APPLICATION OF NANO *ACACIA NILOTICA* AND NANO TITANIUM DIOXIDE (TiO_2) FOR THE REMOVAL OF GLYPHOSATE- A COMPARATIVE STUDY

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Abstract— The use of low cost and locally available adsorbents have been identified for the removal of glyphosate from aqueous solution. This study deals with the removal of glyphosate using *Acacia nilotica* and titanium dioxide (TiO_2) both in the form of nano particles as an adsorbent. Glyphosate is herbicide which is soluble in water and has direct and indirect effects on plant and animal life due to its persistent nature in the environment. Batch experiments were carried out to determine the effect of pesticide concentration, contact time, pH, different dosages of *Acacia nilotica* and TiO_2 and rpm on adsorption efficiency. The results showed that adsorption capacity increased with increased dosage of nano *Acacia nilotica* while the adsorption capacity decreased when the dosage of TiO_2 was increased. Adsorption of the complete series of concentration (200-600 mg/L) and increased with increasing time (2 h) and rpm (200). Optimum condition for glyphosate adsorption was favorable at pH 4. Nano *Acacia nilotica* recorded 82.7 mg/L of adsorption at optimum conditions. Nano TiO_2 recorded maximum adsorption capacity of 78.9 mg/L at optimum conditions. Freundlich isotherms was obtained besides outcomes revealed that Freundlich isotherm model was best suited into it as it supported hetrogenous adsorption due to chemisorption.

Index Terms— Nano *Acacia nilotica*; Nano TiO_2; Glyphosate; Adsorption; Adsorption isotherm.

I. INTRODUCTION

Water pollution problems are arising due to globalization and competition on the international market for food production industries. Most of the pesticides are not degradable and are continuously present in the ecosystem, hence the removal of pesticides in aqueous solution is significant to safeguard environment and human health. The amount of organophosphorous compounds that are purposely or accidentally introduced to the natural environment is a hazardous threat to all forms of life systems. The direct, indirect or combined effects of these compounds in environment is of great concern in terms of biodiversity, ecosystem, sustainability issues and environmental sustainability. Organophosphate refers a group of insecticides which acts on human enzymes through different mechanisms. In India glyphosate consumption reach 8.48 MT in 2013-14, whereas the consumption of glyphosate was 2.89 MT in 2006-07, its almost four fold increase in consumption pattern, which is a great cause of worry. In US, the maximum annual rate for glyphosate is limited to not more than 6.7 kg per hectare for crops and not more than 8.9 kg per hectare for non-crop uses. In agricultural areas, the application rate for glyphosate lies between 0.8 to 4.2 kg per hectare. Surface runoff and water passage through soils are widely known as the most important transport routes for pesticides from fields to receiving aquatic streams.

There has been various methods developed today for the removal of glyphosate (N-(phosphonomethyl) glycine, $HOOC-CH_2-NH-CH_2-PO_3H_2$) from aqueous solution like nano filtration, membrane filtration, solid phase extraction etc. However these techniques are slightly expensive, require lot of time and generate toxic waste products after reaction. This may be due to lack of eco-friendly technological process. In order to capitalize on such faults some other methods like adsorption, photocatalytic reaction have been used to overcome the other methods. Glyphosate is an amphoteric and non-volatile compound where no photodegradation happens and it is completely stable in air. Adsorption process is an effective alternative which uses a large number of organic, natural, synthetic or low cost alternatives in a cheap and effective manner for the removal of pesticides. Various adsorbents which are used recently for the removal of pesticides include watermelon peel, date stones, fertilizer and steel industry wastes, amberlite, soil etc.*Acacia nilotica* adsorbent is one among the large no of adsorbents used and is one of the most important adsorbent used currently. Due to high adsorption capacity, large surface area, amorphous and cylindrical structure and having high purity. Generally the *Acacia nilotica* is used in micro particle size and the adsorption capacity is found to be 76.7 mg/L.The nano TiO_2 is a commercial adsorbent is well known for the environmental applications. The nano particles generally gain some attention through nano particles due to its higher surface area and availability of free vacant spaces.

Hence in the current study an attempt is made to study the *Acacia nilotica* in nano particle size and compared its adsorption efficiency with nano TiO_2 for the adsorption of glyphosate. Thus the study determined the efficiency of nano *Acacia nilotica* and TiO_2 as adsorbents for the removal of glyphosate from aqueous solution. The parameters like pH, dosage, time, rpm and concentration of pesticide, adsorption isotherms, were studied. The SEM (scanning electron microscope) analysis and TEM (transmission electron microscope) analysis adsorption isotherms kinetics were estimated to analyze the ability of adsorption.

II. MATERIALS AND METHODS

PREPARATION OF NANO *ACACIA NILOTICA* AND NANO TIO_2

TiO_2 was purchased from galaxy scientific company, Vellore, Tamil Nadu having a purity of 98 %. To make the particle to nano size we used a planetary mill where the particles are placed. Particles are placed inside the mill based on specific ball to weight ratio of 10:1 and total milling time was kept to 1hr.

Acacia nilotica seeds required for the process is collected from Semmenchery village of Katpadi Taluk in Tamil Nadu. The seeds are collected from the plant. The seeds are placed inside the seed pods. The seed pods are first collected. The collected seed pods are first air dried for 48 and then crushed in order to extract seeds from them. The collected seeds are then washed and air dried again for a period of 5 days. The dried seeds are then crushed with the help of motor and pistil and are then sieved so that they can be further milled in planetary mill.

Nanoparticle size of the particle is made with the planetary mill from VC ceramics, Chennai by maintaining same machining methods like that of TiO_2. After milling the seed powder is converted to nanoparticle size in Figure.1.

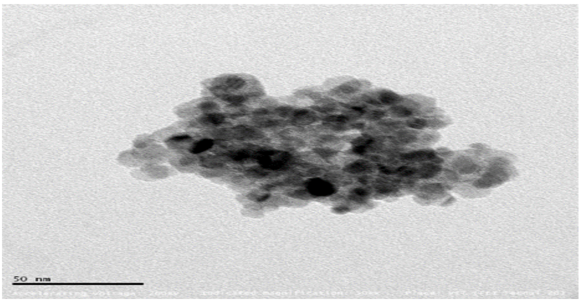

Figure 1:Nano Acacia

The powdered particles of TiO_2 and *Acacia nilotica* are both tested in nanoparticle analyser, SEM (scanning electron microscope) and TEM (transmission electron microscope) in order to know their structure, size and surface morphology. This similar tests are also conducted even after adsorption process in order to know the type of adsorption, type of reaction and surface morphological changes after the adsorption process.

The pesticide used in the glyphosate. Glyphosate used for this process is purchased from erode agro corporation, Katpadi road, Vellore having a concentration of 71 %. As glyphosate gets dispersed in water it can be measured by UV- spectrometry in order to determine the absorbance.

TiO_2 used in the process was of analytical reagent grade (AR) and are prepared with the help of distilled water. Stock solution of 1.583 gm of glyphosate at 1000 mg/L concentration was prepared by diluting 1.583 gm of glyphosate. From the stock solution, desired amount of concentrations was arranged for the experiment.

CHARACTERIZATION OF ADSORBENTS

The morphology of *Acacia nilotica* and TiO_2 surface was recognized using SEM (Jeol JSM- 6390) and TEM (200 KV FEI - Tecnai G 2 20 S - TWIN High resolution transmission electron microscope).

EXPERIMENTATIONS

Adsorption of glyphosate is performed by a batch process in order to attain data of equilibrium. Glyphosate pesticide concentration variation with respect to time in liquid solution was supervised through numerous situations like dosage (0.1, 0.2, 0.3, 0.4, 0.5mg/L) and pH (3, 4, 5, 6, 7, 8), initial pesticide concentration (200, 300, 400, 500, 600 mg/L), rpm (50, 100, 150, 200) and time intervals (30, 60, 90, 120 min). The pH was initially adjusted by either adding 0.1 M HCL or 0.1 M NaOH. Known amount of either *Acacia nilotica* or TiO_2 into 50 mL of glyphosate pesticide solution of identified concentration, pH, temperature and the combination was thoroughly mixed in an orbital shaker maintaining a speed of 200 rpm for 2 hours of time interval to achieve adsorption. Samples was taken at predetermined intervals and centrifuged using research centrifuge by maintaining 10,000 rpm for a period of 10 min. Thereafter the analysis of glyphosate residual in the conical flask was performed using UV-300 Spectroquant pharo spectrophotometer having a wavelength of 345 nm. The glyphosate adjustment graph was created using numerous points of glyphosate concentration versus absorbance having a range of 200 – 600 mg/L and the outcomes are evaluated. The glyphosate adsorbed amounts on to the *Acacia nilotica* and TiO_2 particles (mg/L) was calculated from the following equations (Eq.1, 2).

$$q_t = ((C_o - C_t) / M) \times V \quad (1)$$

$$q_e = ((C_o - C_e) / M) \times V \quad (2)$$

Where Co, C_t and C_e are the initials, at any time t and equilibrium glyphosate concentration (mg/L), respectively; V is the solution volume (L); and M is the *Acacia nilotica* or TiO_2 mass (mg).

ADSORPTION ISOTHERMS AND KINETICS

Adsorption isotherms are of basic importance in the design of adsorption process because they indicate how glyphosate are distributed between the adsorbent and aqueous phase at equilibrium as a result of glyphosate concentration. Whenever an adsorbent comes in contact with pesticide solution, the concentration of pesticide on the surface of adsorbent will increase till the dynamic equilibrium is achieved. At this stage there is a clear distribution of pesticides between the liquid phases. Freundlich isotherm was employed to calculate the adsorption capacity.

Adsorption kinetic study of glyphosate was done by altering the contact time and keeping other parameters in their optimum conditions (adsorbent dose, pH, concentration and rpm).

The kinetic study was studied for contact time ranging from 30 min to 120 min (dosage = 0.5 mg/L for *Acacia nilotica* and 0.1 mg/L for TiO2, pH = 4, concentration = 400 mg/L, rpm = 200) and therefore monitoring the percentage removal of glyphosate by the adsorbent. The data was then represented against the pseudo second order kinetic equation as this method was subjected to heterogeneous occupation and this type of occupation is generally supported by chemical reaction or chemisorption process.

III. CHARACTERIZATION OF THE ADSORBENT

PARTICLE SIZE ANALYSIS OF *ACACIA NILOTICA*

The particle size analysis of *Acaicia nilotica* was carried out in nanoparticle analyser in order to determine the particle size range after the particles are initially broken down and the average particle size achieved was 2948 nm.

SEM ANALYSIS

The surface morphology was observed using scanning electron microscope (SEM), and is performed before and after the adsorption, *Acacia nilotica* in nano size shown in Figure.2 and Figure.3 TiO_2 in nanoparticles shown in Figure.4 and Figure.5.

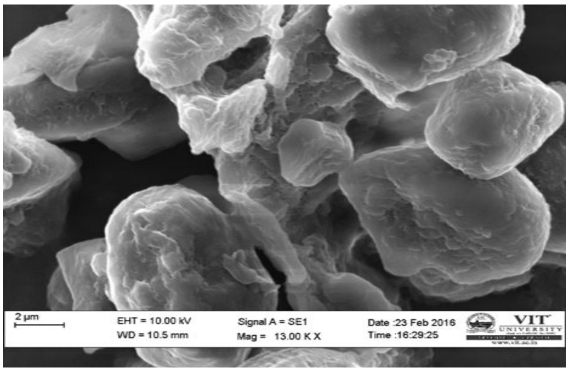

Figure 2:Nano Acacia before adsorption

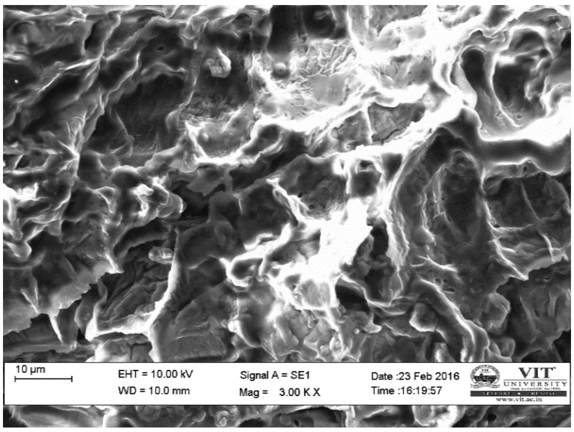

Figure 3:Nano Acacia after adsorption

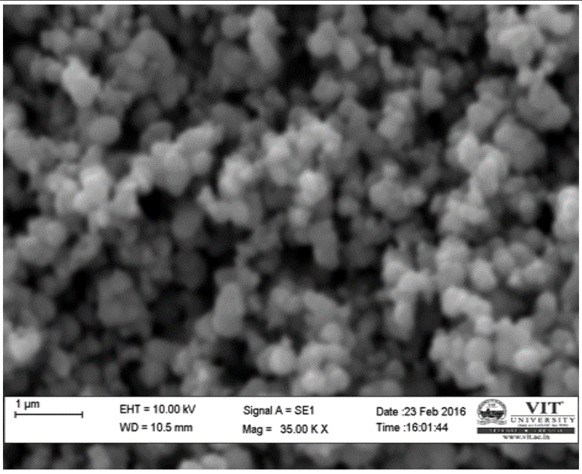

Figure 4:Nano TiO_2 before adsorption

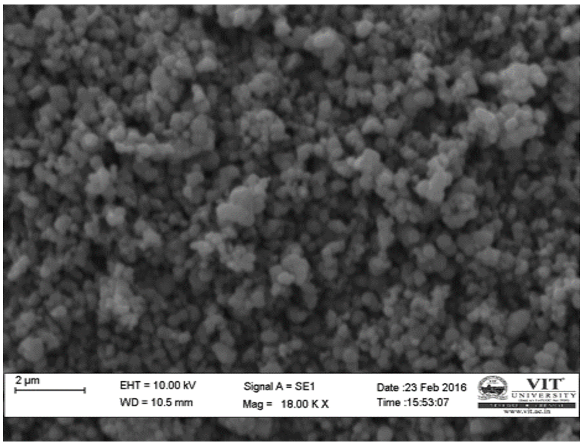

Figure 5:Nano TiO_2 after adsorption

TEM ANALYSIS

TEM analysis is performed in order to know the size of the adsorbent material. Here TEM analysis is performed using 200 KV FEI-Tecnai G2 20 S-TWIN High resolution transmission electron microscope.

It is clearly visible from the image Figure. 6 that the form of the seed particles is in an amorphous form and having an irregular morphology. Figure. 7 shows that the form of the nano TiO_2 particles as in a crystalline form and has a spherical structure.

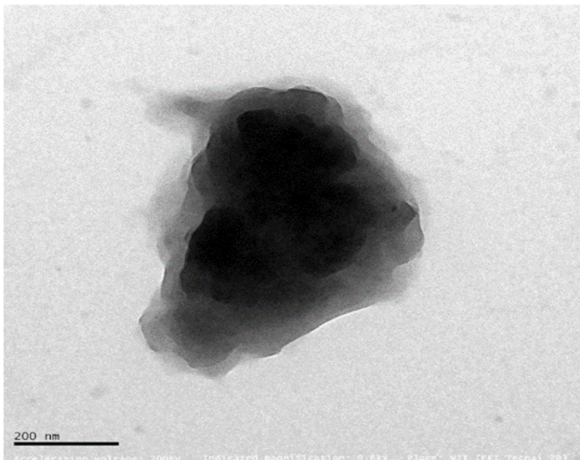

Figure .6: *Acacia Nilotica* having a particle range of less than 100nm

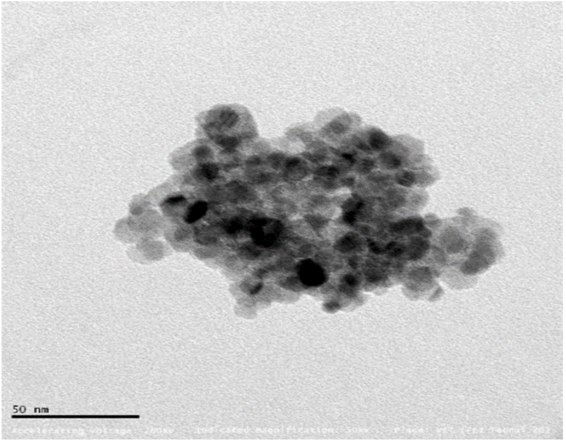

Figure .7:TiO_2 having particles in less than 20nm size

ISOTHERM- CALCULATION

Adsorption isotherms are calculated in this process Freundlich process is used to tell the rate of reaction carried out.

$$q_e = (C_o - C_e) \times V/m \quad (3)$$

Where C_o is initial concentration; C_e is the final concentration; V is the volume of pesticide solution and m is the mass of adsorbent.

Freundlich is calculated using by the relation of log $c_e$and log q_e and the graphs have been plotted.

IV. RESULTS AND DISCUSSION

ACACIA NILOTICA (NANO) & NANO TIO_2

EFFECT OF CONTACT TIME

In order to discover out the optimal time of contact 0.5 mg of *Acacia nilotica* nanoparticles and 0.1mg of nano TiO_2 was added to 250 ml erlenmeyer flask containing 50 ml of glyphosate pesticide having a concentration range of 400 mg/L at 28°C. The pH of the solution was maintained at 4 by using 0.1 M of HCL. The mixture was shaken in an orbital shaker at 200 rpm and samples was collected regularly for every 30 min of time interval. The collected samples was centrifuged at 10,000 rpm for 10 min to separate the adsorbent from the solution. The removal of glyphosate by adsorption onto *Acacia Nilotica* and TiO_2 was found to be slow during initial time intervals and increased rapidly over increased contact time. This clearly tells us that large no of vacant sites are gets occupied as the contact time goes on increasing, which therefore tells us that adsorption takes place over increased contact time in the case of *Acacia Nilotica* and indicates that TiO_2 when made to nanoparticle size has better adsorption capacity when compared to the adsorption range of *Acacia nilotica* particles. Therefore for stability studies time of contact was maintained for 120 min.

EFFECT OF DOSAGE

The effect of *Acacia nilotica* and TiO_2 is studied by varying the dosage for adsorption of glyphosate, the experiment was performed underneath various conditions prescribed in the former level having a contact time of 2 h and varied dosage (0.1, 0.2, 0.3, 0.4 and 0.5 mg/L). The effect of *Acacia Nilotica* and TiO_2 dosage for the removal of glyphosate. There has been a shift showing where the increase in *Acacia Nilotica* and TiO_2 dosage from 0.1 to 0.5 mg. *Acacia nilotica* adsorbent achieved an extreme capability of 81.15 mg/L at 0.5 mg dosage, whereas TiO_2 adsorbent achieved an extreme capability of 73.7 mg/L at 0.1 mg dosage. Increment in adsorption capacity with adsorption dosage was expected subsequently when the particles of adsorbent increases and therefore additional surface area was freely vacant. Though parallel explanations can be seen in literature which suggested that amount adsorbed increase with the amount of adsorbent increase. So, as a result 0.5 mg/L of acacia adsorbent and 0.1 mg/L of TiO_2 adsorbent was subsequently used to perform experiments for this work. But in the case of TiO_2 it's different. Here the collision of particles of TiO_2 led to the minimum usage of TiO2 particles for the adsorption study. There are also such studies indicating the minimum use of nano TiO_2 particles for the adsorption process.

EFFECT OF INITIAL pH

The effect of pH on the adsorption of pesticide on to *Acacia nilotica* and TiO_2 at 28°C and glyphosate initial concentration of 400 mg/L is revealed. The quantity of glyphosate adsorbed on to *Acacia nilotica* and TiO_2 amplified by lowering pH and the maximum quantity of glyphosate adsorption is carried out at pH 4 (77.7 mg/L for acacia nanoparticles and 64.2 mg/L for nano TiO_2 particles).

The pH solution can control the electrostatic exchanges between the adsorbent and the adsorbate. The adsorbent potential is zero at isoelectric point (IEP) whereas pH_{IEP} for *Acacia nilotica* and TiO_2 is internal range of 3.5 and 4.5 from the study, where IEP otherwise called as isoionic point is the point where amino acid does not mitigate in an electric field. Although the external layer of the adsorbent transports positive potential of pH, lesser than IEP, it has negative potential of pH, where the values is greater than IEP. At pH of 4, *Acacia nilotica* and TiO_2 surfaces has positive potentials and therefore no electrostatic dispersions take place among glyphosate pesticide and the positively charged surfaces having higher adsorption. Therefore when pH $>pK_a$(glyphosate, pK_a= 4), the phenols gets dissociated thereby forming anions of phenolate, therefore the surfaces of *Acacia nilotica* and TiO_2 has negatively potential where electrostatic repulsions gets induced between the similar charges thus depressing the adsorption values. In aqueous media the phenolate ions generally gets soluble and adsorption can take place when the stronger adsorbate water bonds must are broken. Comparable outcomes was described for adsorption with the help of *Acacia nilotica* and TiO_2. Thus all the experiments should be performed at pH $\leq$ 4.

EFFECT OF CONCENTRATION

The initial glyphosate concentration having a range of 200-600 mg/L for the adsorption of glyphosate on to *Acacia nilotica* and TiO_2. The initial pesticide concentration varied from 200-600 mg/L the amount of glyphosate adsorbed per unit weight of *Acacia nilotica* at equilibrium conditions and the constant temperature is 28°C reached 76.6 mg/L for *Acacia nilotica* and 72.7 mg/L for TiO_2. It is clearly understandable in the detail that concentration delivers a significant factor to overcome the resistance of whole mass transfer. Furthermore the rise of initial concentration of glyphosate for mass of (0.5 g) generates an excessive surge of molecules of pesticides in the aquatic media but from the study it is clearly visible that adsorption took place for the entire range of concentration. Therefore higher interaction took place between *Acacia nilotica* and glyphosate than TiO_2.

Effect of rpm

Samples was collected at different periods (30, 60, 90 and 120 min). The effect of rpm for the removal of glyphosate using *Acacia nilotica* and TiO_2 dosage. It was found that the adsorption increased rapidly with the increase of *Acacia nilotica* dosage, where 200 rpm was achieved for both *Acacia nilotica* particles and TiO_2 particles. Adsorption of 65.9 mg/L took place for TiO_2 and 77.6 mg/L for *Acacia nilotica* at rpm of 200.

Isotherms

Nano TiO_2 adsorption isotherms

Adsorption isotherm studies was performed with different concentrations of herbicide called glyphosate ranging 0.1 mg/L to 0.5 mg/L. Adsorption equilibrium isotherm data's was analysed based to the right form of Freundlich adsorption isotherm equation respectively.

$$Lnq_e = (1/n)\, LnC_e + LnK_F \qquad (5)$$

Where C_e(mg/L) is the equilibrium concentration of glyphosate, K_F $[(mg/g)(L/mg)^{1/n}]$, n are the Freundlich isotherm constant terms indicating adsorption intensity and capacities respectively and q_e (mg/L) is the level glyphosate adsorbed at equilibrium,. The values of Freundlich parameter was calculated from the intercept and slope of linear plots of Lnq_e against LnC_e. The isotherm constants and coefficients of correlation are shown and recorded below in Table. 1

Table.1 Freundlich isotherm values for TiO_2 and *Acacia Nilotica*

Freundlich isotherm	n	K_F	R^2
Nano TiO_2	0.19	31.30	0.87
Acacia Nilotica	0.25	6.54	0.91

From the Table. 1 it can be said that the process of adsorption can be clarified by Freundlich model by relating the results with the values of correlation coefficients. Which means the the surface is prevailed by heterogeneous occupation. Freundlich parameter values, K_F and n are 31.3 and 0.19 respectively. Relatively n < 1 indicate that adsorption remains positive over the entire range of concentration, while studies where n > 1 indicates that adsorption has increased at higher concentration but downgrades at lower concentrations. In the present study, different concentrations are favorable over the complete series of concentrations.

***ACACIA NILOTICA* NANO SEED POWDER**

Adsorption study can be described by Freundlich model by associating the outcomes with the values of correlation coefficient. This means the surface is predominated by that heterogeneous occupation. Freundlich parameters K_F and n are 4.78 and 0.23 correspondingly. Relatively n < 1 indicates that adsorption is favorable over the entire range of concentrations, while studies where n > 1 indicates that adsorption is suitable at higher concentrations but less effective at lower concentrations. In the present study, entire range of concentrations are favorable for adsorption studies.

KINETIC STUDIES

KINETIC 2ND ORDER FOR NANO TIO_2

If the rate of sorption in a second order mechanism, the pseudo second order chemisorption kinetic rate equation is expressed as

$$(1/qt) = (1/K_2 q_e^2) + (t/q_t) \qquad (6)$$

The contact time is t (min) and the volume of solute adsorbed at equilibrium at a given time is q_e (mg/L) and q_t (mg/L). The plot of t/q_t against t should give a linear association and from which slope and intercept (q_e and K_2)can be determined by the plot respectively, when the pseudo second order is relevant. Correlation coefficient value of linear regression is R^2. The experimental data was best fitted using linear model. It was detected that the value of q_e value 6.78 mg/L and K_2 is 0.0391 respectively. Therefore coefficient of linear regression correlation value R^2 is 0.949. The sorption of a pesticide by an adsorbent may implicate a chemisorption is centered on the pseudo second order model.

KINETIC SECOND ORDER FOR *ACACIA NILOTICA* (0.6MM)

The value of q_e is 0.39 mg/L and K_2 is 0.021 is noted. Correlation of linear regression coefficient R^2 is 0.999. The sorption of a pesticide by an adsorbent may comprise a chemisorption is characterized created on the hypothesis of the pseudo second order model.

KINETIC SECOND ORDER FOR *ACACIA NILOTICA* (NANO)

The value of q_e is 0.283 mg/L and K_2 is 0.013 is noted. Correlation of linear regression coefficient R^2 is 0.999. The sorption of a pesticide by an adsorbent may comprise a chemisorption is characterized created on the assumption of the pseudo second order model.

CONCLUSION

The interest of this study is the use of agricultural solid waste particles i.e. *Acacia nilotica* and titanium dioxide as low cost modified adsorbents in the elimination of glyphosate pesticide from liquid solutions. It has outstanding adsorption capabilities compared to other types of adsorption. This experiment also investigated the adsorption of glyphosate on to *Acacia nilotica* in the form of both micro, nanoparticles and TiO_2 in the form of nanoparticles at numerous circumstances. The trace amount of *Acacia nilotica* (0.5 mg) and Titanium dioxide (0.1 mg) was used as best adsorbents to remove glyphosate where significant adsorption for glyphosate pesticide is shown. High specific area of particles and the lack of internal scattering resistance may be the root cause. The consequences backed that the adsorption capacities reduced as pH improved but increased when the dosage of *Acacia nilotica* increased whereas the adsorption increased when the titanium dioxide dosage decreased. The best fitting isotherm model was Freundlich isotherm and heterogeneous employment of the surface occurs while the kinetic studies states that chemisorption is taking place.

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