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Adsorptive removal of phosphates from wetland waters using silica molyb date adsorbent

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Abstract

World's most productive and valuable ecosystem is the wetlands. Quality and functions of wetlands have been affected adversely by deforestation, fertilizers, and pesticides among others. Pollution by phosphates affect aquatic life as they have serious side effects at very low levels. Silica molybdate was prepared by first chlorinating silica sand using phosphorous pentachloride (PCl_5) to give chlorinated silica. Amination of chlorinated silica was done using Ethylenediamine (EDA) and later molybdate was chemically grafted to the aminated silica to yield silica molybdate. Silica molybdate was used to reduce the levels of PO_4^{3-} residues from wetland ecosystem.. Molecular structure of the silica molybdate material was characterized using Fourier Transform Infrared (FT-IR). FT-IR results showed Adsorption bands at 854cm^{-1} and 542cm^{-1} which were attributed to Mo=O and Mo-O stretching in molybdate. Peaks observed at 1388 and 1662cm^{-1} were attributed with the vibration mode of Mo-OH bond and bending mode of adsorbed water. Spectra peaks observed at 542, 634.58 and 898.97 cm^{-1} were attributed to the adsorption of molybdate. The physical adsorption parameters which were examined using batch adsorption system were; temperature, pH, contact, time, initial concentration using sorption models, adsorption kinetics and thermodynamics. Results showed that optimum pH for biosorption of PO_4^{2-} was 6.0, optimal contact time was 30 minutes, optimum temperature was 45 °C. The experimental results obtained showed that the maximum phosphate adsorption of silica molybdate was achieved at 194.93mg/g at adsorption optimal conditions of pH, temperature and contact time. The phosphate removal based on silica molybdate will offer several benefits such as low cost, effectiveness and reliability to lower the levels of phosphates in wetland waters as compared to commercial activated carbon. Based on the adsorption efficiency values obtained from this study and comparing them with adsorption efficiency reported in the literature, it can be concluded that silica molybdate is super adsorbent for the removal of phosphates from wetland waters.

Keywords: Wetland pollution; Phosphates; Adsorption; Silica molybate

1. Introduction

The most valuable and productive ecosystem in the world is the wetlands. The earth's surface covered by the wetlands is 15%. Wetlands offer 40% ecosystem services is in the world. These services include habiting aquatic animals and plants, cultural identity, opportunity for tourism among others. Improving water quality, reducing food wastage, and managing anthropogenic release of greenhouse gases are among three regulating services with global significant. Wetlands are capable of trapping pollutants and nutrients in their soils. Trapping of nutrients by the wetlands leads to water purification [1]. The reduction of vegetation cover, especially within the Mount Elgon, Mau complex, the Aberdare range, and Mount Kenya ecosystems which is considered as the main water catchment

basins has resulted to the decline of water quality and functions of wetlands. The hydrological cycles and wetland capacity to supply water has been affected. The ecological balance of wetlands has been affected by the introduction of alien species. Inadequate management capacity, increased human population, un-favorable climate, poverty prevalence, inappropriate land uses, land fragmentation and inappropriate conversion of wetland are the main driving forces of the adverse effect in wetland ecosystems and biological diversity [2]. They tap pollutants like phosphorous and heavy metals in their soils and transform nitrogen into an easier form for plants to take in [3].

About 2% of the earth surface is mainly covered by fresh water. Water bodies are mainly targeted by industries by discharging industrial effluents to water bodies leading to pollution. Waste water is harmful not only to aquatic life but also has highly harmful to human life. [4]. Pollution in the environment should be handled in a special way as it's a serious matter affecting many organisms at every level. Water is the mostly adversely affected environmental resources [5].

High amount of phosphate ions in water bodies leads to growth of aquatic plants that are harmful algae as well as lowering the amount of dissolved oxygen which affects the aquatic life. Ortho-phosphate is the principle phosphorous compound found in waste water with minimal amount of organic phosphates [6]. Maximum contaminant level for phosphate has been set by United State Environmental Protection Agency to be $\leq 20\mu g/L$ [7]. Phosphorous compounds which are mostly found in waste water are soluble. A small fraction of phosphate can be removed by precipitation. Biological treatment involves use of biochemical process to remove phosphates from waste water. There are more phosphates in water than what biochemical technology can handle. Primary and secondary waste water treatment can remove about 20-30% of phosphorous. There is need to come up with any adsorbent which can lower the levels of phosphates in wetland waters [8].

Currently, Methods used to reduce the levels of pollutants from water include adsorption, liquid-liquid extraction and precipitation. Adsorption method has been used for long a time as a way of purification and separation process in industries. Adsorption method has advantages such as operation simplicity, high efficiency and economy ease [9]. Studies utilizing adsorption techniques have been conducted with a significant interest in lowering the amounts of contaminants in waste waters and aquatic environments [10]. Various materials have been used to prepare adsorbents which are used to purify water. Adsorbents commonly used include; activated carbon, zeolite, chitosan, industrial waste and clay minerals among others. Activated carbon has shown excellent ability to remove organic such as phenolics, pharmaceuticals, dyestuffs, pesticides and metal ions due to its high porosity nature [11]. Although the application of activated carbon is very wide, it is expensive [12]. Activated carbon adsorbents are also nonselective. They are not recommended for lowering the levels of aqueous concentration below the required limits [13]. Adsorption efficiency of adsorbents is affected by factors such as pH, temperature, time and initial concentration of the pollutant.

The aim of this study was to determine the efficiency of modified silica in removal of phosphates from wetland water.

2. Materials and Methods

2.1 Materials

Silica sand used as raw material to produce silica molybdate, Ethylenediamine (EDA), phosphorous pentachloride (PCl_5) dimethyl formamide (DMF), hydrochloric acid (HCl, 37 %), sodium molybdate, sodium hydroxide (NaOH) and methanol analytical grade were purchased from Sigma Aldrich and were used without any further purification. All solutions were prepared using double deionized water.

2.2 Preparation of Silica Molybdate

Synthesis of silica molybdate was prepared in three steps. The first step involves chlorination of raw silica. 2.0g of raw silica was put into 250cm^3 three necked flask and 25 ml of DMF was added while stirring with magnetic stirrer. 1.5g of phosphorous pentachloride (PCl_5) was added dropwise to the raw silica suspended in DMF. The mixture was refluxed for 2hrs, filtered and washed with deionized water then dried under vacuum at 70°C for 24hrs. The second step involved the amination of chlorinated silica. 5.0g of chlorinated silica was reacted directly with 25ml ethylenediamine. The resulting mixture was filtered washed and dried in a desiccator for 48hrs [14]. The last step involved grafting of molybdate to the aminated silica. 1.0g of aminated silica was mixed with 1.0g of sodium

molybdate suspended in 25ml DMF. The resulting solution was refluxed for 3hrs at 80°C. The resulting mixture was filtered by vacuum filtration, washed and dried in the desiccator for 48hrs.

2.3 FT-IR characterization of the adsorbent

FT-IR analysis was done for raw silica (RS), chlorinated silica (CS), aminated silica (AS) and silica molybdate (SM)

1.0 mg of each sample of RS, CS, AS and SM were mixed thoroughly with 50.0mg of potassium bromide (KBr). The mixture was pulverized and then pressed in a vacuum into pellets. The pellets were then put into spectrophotometer machine (FT-IR 8400 model Shimadzu Tokyo Japan) for analysis. The adsorbent spectra were measured in a wavelength range 4000cm^{-1} to 400cm^{-1} [15]

2.4 Adsorptive process for the removal of phosphate

Phosphate adsorptive capacity of silica molybdate was studied at various parameters such as pH, temperature and contact time. The concentration of phosphate was varied from 20ppm-60ppm. The absorbance was measured at 542 nm on UV-Vis spectrometer. The effect of pH on the phosphate solution was investigated in the range of 3-8 adjusted using NaOH and HCl solutions with the aid of pH meter. Contact time was varied from 30-150 minutes and temperature varied from 25°C to 45°C. The adsorption experiments were carried out at a stirring speed of 150rpm.

2.5 Adsorption isotherms

The adsorption capacities were investigated by adding 0.02g of functionalized silica molybdate separately to 100 ml of changing initial concentration of the model solution at optimum pH 6.0. The mixture was agitated at 150 rpm for contact time 1 hr at constant temperature of 45 ± 1 °C after which the mixtures were filtered and the amount of phosphates in the filtrate was analyzed using UV-Vis. The entire procedure was done in three replicates. The amount of phosphates adsorbed by functionalized silica molybdate during the batch experiments were calculated by the expressed in Equation 1.

$$qe = (ci - ce)/M \times V \quad \text{.....equation (1)}$$

where, *qe* is the quantity of phosphates uptake per unit functionalized silica molybdate at equilibrium, *Ci* is the initial concentration of phosphates in ppm, *Ce* is the equilibrium concentration of phosphates in mgL^{-1}, *M* is the mass of the silica molybdate adsorbent in grams and *V* is the volume of adsorbate in L [16, 18].

The removed percentage of phosphates in solution were calculated using Equation shown below,

$$\boldsymbol{R}\% = (\boldsymbol{Ci} - \boldsymbol{Ce})/\boldsymbol{Ci} \times \mathbf{100} \quad \text{..... Equation (2)}$$

Where R% is the percentage removal of phosphates in the solution, Ce and Ci are the equilibrium and the initial concentration of phosphates respectively [16]. The data obtained was analyzed using sorption models/ isotherms to determine the amount of phosphates removal. Langmuir and Freundlich equations, Equation 3 and 4 respectively were used in determination of absorption capacities of the adsorbent [18].

$$Ce/qe = 1/qmax \,.b + ce/qmax \quad \text{.....equation (3)}$$

$$x/m - K_f C_e^{\,1/n} \quad \text{.....Equation (4)}$$

2.6 Adsorption kinetics

Chemical kinetics was applied to determine the rate controlling mechanism which involves pathway process of chemical reaction and mass transfer rate [19]. The obtained data were analyzed by applying pseudo-first order and pseudo- second order model [20]. Pseudo-first order kinetic model (equation 3) considers the rate at which adsorption active sites are occupied proportional to the number of unoccupied sites [19].

Log (qe-qt) =log qe-K_1t……equation (5)

Where k_1 is the pseudo-first order sorption rate constant (min^{-1}), qe is the quantity adsorbed at equilibrium (mg/g) and qt is the quantity adsorbed at time t (mg/g). qe and k1 are determined from the slope and intercept of the plot of log(qe-qt) against t respectively [21].

Pseudo-second order kinetic rate equation is given as:

$\Delta qt/dt = k_2 (qe-qt) (qe-qt)^2$……..Equation (6)

Rate constant of pseudo-second order sorption is given as K_2 (g mg^{-1} min^{-1}). The equation is integrated and rearranged to obtain equation 5:

$t/qt = (1/K_2qe^2) + (t/qe$…….Equation (7) A graph of t/qt versus t is plotted to give a linear relationship. From the graph qe and K_2 was determined from the slope and the intercept of the plot respectively [21].

3. Results and Discussion

3.1 Characterization of raw and modified silica

FT-IR spectra of raw silica (Figure 1) showed broad bands at 3435cm^{-1} and 1647cm^{-1} which were assigned to the stretching and bending vibrations of the silanol groups (Si-OH) respectively. The bands found at 1051 and 794 cm^{-1} are the characteristic anti-symmetric and symmetric stretching modes (Si-O-Si) of SiO_4 [22]. A small band found at 970cm^{-1} was allocated to Si-OH stretching mode and the band at 433cm^{-1} was assigned to Si-O-Si bending vibrations.

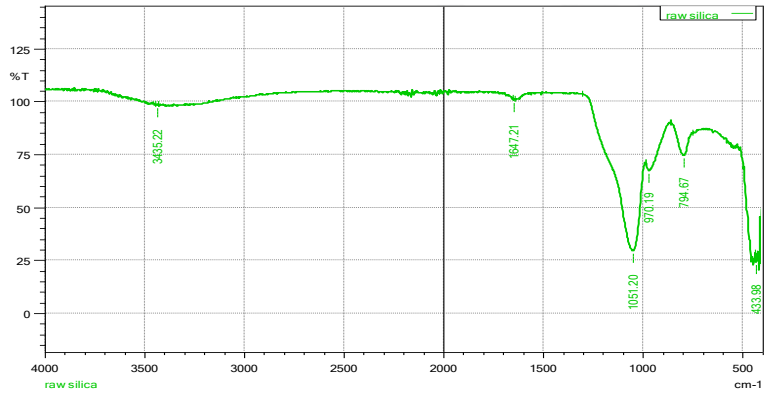

Figure 1: FT-IR spectrum of silica sand

FT-IR spectrum of chlorinated silica (Figure 2) showed the shifting of the existing bands, disappearance of other bands and appearance of others. The new bands appeared due to adsorption frequencies of carboxylic, hydroxyl and halogen group [21]. Appearance of new adsorption peaks was observed at a frequency 663cm^{-1} which was attributed to C-Cl bond stretching vibration which ranges from 850cm^{-1} to 500cm^{-1}. The frequency band at 1163.10cm^{-1} assigned to C-OH stretching vibrations in raw silica sand disappeared due to replacement of –OH

group with the halide [20]. The absorption peaks of various wavelengths were identified after chlorination due different functional groups. These were 1653 cm^{-1}. assigned to C=O stretching of carboxylate, 1493.89 cm^{-1}.attributed to C=H bending and 1390.45 cm^{-1}.due to OH bending [21].

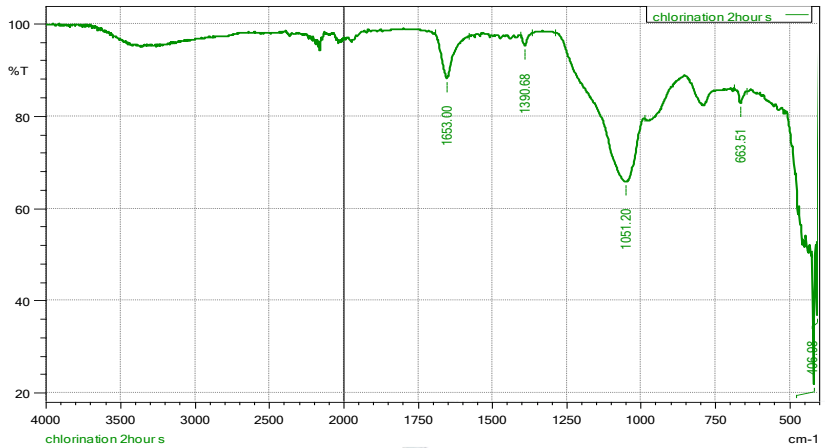

Figure 2: FT-IR spectra of chlorinated silica sand

FT-IR spectrum of aminated silica (Figure 3) gave a new band at 3356cm^{-1} which was attributed to stretching vibrations of the NH_2 group. NH_2 bending vibrations of SiO_2-NH_2 emerges at 1604cm^{-1}. The displacement of the band at 1614cm^{-1} corresponds to the bending of OH bonds and also angular deformation of the N-H. Amine band at 1604cm^{-1} is an indication of ethylene-1,2-diamine immobilized in the silica material.

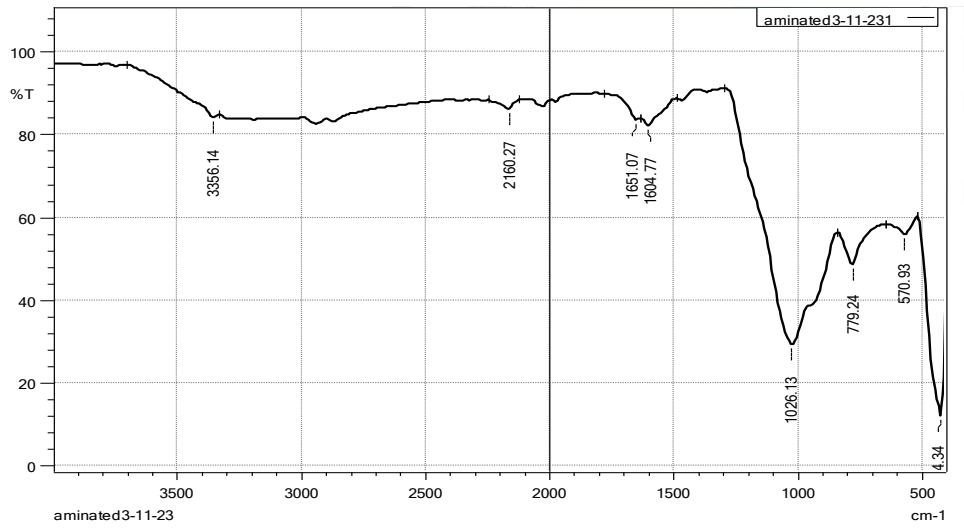

Figure 3: FT-IR spectra of aminated silica sand

FT-IR spectrum of aminated silica bound with molybdate (Figure 4) gave adsorption bands at 854cm^{-1} and 542cm^{-1} were attributed to Mo=O and Mo-O stretching in molybdate. Peaks observed at 1388 and 1662.64cm^{-1} were attributed to the vibration mode of Mo-OH bond and bending mode of adsorbed water. Spectral peaks observed at 542, 634 and 898.97 cm^{-1} were attributed to the adsorption of molybdate on the mesoporous silica [22].

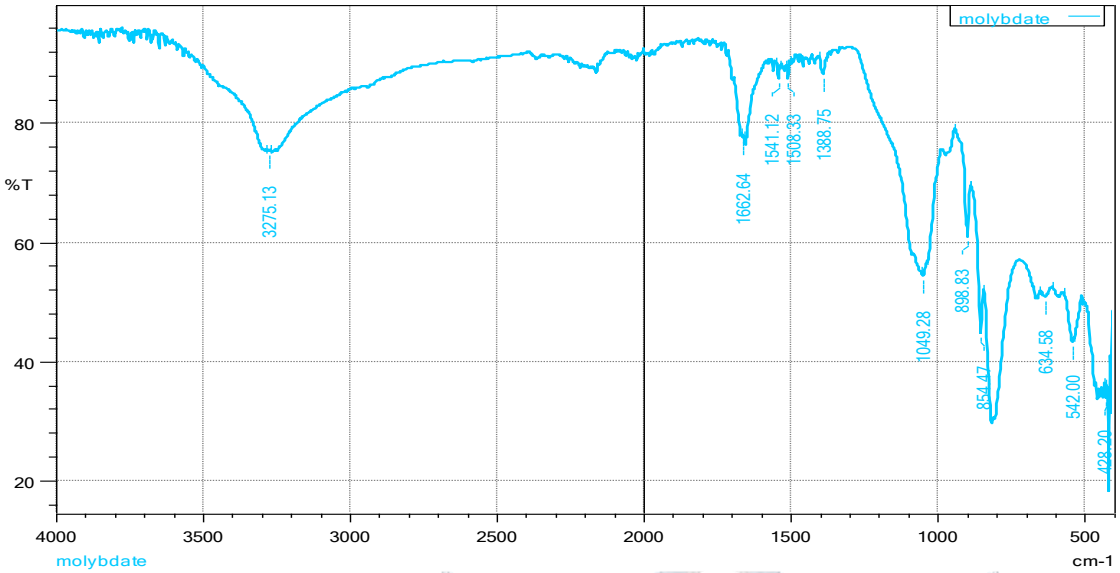

Figure 4: FT-IR spectrum of silica molybdate

3.2 Effect of initial solution pH

One of the most important parameters which influences the sorption of both cation's and anions at the solid liquid phase is the pH of the aqueous solution. The anion exchange capacity is strongly affected by the surface chemistry of the solid and the pH of the solution [25]. The effect of pH on the adsorption of phosphates ions by functionalized silica molybdate was attributed to the fact that change in pH causes significant change to the surface charge and the behavior of the functional groups on the adsorbent surface [26]. The results on the effect of pH on the adsorption of phosphates ions shows that as the pH is raised from 4-6, removal efficiency of phosphates ions is increased (Figure 5). Increase from pH 4-6 is attributed to the high density of positively charged ions. At pH 6 the maximum removal efficiency of phosphates ions was observed to be 94.2 %. A value of pH was selected as the optimal pH for more adsorption experiments in order to achieve suitable removal efficiency and phosphate uptake capacity. At pH 7 removal percentage was observed to be 52.2 % at pH 7 and 39.1% at pH 8. Increasing the pH from 6-8, removal efficiency of phosphates ions decreased. The tendency could be due to the competition between the extra OH^- ions and negatively changed phosphate ions. Similar results have been reported in the studies carried out on the phosphate removal using polyethylenimine functionalized silica-based materials [26]. According to Ovakouak and Youcef, the reduction in the amount of phosphate ion removed in the basic pH is caused by the increase of negative charge on the surface of the adsorbent (Ovakouak and Youcef 2016,)

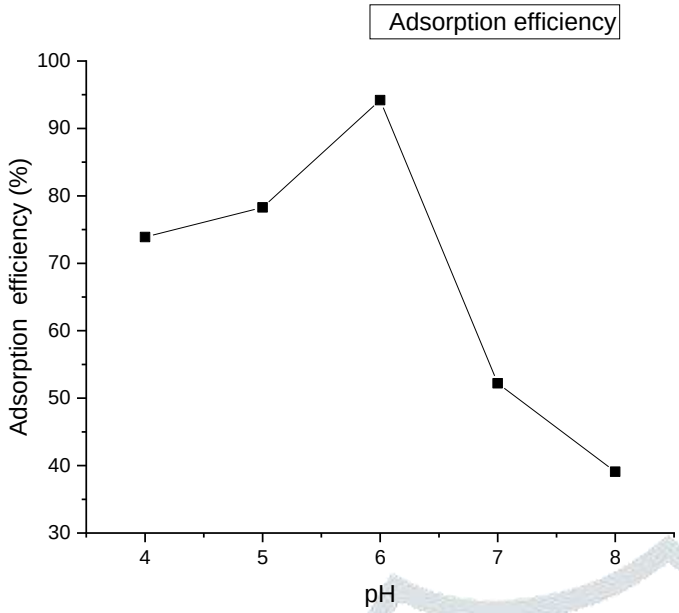

Figure 5: Variation of adsorption efficiency against pH

(Experimental conditions: shaker speed 150rpm, adsorbent dosage 0.02g, temperature 25±1℃ and pH 4-9 and contact time 60 minutes)

3.3 Effect of temperature on the adsorption of phosphates

By increasing the temperature of the circulating water adsorption capacity and the rate at which phosphates are adsorbed increased significantly (Figure 6). Increase in temperature promotes the adsorption capacity of the adsorbents for PO_4^{3-}. Movement of ions increases in circulating water with an increase in temperature due to increase in kinetic energy. This accelerates the movement rate of phosphate ions to the surface of the adsorbent increasing the adsorption capacity of adsorbent for phosphate ions [27]. The increase in removal efficiency with the increase in temperature shows that the phosphate adsorption process was endothermic in nature [28]. Similar results were reported in adsorption of Cr(vi) from aqueous solution by adsorbent prepared from paper mill sludge; kinetics and thermodynamic studies [28].

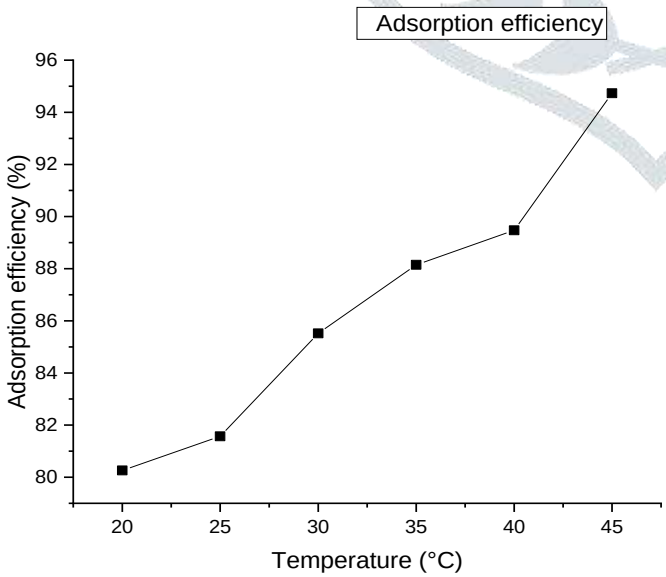

Figure 6: Variation of adsorption efficiency against temperature

(Experimental conditions shaker speed 150rpm, adsorbent dosage 0.02g, temperature 25-45℃ and pH 6.0 contact time 60 minutes)

3.4 **Effect of contact time on the adsorption of phosphate ions**

Removal efficiency of phosphate was investigated as a function of contact time, at pH 6.0, initial concentration 30ppm and adsorbent dosage 0.02g (Figure 7). It was observed that the removal efficiency of phosphates increased with an increase of contact time to a maximum of 60 minutes after which it continued to a lower rate until saturation [29]. Contact time enables diffusion and adhesion of adsorbate particles to take place. Addition of time no longer increased the adsorption of phosphates ions because the active site had started to release the phosphate back into the solution. At the beginning of the adsorption process the vacant sites of silica molybdate are more. After 60 minutes the graph of adsorption efficiency against time is a straight line indicating that all the vacant sites if silica molybdate have been utilized. Similar results were reported in study on adsorptive removal of phosphates from aqueous solution [29].

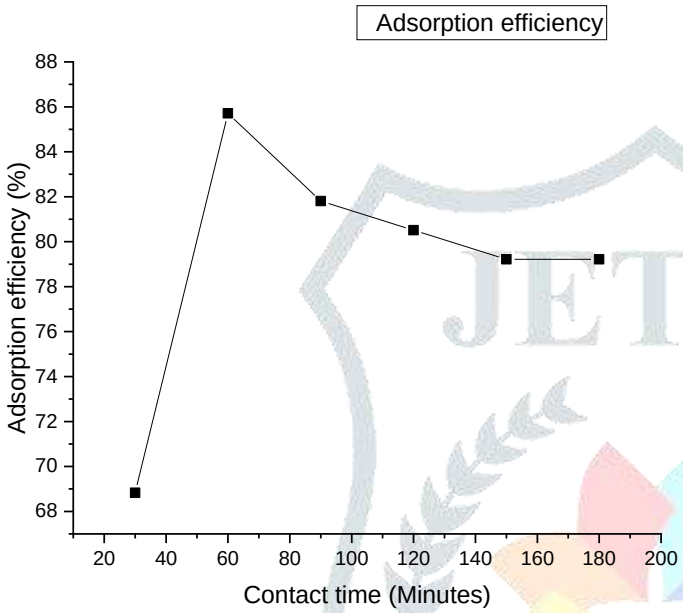

Figure 7: Variation of adsorption percentage against contact time

(Experimental conditions shaker speed 150rpm, adsorbent dosage 0.02g, temperature 25±1℃ and pH 6.0 contact time 30-180 minutes)

3.5 Adsorption isotherms

The first theoretical treatment of nonlinear sorption is the Langmuir model which suggested that the uptake occurs on the homogeneous surface by monolayer sorption without the interaction between the adsorbed molecules [30]. The equation of Langmuir was used for adsorption equilibrium of phosphate ions into the silica molybdate. Linear equation of Langmuir is given as follows; ce/qe = 1/q max .b + ce/q max. Ce the equilibrium concentration of the adsorbate in mg/L. Qe refers to the amount of phosphates ions adsorbed into the silica molybdate at equilibrium (mg/g) and q max (mg/g) is the Langmuir constant related to adsorption capacity and b (L/mg) is the Langmuir constant related to the energy of adsorption [30]. The linear plot of ce/qe verses ce (Figure 8) of silica molybdate showed that the adsorption process obeyed the Langmuir isotherm model according to the correlation coefficient value $R^{2,}$ Qmax and b which were obtained from the slope and the intercept respectively. The essential features of Langmuir isotherm is expressed in terms of a dimensionless constant separation factor or equilibrium parameter Rl expressed as Rl = 1/(1+b.co) [30].

The expression of Freundlich isotherm encompasses the exponential distribution of active sites and the surface heterogeneity. The constant Kf and nf numerical values were determined from the intercept and slopes of respective plots. Relative adsorption capacity of the adsorbent is indicated by the constant Kf relating to the bonding energy referred to as adsorption distribution coefficient. This value represents the quantity of the metal ions adsorbed in the adsorbent at equilibrium [19]. Heterogeity factor is known as nf. Adsorption process is linear when nf=1. If the

adsorption process is chemical nf < 1and a physical process when the value of nf > 1. When the value of 1/nf is less than 1 adsorption is the predominant process taking place [30].

Experimental results obtained were integrated into Langmuir and Freindlich isothermal model. Langmuir plot of phosphate by silica molybdate is shown in Figure 8 and Freindlich plot for phosphates by silica molybdate is shown in Figure 9. The values of Langmuir and Freindlich constant of phosphates by silica molybdate is listed in Table 1. Freindlich equation is better obeyed by the system than Langmuir one as is evident for the values R^2 in Freindlich model.

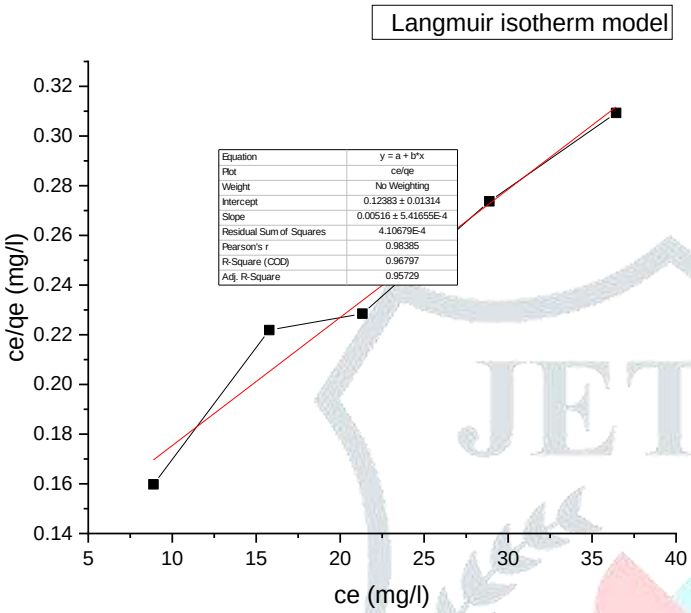

Figure 8: Langmuir adsorption isotherm for adsorption of phosphates ions into silica molybdate adsorbent for 1hour agitation**.**

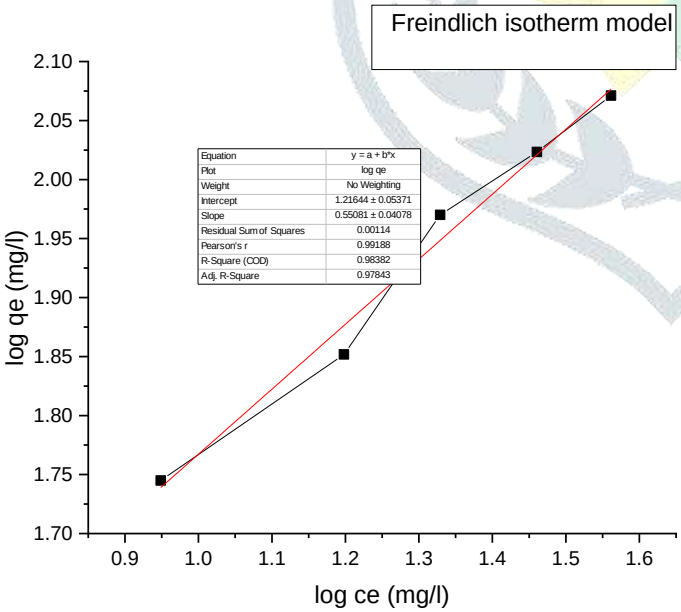

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Figure 9: Freundlich adsorption isotherm for adsorption of phosphates ions into silica molybdate adsorbent for 1hour agitation

Table 1: Results of Langmuir and Freundlich isotherms for phosphates adsorption capacities

Langmuir isotherm			Freudlich isotherm		
Q(max) (mg/g)	Rl dm^3/mg	R^2	1/n	K f (mg/g)	R^2
194.93	0.2870	0.95814	0.5501	16.45	0.97164

3.6 Adsorption kinetics

From the results in Table 2 and Figure 10 and 11 show the linear plot of log(qe-qt) versus t for the lagergren pseudo-first order model and t/qt versus t for lagergren pseudo- second order for biosorption of PO_4^{3-} into silica molybdate. The equilibrium rate constant of pseudo-first order sorption K_1 was observed to be 0.0027 and the correlation coefficient R^2 was found to be 0.9491. The equilibrium rate constant of pseudo-second order model K_2 was 0.00386 mg/g min^{-1} and the correlation coefficient R^2 was 0.89551. The pseudo-first order equation fitted well with correlation coefficient R^2 0.9491 closer to unity.

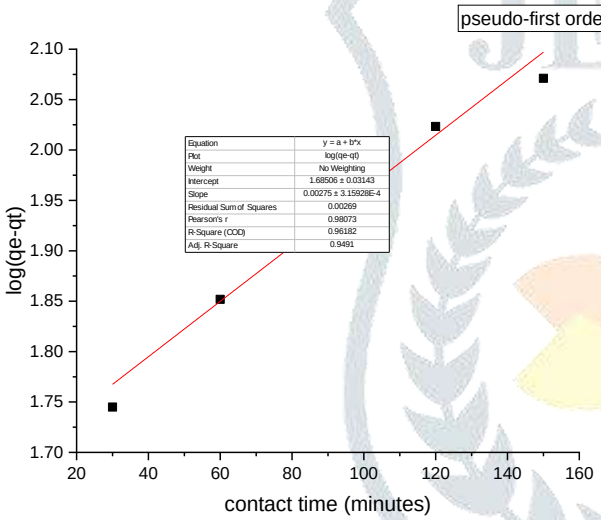

Figure 10: Linear plot of log(qe-qt) versus t for the lagergren pseudo-first order model

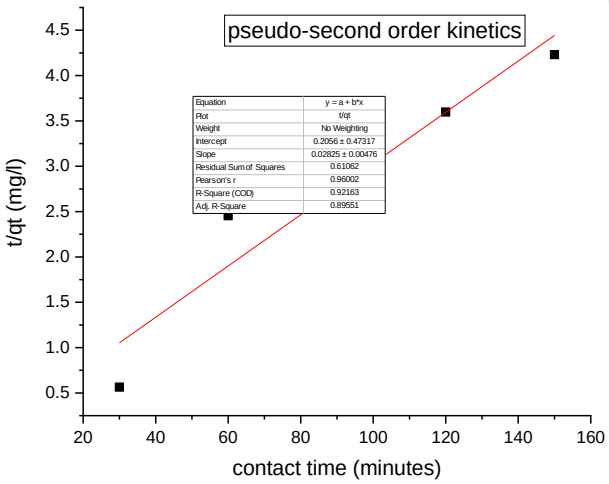

Figure 11: t/qt versus t for lagergren pseudo- second order

Table 2: Kinetics parameters for adsorption of phosphates into silica molybdate

Phosphates	Pseudo-first order K_1			Pseudo-second order K_2		
Parameters	Qe(mg/g)	K_1(mg/g min^{-1}	R^2	Qe(mg/g)	K_2(mg/g min^{-1}	R^2
	48.42	0.0027	0.9491	35.46	0.00386	0.89551

3.7 Comparison of silica molybdate as an adsorbent with commercial activated carbon

Table 3 gives the theoretical adsorption efficiency from batch adsorption experiments of silica molybdate with other previously reported results from activated carbon used as an adsorbent for phosphates adsorption. Based on the adsorption efficiency values it can be concluded that silica molybdate is super adsorbent for the removal of phosphates from wetland waters.

Table 3: Comparison of adsorption capacity of silica molybdate with activated carbon for adsorption of phosphates

Adsorbent	Adsorption efficiency (%)	Reference
Silica molybdate	94.73	This study
Activated Carbon from Ampelodesmos Mauritani Cos Stem (ACAMCS)	75	[6]
Powder activated carbon (PAC)	51.62	[32]
Granular activated carbon (GAC)	40.29	[32]

4.0 Conclusion

Characterization analysis reveals that silica molybdate contains unique properties as an efficient adsorbent. Several properties such as; functional groups, surface modification and thermal stability in silica sand was improved after functionalized silica with amine and molybdate. The optimum experimental conditions for achieving maximum phosphate removal were as follows; pH 6.0, initial phosphate concentration 30ppm, contact tome 60 minutes, the temperature of the solution 45°C and shaking speed 150rpm. Equilibrium data were described by Langmuir and Freindlich adsorption isotherms. The maximum sorption capacity for phosphates was found to be 194.93mg/g. For adsorption of phosphates in silica molybdate, Freindlich adsorption model was best obeyed according to the correlation coefficient R^2= 0.97164 as shown in Figure 9. Pseudo-first order kinetics model was best obeyed in the adsorption of phosphate in silica molybdate. The present measurements show the feasibility of silica molybdate with different characteristics as potential sorbents for phosphates. Silica molybdate prepared in this study for adsorption of phosphate ions is highly efficient adsorbent as compared to activated carbon but more data is required before conclusive statements can be made.

Conflict of interest

The authors declare that they have no conflict of interest

Acknowledgement

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