species decrease the adsorption on catalyst surface by increasing temperature. As the temperature raise above 51 degree the reduction in absorption result because the failure of sorption force that was necessary for the adsorption of dye molecule on catalyst surface (Asgher and Bhatti 2012). The second reason for such behavior may be deactivation of surface actively binding site at high temperature that lead the poor bio sorption efficiency. The effect of the temperature by peanut shell for the exclusion of brilliant green dye from media

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by raised in temperature from 11 to 61 degree resulted in decrease of the adsorption capacity that is an exothermic nature (Aziz, Abbas et al. 2012).

Effect of the initial dye concentration

The sorption ability of nanocatalyst is dependent on initial concentration of dye solution. This experiment was performed to measure the effect by changing the concentrations of dye from 5-100 mg/L on adsorption capacity of nanophotoctalyst for removal of cationic dye from wastewater under optimum condition of pH 6, 8 and 10, 90 min contact time,0.05 g/25 mL dose, 30°C temperature and 120 rpm shaking speed. The obtained results are shown in Fig. 3.5.

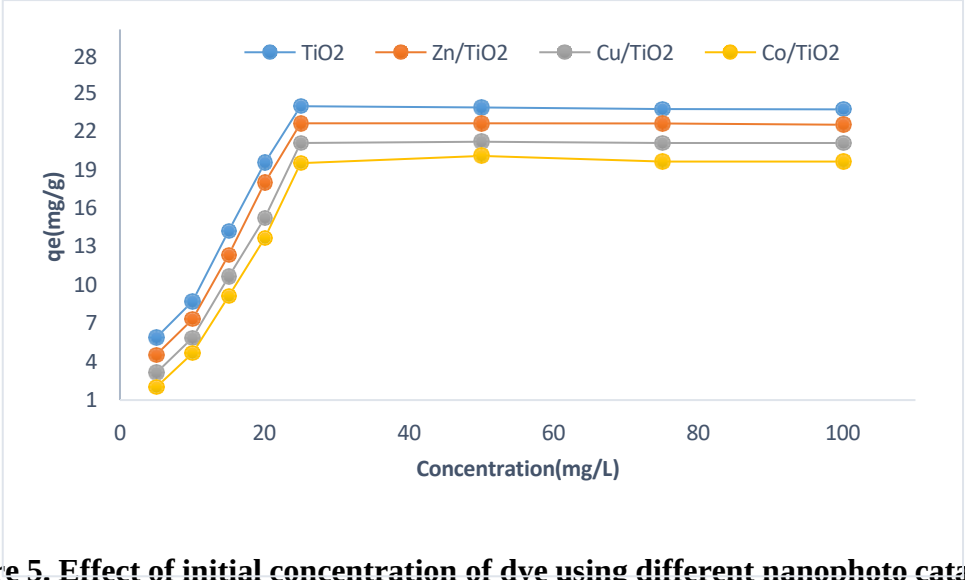

Figure 5. Effect of initial concentration of dye using different nanophoto catalyst

Condition: Shaking speed 120 rpm, time 90 min, and effect of initial dye concentration with different catalyst The above results show actions of the sorption capacity of the dopant and pure titanium dioxide nanophotocatalyst under varying initial concentration of dye from 5 to 100 mL in keeping other parameters constant. The given results that come after the experiment showed that higher absorption arise at 50 mL by

the all type of nanophotocatalyst as well as their dopant agents like TiO_2 (23.892), Cu/TiO_2 (21.213), Co/TiO_2 (20.102), and Zn/TiO_2 (22.654) respectively for the removal of Actacryl Green □-2□ dye. The given result represents that adsorption efficiency increase rapidly till 50 mL then attain equilibrium.

The reason behind above mentioned results is, the initial concentration of dye provides significant forces to reduce the resistance in mass transfer among two phases and to attain equilibrium between catalyst surface and concentration of dye. (Fayoud, Tahiri et al. 2016) showed initial concentration effect on eosin blue (EB) dye solution by changing dye concentration from 5-25 mg/L at fixed dose of Zr loaded rGO catalyst. The results clearly showed that the speed of removal was improved by

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increasing concentration of dye in solution from 5-20 mg/L and remains constant with further raising the dye concentration. This effect was observed as the amount of active sites on the catalyst surface covered by the more availability of dye molecules which retarded OH radical's generation on catalyst surface which leads to saturation limit. Beyond saturation limit molecules of dye was not completely adsorbed on catalyst surface due to the unavailability of active sites on the surface of catalyst.
(Yagub, Sen et al. 2012) present the same consequences of the initial dye concentration on the adsorbent capability to exclude methylene blue. The same result presented as the initial concentration of the dye increased from 5 to 60mg/L the absorption ability raised from 33.2 to 123.8 mg/g and next equilibrium attained by the overcome of the dynamic balance between adsorbent surface and concentration of dye respectively. (Patil, Shedbalkar et al. 2016) reported that the prepared nanoparticles were used for the removal of BG dye solutions prepared at different concentrations (50 to 90 mg L−1). Each study was subjected to a runtime of 180 min. For 0.025 g, the removal rate gradually increased and attained a maximum value of 19.30, 24.7 and 25.13% at concentrations 50, 60 and 70 mg L−1 respectively. Upon ionization, the active sites are created in the form of negative charges on the peripheral of the PAPE and the dye molecules become positively charged. Due to electrostatic interaction, the dye molecules are adsorbed onto the surface of the nanoparticles until the critical level is reached. It is observed that, on increasing the dye concentration (80 and 90 mg L−1), the removal capacity of the nanoparticles decreased and the final residual concentration of the dye increased. This inhibited tendency can be ascribed to the mitigation of active sites present over the surface of the nanoparticles. It is due to the larger surface area, active sites and increased pore density, 0.05 and 0.075 g of PAPE achieved significant dye removal capacity (50 and 60 mg L−1 of dye conc.). Moreover, for 0.05 g, a steady decrease is 53 observed in the removal rate at 70, 80 and 90 mg L−1 and for 0.075 g, there is a minimal decrease at 90 mg L−1. This is due to the lesser availability of active sites and lower driving force of the dye molecules from the solution to the surface of the nanoparticles at higher concentrations. However, the adsorption capacity of the nanoparticles increased with initial dye concentration due to the concentration gradient of the dye molecules between the solution and the adsorbent.

Effect of electrolytes on the biosorption of selected cationic dye

The productions of fabrics, large quantity of salts in different dyeing ways are used (Aksu and Balibek 2010). Therefore, the concentration of salt in textile wastes liquid is although an important parameter that is responsible for governing the both electrostatics and non-electrostatic relations among the dyes molecule and catalyst surface which distresses the efficiency of biosorbent for the removal of dye (Doğan, Abak et al. 2008). The presence of several concentrations and their effect (0.1-0.5M) of different salts (NaCl, $AlCl_3.6H_2O$) on the bio sorption use of chosen best effective catalyst (TiO_2, Zn/ TiO_2, Cu/ TiO_2 and Co/ TiO_2) for the elimination of carefully chosen cationic dye in optimal conditions was detected. The results are displayed in Fig. 3.6. The occurrence of salts be able to generate two kinds of effects. It can increase or decline in bio sorption capacity of catalyst. From certain values, it was

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determined that the adsorption possible of selected catalyst for the cationic dyes was reduced by the salt increasing amount and it can be owing to facts that the ionic salt separated by the electrostatically attraction between the contrary the charge of dyes particle and the presence of functional group on photocatalyst.
(Asgher and Bhatti 2010) also exposed the similar result of ionic ability on the exclusion of cationic dye by means of dead aerobic granulated sludge. As the decrease in adsorption budding was noticed by raising the electrolyte (NaCl) dosage from 0 to 3% in sorption experiment. The main decreasing in bio sorption ability from 17.87 -9.56 mg/g was observed as the NaCl concentration was raised as of 0 to 1 percent. After that, the increase in absorption starting 1- 4%, the minor decrease in bio sorption ability was examined. (Ngoh and Nawi 2016) moreover perceived the identical effect of NaCl onto adsorption efficacy seeds of dombiya willaichi for the elimination of reactive blue 41 from the waste of water. The effectiveness bio sorption of catalyst for reactive dye was diminished from 83.25 to 73.2 percent by improving the NaCl concentration as of 0.01 to 0.1 mol/L.

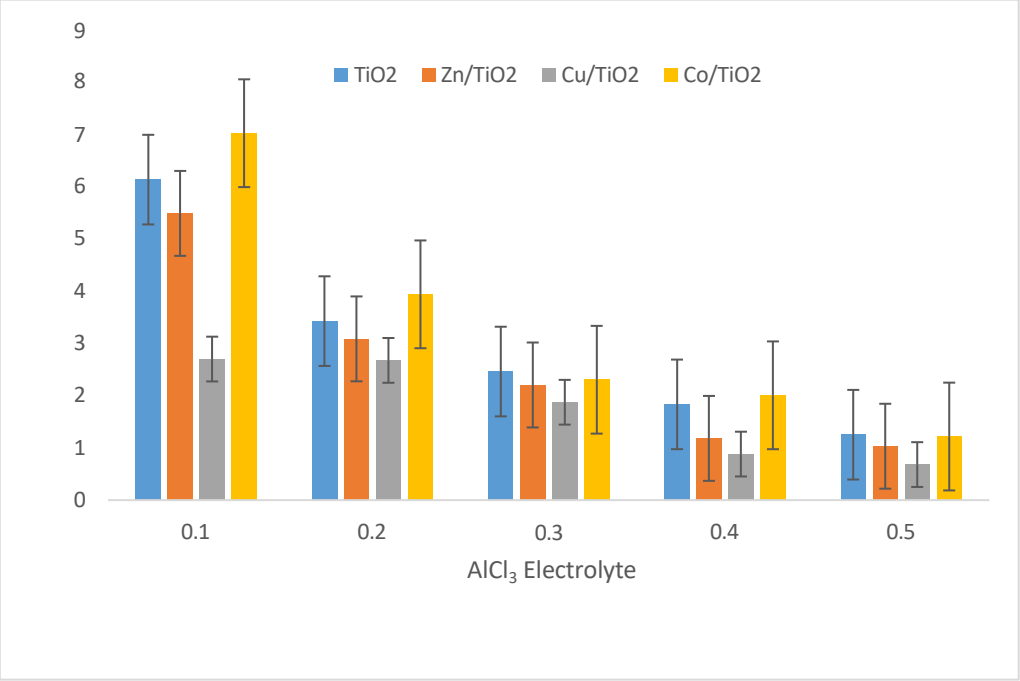

Figure 6. Effect of AlCl3 electrolytes at optimum conditions of pH, initial dye concetration, stirring time and 120 rpm speed for various nanoparticles TiO2 , Zn/TiO2, Cu/TiO2 and Co/TiO2 at optimum values of pH 6,8, and 10, 120 rpm shaker speed, , temperature 30 °C for 90 minutes.

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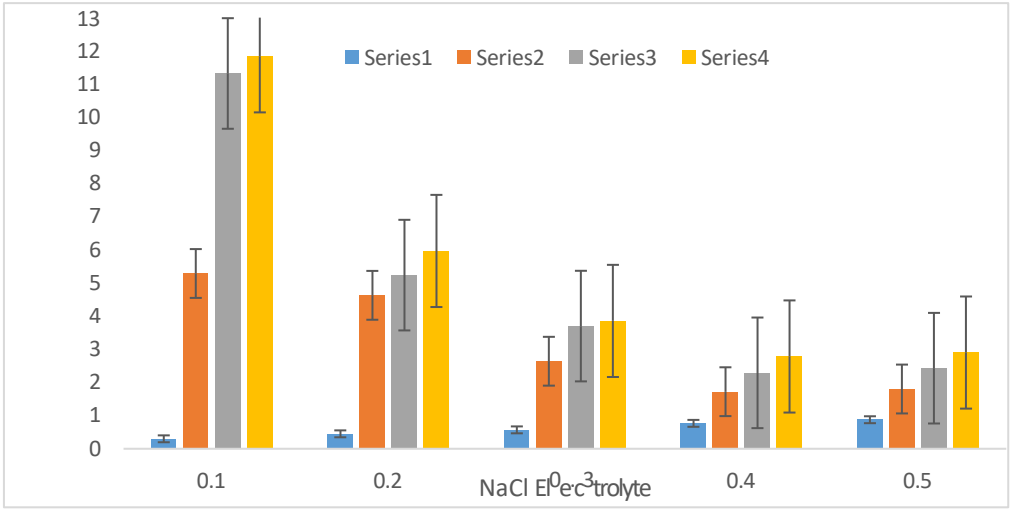

Figure 7. Figure 6. Effect of Nacl electrolytes at optimum conditions of pH, initial dye concetration, stirring time and 120 rpm speed for various nanoparticles TiO2 , Zn/TiO2, Cu/TiO2 and Co/TiO2 at optimum values of pH 6,8, and 10, 120 rpm shaker speed, temperature 30 °C for 90 minutes.

Effect of surfactants/detergents on the biosorption of acid dyes

The application of various surfactants and detergents in fabric industries is very communal during various process and the incidence in fabric wastewater also effects the biosorption effectiveness of biomass. The influence of 2% concentration of all these surfactants (SDS, CTAB and Triton X-100, Arial) and one detergent (Excel) on the biosorption proficiency of various biomass (TiO2, Zn/TiO2 and Cu/TiO2, Co/TiO2) for the actacryl green □-2□ dye from solution containing dye was examined respectively and results are written in Fig. 3.7. As of these results, it was observed that the bio sorption ability of Cu/TiO2, Co/TiO2 for reactive blue dye from dye containing was lessened meaningfully because of the occurrence of various surfactants and cleaners. The reason is that such decreasing could be the presence of opposition between the surfactants and the dye molecules for attaching to bio sorbent surface (Sadaf, Balal et al. 2024). The results indicated the weighty decrease in biosorption capability of all biosorbents for their cationic dye in the existence of an anionic surfactant, SDS. It could be due to construction of electrostatic repulsion between the molecules of SDS and dye anions.

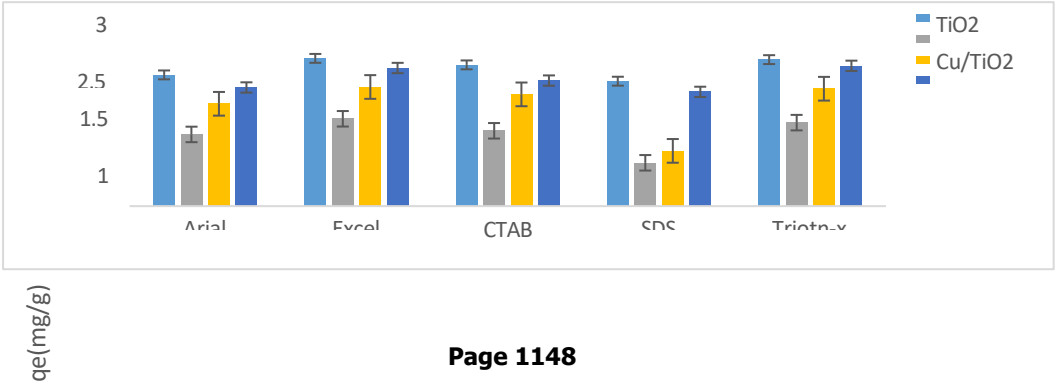

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Figure 8. Effect of surfactant at optimum conditions of pH, initial dye concentration, stirring time and 120 rpm speed for various nanoparticles TiO2 , Zn/TiO2, Cu/TiO2 and Co/TiO2 at optimum values of pH 6,8, and 10,120 rpm shaker speed, (0.05 g) dose, , temperature 30 °C for 90 minutes.

Kinetic studies

Sorption of kinetics, representative the uptakes of catalyst, is a chief characteristic that represent vital information about the pathways of reaction and their probable uses as well as application. For designing of any batch photo sorption system, the determination of absorption kinetics is very important stage. For the selection of optimum experimental operating parameters for large complete scale batch system, information about solute uptake kinetics is necessary. For the investigation of degradation mechanism and possible rate controlling steps like mass transfer and chemical processes, the applicability of different kinetic models such as pseudo-first-order, pseudo-second-order and intra particle diffusion have been checked to investigate the sorption experimental data of actacryl green dye using different types of photocatalyst.

Pseudo-first-order kinetic model

Pseudo-first-order kinetic model is appropriate for the investigation of liquid/solid degradation systems. According to pseudo-first-order kinetic model, the change in concentration of dye as function of time is directly proportional to the power one. The linear integrated equation of pseudo-first-order kinetic model is given as follow (Yuh-Shan 2004) .

$$Log\,(qe - qt) = logqe - \frac{k1.}{2.303}\,t \quad (1)$$

In this equation, t stands for the equilibrium time (mint), qt and qe show the photo degradation capability (mg/g) values at equilibrium and any time t correspondingly whereas the k1 stands for the pseudo first order rate constant (L/min). Both k1 and theoretical qe values were calculated from the slope and intercept by scheming the graph between log (qe - qt) and t respectively.

Pseudo-second-order kinetic model

The sorption mechanism for the whole range of contact time can be understood by the successful application of pseudo-second-order kinetic model (Ho and McKay 1999). The differential equation of pseudo- second-order is given as follows:

$$\frac{Dqt}{dt} = k2\,(qe - qt)2 \quad (2)$$

In this equation, k2 (g.mg-1.min-1) stands for the 2nd order rate constant of sorption

$$\left(\frac{t}{\ }\right) \quad \frac{1}{\ } \quad \frac{t}{\ }$$

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route. By integrating and the applying of boundary conditions, t=0 to t=t and q=0 to q=qt, the straight form of pseudo-second-order is shown as:

(3)

The second-order-rate constant value k2 (g.mg-1.min-1) and the theoretically calculated value qe (mg.g-1) can be calculated from the value of intercept and slope correspondingly by scheming the t/qt verses t. The k2 value, qe calculated, qe experimental and R2 for the subtraction of dye using various kinds of chosen catalyst are shown in Table 4.1

Intraparticle diffusion kinetic model

The degradation route of molecules of dye from waste water on the catalyst surface takes place in numerous phases. The intra particle diffusion route can be clear in three main phases for the degradation of
nanophotocatalyst particles on to the surface of nano catalyst. The first stage contains the transmission of sorbate molecules from bulk phase to catalyst outer side through molecular diffusion which is identified as film or surface diffusion. In second step, internal diffusion occurs in which the sorbate particles carriage to the internal locations from catalyst surface. The third step contains the interaction of catalyst molecules from internal location to interior pores surfaces. The general degradation process rate is measured by slow stage identified as rate determining step (Kumar and Ahmad 2011).

$$qt = kpit^{\frac{1}{2}} + ci \quad — \qquad (4)$$

In this equation, Ci specifies the thickness of boundary layer whereas the Kpi (mg/g min1/2) denotes the rate constant of intraparticle diffusion. Their values can be calculated from the value of intercept and slope by scheming the qt against t1/2 respectively. The Kpi, Ci and R2 values of bio sorption processes of cationic dye using various respective chosen nanophotocatalysts are given in Table 3.1.

Table 3.1 Kinetic modelling of experimental data obtained for dye removal using different nanoparticles

Kinetic Models	TiO2	Zn/TiO2	Cu/TiO2	Co/TiO2 Pseudo-1st order
k1 (L/min)	-0.0086	-0.0087	-0.0054	-0.0503
qe exp (mg/g)	23.6432	22.554	21.431	20.543
qe cal (mg/g)	14.9589	14.5044	8.3849	8.0649
R^2	0.8133			

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0.8180
0.9639 0.9628

Pseudo-2nd order

k2 (g/mg.min)	0.001963	1.28005	0.01278	1.2039
q_e exp (mg/g)	23.6432	22.554	21.431	20.543
q_e cal (mg/g)	24.5700	23.4748	18.1159	21.1864

R^2 0.9518
0.9977
0.9978 0.9972

Intraparticle diffusion

8.9575	8.9266	8.4921	8.6485

Kpi (mg/g.$min^{1/2}$) Ci

R^2
- 19.977

0.9994
-20.807

0.9984
-19.9 -21.592
0.9934 0.9993

The suitability of pseudo-1st order-kinetic model was not greatly better on the degradation courses of TiO_2, Zn/TiO_2, Cu/TiO_2 and Co/ TiO_2 and the suitability of pseudo-2nd-order kinetic model was far better on the kinetic data of first due to very close settlement between the experimental and calculated degradation capability values (mg/g). The intra particle diffusion model displayed the little suitability with smaller value of correlation coefficient (R2) for all applied catalyst for the removal of actacryl green dye.

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Absorption isotherms

The isotherm of absorption has important significance in the calculating of bio sorption systems and their facts showed the attraction among the molecules of dye and nanophotocatalyst and also give indication about mechanism bio sorption (Janaki, Sailatha et al. 2015). This isotherm represents the relation among the quantity of sorbate sorbed by unit amount of sorbent and rest amount of sorbate in test solution at constant temperature under investigational equilibrium circumstances (Rangabhashiyam, Anu et al. 2014). For the useful appliances of biosorption system, it's vital to do biosorption isotherm being studied on the base of several biosorptional isotherm models (Bettini, Della Foglia et al. 2015). The experimental equilibrium biosorption data can be examined using various biosorption isotherms such as Langmuir, Freundlich, Timken, Harkins–Jura and Doubinin-Radushkevich (D-R) and so on.

Langmuir bio sorption isotherm

According to Langmuir isotherm, the degradation of dye from waste water on the surface of bio sorbent that lie on the constant integer of binding active centers take place by monolayer growth and no further sorbate attach more on the active site after monolayer development. The linear equation of isotherm Langmuir is shown below as (Harter and Smith 1981).

$$\frac{Ce}{qe} = \frac{1}{qmb} + \frac{Ce}{qm} \quad (5)$$

In the above equation,

qm = (mg/g) is the maximum biosorption capability

b = (L/mg) Langmuir constant shows the biosorption energy Ce = (mg/L) stands for the at equilibrium sorbate concentration

RL = is of Langmuir biosorption isotherm another significant factor and can be calculated by using the equation (Herrmann, Disdier et al. 1981).

$$RL = \frac{1}{1+bc_{\circ}}$$

Here, RL is dimensionless constant also called as equilibrium or separation factor while Co and b represent the initial dye concentration and the Langmuir constant respectively. The RL value suggests the biosorption nature whether the bio sorption is favorable if 0<RL<1, if RL > 1 it will be unfavorable and RL is equal to 1 and zero showed the straight or irreversible respectively. The qm and b used to find the values of slope as well as intercept by scheming the graph between Ce and Ce/qe.

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Freundlich biosorption isotherm

According to Freundlich bio absorption isotherm, the biosorption proceeds via creation of multilayer which represent the different nature of the surface of bio sorbent, intact between the particles sorbed and imbalanced distribution of sorption heat on bio sorbent surface (Kumar and Porkodi 2006). The expression for Freundlich biosorption isotherm is shown below.

1

In above equation,

$$\boldsymbol{logqe} = \boldsymbol{logkF} + \frac{\boldsymbol{logCe}}{\boldsymbol{n}} \quad (6)$$

qe and Ce = biosorption capability (mg/g) and dye concentration (mg/L) at equilibrium KF = stands for Freundlich constant (mg1-(1/n) L/n g-1)

n = represents the biosorption intensity

The constants of Freundlich isotherm are empirical in nature and their value depends upon various environmental parameters (Rangabhashiyam et al., 2014). The anomaly of biosorption from the linearity can be achieved by the value of n (Arias and Sen 2009). The value of n=1 shows the linear biosorption and its value < unity indicate the chemical nature of adsorption process and its value > shows the positive adsorption procedure (Salleh and McMinn 2011). The KF and n values can be attained from the intercept and slope value by scheming the linear graph between the log qe versus log Ce correspondingly.

Temkin biosorption isotherm

This model consists of two assumptions the first consist of the heat of adsorption in layer of sorbate molecules decrease the linearity with the coverage of surface due to the interaction among the sorbent and sorbate. The second assumption mainly concern on the binding energy distribution on to the surface of biosorbant or catalyst binding site are uniform in nature (Temkin 1940).

The linear representation of the temkin biosorption isotherm is given below:

$$\boldsymbol{qe} = \boldsymbol{BlnA} + \boldsymbol{BlnCe} \quad (7)$$

In this equation, B=RT/b

R = show the universal gas constant (8.314 J mol-1 K-1), T = represent the absolute temperature (K)

b = show the Temkin bio sorption constant

A = symbolizes the Temkin equilibrium binding constant (L/mg)

B = the constant that is correlated to bio sorption hotness (J/mole)

The value of A and B can be obtained from the intercept and slope values by plotting the graph among the qe and ln Ce correspondingly.

Harkins–Jura biosorption isotherm

In this model of isotherm the absorption takes place by forming sorbate multilayer on catalyst surface by the heterogeneous dispersal of the pores (Harkins and Jura 1944).

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The linear equation of that model can be given as:

1

$$\overline{qe2}$$

$$\boldsymbol{B}$$

$$= (\boldsymbol{-}) -$$

$$\boldsymbol{A}$$

$$\mathbf{1}$$

$$(\ ) \qquad -$$

$$\boldsymbol{A}$$

$$\boldsymbol{logCe} \qquad (\mathbf{8})$$

In the above equation,
A = show the Harkins–Jura isotherm factor
B = indicate the Harkins–Jura isotherm constant.

Table 3.2 Equilibrium modelling of data for the removal of actacryl green dye

Equilibrium models	TiO2	Zn/TiO2	Cu/TiO2	Co/TiO2
Langmuir				
qm Cal (mg/g)	24.3903	23.5849	21.2342	19.305
qm Exp (mg/g)	23.99	22.654	21.112	19.543
b	0.000984	0.00529	0.0127	0.04539
RL				
R^2	0.871	0.785	0.055	0.086
Freundlich				
qm Cal (mg/g)	15.2932	10.6623	9.3152	5.6724
R^2	0.9928	0.9697	0.9908	0.9807
KF	15.3178	7.8922	3.0429	1.2175
n	6.1881	2.8344	1.4705	1.1027
R^2	0.6317			
0.2796				

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0.4097 0.2976

Temkin				
qm Cal (mg/g)	2.8378	2.2578	1.0336	1.128
A	0.5322	0.2481	0.1709	0.1282
B	9.0898	2.3721	0.4805	0.39616

R^2 0.5329
0.3053
0.3863 0.6329

Harkins-Jura				
qm Cal (mg/g)	5.15	77.102	56.162	45.80
A	-16.9779	-0.0508	-0.8913	-1.3734
B	-4.4974	-0.5680	-1.002	-1.5205

R^2 0.6794
0.2610
0.2859 0.3808

The suitable aptness for Temkin isotherm was also checked. The Langmuir model was best fit for our experiment because the experimental and calculated values closed and R2 also satisfied. Harkins jura isotherm indicated the least aptness on the equilibrium data of all because of great variation between the experimental qm and calculated qm (mg/g) and low values of R2.

Thermodynamic studies

Thermodynamic study is best way to get information about the nature of adsorption procedure. The values of thermodynamic factor like Gibbs free energy change as well as entropy change (ΔG^o and ΔS^o) were concluded using the adsorption thermal records for the exclusion of acataryl green □-2□ dye by using dopant photo catalyst. The ΔG^o were calculated at different temperature for act acryl green dye by using the equation shown below

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$$\triangle G^{\circ} = \triangle H^{\circ} - T \triangle S^{\circ} \quad (9)$$
$$\triangle G^{\circ} = -RTlnKd$$

Above equations showing
Kd = qe/Ce is called the thermodynamic equilibrium constant
R = indicate the general gas constant (its values is 8.314 J/mol K) T = temperature in (K) is absolute temperature
The values of ΔH^{o} and ΔS^{o} for cationic dye was determined by the values of slope and intercept making the ln Kd verses 1/T with help of following Van t hoff equation.

$$(Kd) = \frac{\triangle S^{\circ}}{R} - \frac{\triangle H^{\circ}}{R} \times 1/T$$

If the values of ΔG^{o} positive, then bio sorption of cationic dye using numerous kinds of bio sorbents was non spontaneous in nature. The negative ΔS^{o} values indicated the decreasing in ailment on solid and liquid boundary through out every bio sorption process for the subtraction of cationic dyes by using various kinds of dopant photo catalyst.
The values of thermodynamic factor like Gibbs free energy change (ΔG^{o}), enthalpy change (ΔH^{o}) and entropy change (ΔS^{o}) were concluded by using the bio sorption thermal records for the exclusion of act acryl green dye by using various chosen catalyst. The result presented in the table 3.3.

Table 3.3. Thermodynamic modelling data obtained for act acryl green dye removal.

Thermodynamc Model	308	310	317	324	331	338
TiO2 NP						
ΔG° (KJ/mol)	-3471.24	-4913.17	-6025.12	-8555.23	-6570.63	6401.53
ΔS° (J/K.mol)	97.18					
ΔH° (KJ/mol)	-2523					
Zn/TiO2 NP						
ΔG° (KJ/mol)	-2761.05	-3639.84	-4931.69	-6369.99	-5429.23	-5607.52
ΔS° (J/K.mol)	93.51					

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ΔH° (KJ/mol)	-2525					
Cu/TiO2 NP ΔG° (KJ/mol) ΔS° (J/K.mol) ΔH° (KJ/mol)	-2061.34 90.93 -2521	-2902.92	-4291.13	-5135	-4856.4	-4819.3
Co/TiO2 NP ΔG° (KJ/mol) ΔS° (J/K.mol) ΔH° (KJ/mol)	-1628.06 78.47 -2191	-2320.74	-3503.98	-4456.42	-3969.64	-3979.32

The obtained thermodynamic parameters values are presented in the above table. The –Ve values of ΔH show the exothermic nature of process for the decay of all basic dyes. The negative values of ΔS represent the decrease in dis-orderness on the liquid and solid phase to each types of adsorbents for the removal of basic dye (Mittal, Chisti et al. 2013). The –Ve ΔG values specify the spontaneous type of reaction.

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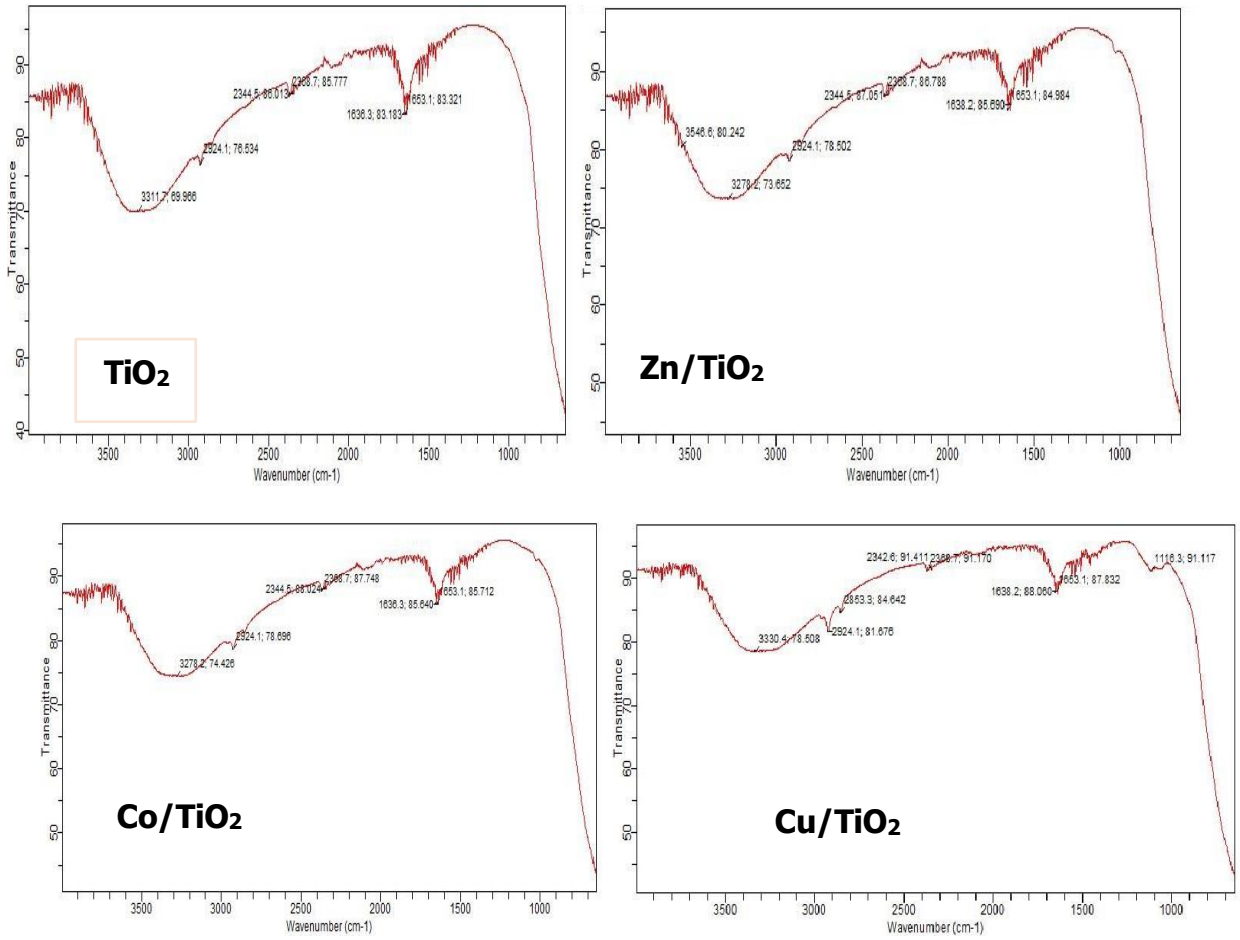
Characterization

FTIR Spectroscopy



TiO2

Figure 4.1 illustrate the FTIR spectra of TiO_2 NPs. The metal oxides naturally showed interatomic vibration absorption band in visible region or less than 1000cm^{-1}. The stretching and bending vibration of H_2O and hydroxal group is resemble, this give absorption peak at 3311, 2924,2344, 2924, 2344, 1638 and1653 respectively.

Zn/TiO2

Figure 4.1 illustrate the FTIR spectra of Zn /TiO2 NPs. The metal oxides naturally showed interatomic vibration absorption band in visible region or less than 1000cm^{-1}. The stretching and bending vibration of H_2O and hydroxal group is resemble, this give absorption peak at 3546, 3278, 2924, 1653 and1636 respectively.The peaks at 3546 represent the hydroxal peak due to presence of water in sample. The peak near the 1000 cm^{-1} represent the sample absorption peak.

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Co/TiO2

Figure 4.1 illustrate the FTIR spectra of Co /TiO2 NPs. The metal oxides naturally showed interatomic vibration absorption band in visible region or less than 1000cm^{-1}. The stretching and bending vibration of H2O and hydroxal group is resemble, this give absorption peak at 3278, 2924, 2344,1656 and1636 respectively. The peaks near 3278 represent the hydroxal peak due to presence of water in sample. The peak near the 1000 cm^{-1} represent the sample absorption peak.

Cu/TiO2

Figure 4.1 illustrate the FTIR spectra of Cu /TiO2 NPs. The metal oxides naturally showed interatomic vibration absorption band in visible region or less than 1000cm^{-1}. The stretching and bending vibration of H2O and hydroxal group is resemble, this give absorption peak at 3330, 2924, 2853,2342,1638 and 1116 respectively. The peaks near 3330 represent the hydroxal peak due to presence of water in sample. The peak near the 1000 cm^{-1} represent the sample absorption peak.

Conclusion

Water pollution is a kind of pollution that contaminate water bodies (rivers, ground water ,oceans and lakes) and hazard for health because of pollutants present in it. The dye is pollutant that is present in water and cause health risk for humans that discharge from industries.by increasing the population of the world the
demand of industries will be increased so pollution is increasing day by day. Dyes are non-biodegradable, lethal and damage kidney, brains and reproductive system. For the treatment of waste water dye several methods are used like chemical oxidation biological method, coagulation and sedimentation but there is some limitation that chemical methods are costly as these require large amount of oxidant and electricity consumption for decomposition of complex dye biological method are not effective, these are unsafe to environment difficult to degrade and threat for the life of humans. Different nanophotocatalyst will be synthesized by different methods and used for the degradation of dyes. Titanium dioxide is bright catalyst due to its promising properties as environmentally friendly, safety and availability. To remove one of the cationic dye was actacryl green □-2□ by pot catalyst TiO2, Zn/TiO2, Co/TiO2, and Cu/TiO2. After the synthesis of photocatalysts by sol gel method optimization of the parameters were done to find the optimum condition of in each cases. These appropriate conditions were help us to remove cationic dye from waste water. The batch study was completed to develop the sequence parameter the range of pH start from 2-12, catalyst dosage 0.05-
0.7. initial dye concentration 5-100mg/L, and finally temperature start from 345-65C. The optimum pH was different for different catalyst but all was nearly in basic values. Different kinetic models like pseudo1st order, pseudo 2nd order and equilibrium models such as Langmuir and freundlich and thermodynamic parameter as gives free energy, entropy and enthalpy was observed. Characterization was done by FTIR were sample gives different absorption peaks.

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