

Article

Synchronous Adsorption of Cadmium and Lead ions from Aqueous Media by Rice Husk Ash and Sodium Dodecyl Sulfate Combination

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Abstract: In this study, the synchronous removal of Pb²⁺ and Cd²⁺ ions from aqueous solutions by colloidal particles made from rice husk ash (RHA) in aqueous sodium dodecyl sulfate (SDS) solution was investigated. The RHA derived from rice husk waste generated from the rice mills in Wukari, north-eastern Nigeria was combined with sodium dodecyl sulfate (SDS) for the metal ions adsorption. The adsorption studies under different experimental conditions were optimized and the removal of Pb²⁺ and Cd²⁺ ions was highly pH dependent. The results indicated that pH 8.0 was the optimum for the removal of the metal ions. Adsorption equilibration time was achieved in 2 hours with maximum removal efficiency of the metals ions attained at 71.8 and 88.9 % for Pb²⁺ and Cd²⁺ respectively. The equilibrium data were satisfactorily fitted to Langmuir and Freundlich isotherms. The Langmuir isotherm models gave a better representation of the data than the Freundlich isotherms. The RHA-SDS combination showed higher adsorption capacity for Cd²⁺ ion compared to Pb²⁺ ion under the experimental conditions in the single and binary solutions. The study showed that RHA-SDS synergy can be effectively used for the removal of Pb²⁺ and Cd²⁺ ions from wastewater with higher efficiency compared to the use of RHA alone.

Keywords: Lead, Cadmium, Adsorption, Rice husk Ash and SDS micelles

1. Introduction

The removal of heavy metal ions which constitute environmental pollutants has been a broad area of research. A lot of attention has been given to these study areas because of the threats and toxicity of these metals even at trace quantities. Cadmium and lead have been classified as the most potentially toxic metals with deleterious effects on humans, animal and plants. They exhibit high degree of solubility and hydration [1] hence can contaminate water bodies, soil, plants and can be easily transported across food chains from plants to animals and humans. These metal ions are often discharged by a number of industrial processes into fresh waters and marine environment, leading to widespread pollution. The removal and extraction of these metal ions from water and waste water has become a challenge for researchers. Many techniques have been developed and employed to extract these metal ions from aqueous solutions. Conventional techniques with varying levels of removal efficiencies for these metal ions include: ion-exchange, reverse osmosis, electrochemical treatment, evaporative recovery, and adsorption [2, 3, 4]. These processes come with their attendant shortcomings such as high material and operational costs, limitations in some pH range and expertise requirement. Adsorption techniques however, have become quite prominent in heavy metal ions removal and remediation recently due to the low cost of the adsorbent materials, high efficiency and economic operational cost [5]. Another reason this method has gained wide application and acceptability, is also, due to the wide arrays of agro-allied materials that can serve as adsorbents whether modified or not. Materials that could have been discarded as wastes are finding useful applications in environmental pollution abatement.

The use of rice husk ash for adsorption of heavy metal ions is one of the most effective techniques for the treatment of heavy metal contaminated aqueous systems. The search for new, available and abundant low cost feed stocks has made materials from agricultural wastes stand out as some possible alternatives both in environmental and economic terms. Agricultural materials such as banana and orange peel [6]; maize, sunflower waste [7]; coconut husk and shell [8]. These materials have been reported to adsorb different pollutants such as heavy metal ions, dyestuff and other toxic pollutants [9]. The applicability of rice husk ash (RHA) in adsorption studies has been reported by Vimal et al, where mesoporous rice husk ash was characterized and employed in the removal of Cd (II), Ni (II) and Zn (II) ions from aqueous solutions [10]. Feng et al studied the removal of lead and mercury from aqueous systems using RHA as adsorbent [11]. The use of rice husk and rice husk ash for adsorption of heavy metal ions is on the increase due to the volume of the rice husk generated from rice processing mills yearly worldwide. Millions of metric tons of rice husk ash (RHA) are generated annually from major rice producing countries [12]. Rice husk is finding useful applications including its use as fuel for heat generation in various drying processes. This combustion process produces rice

husk ash (RHA) readily available for utilization.

This study focused on the surfactant enhanced and synchronous adsorption of cadmium and lead ions by rice husk ash (RHA) as adsorbent. The abundance of the RHA and its very high potential as adsorbent has motivated this research study. Anionic surfactant micelles have strong affinities for binding of divalent metal ions and were thus employed as adsorption aid or co-adsorbent. The study reports the enhanced and competitive removal of cadmium and lead ions from aqueous systems using the micellar solution of sodium dodecyl sulfate (SDS). Also reported are the effects of factors such as adsorbent dose, initial concentration of metal ions, initial solution pH, anionic surfactant concentration, contact time and temperature on the adsorption efficiency of these metal ions from bulk solutions. It is discovered herein, that the combination of the useful properties of rice husk ash (RHA) and that of anionic micelles of SDS, could introduce a modified adsorbent matrix with many applications and superior adsorption capabilities.

2. Materials and Methods

2.1. Adsorbent and Its Characterization

Rice husk ash (RHA) was obtained from the local rice mills in Wukari, north-eastern Nigeria. The as-received RHA was properly sieved with a sieve of known mesh size to remove contaminating particles followed by washing with deionized-distilled water to remove any traces of impurities, after which it was dried in the oven at 100°C for 4 hours. The oven dried RHA was milled to reduce the mean particle size and increase specific surface area in a porcelain jar and microspheres of high alumina as the milling medium.

Quantitative chemical analyses of the RHA were accomplished using standard procedures. Proximate analysis was carried to determine the various constituents of the RHA. Bulk density was determined using Archimedes' principle [13], particle size analysis was by sieve analysis using standard sieves. Simple specific surface area of the RHA was determined by Sears method [13]. The point zero charge (PZC) was determined for the RHA using the solid addition method [14] viz: to a series of 100 ml conical flask, 45 ml of 0.1M KNO₃ solution was transferred. The pH₀ values of the solutions were roughly adjusted from 2 to 12 by adding either 0.1M HNO₃ or NaOH. The total volume of the solution in each flask was made exactly to 50 ml by adding the KNO₃. The pH₀ of the solutions were accurately recorded. RHA (1g) was added to each flask and securely capped, immediately. The suspension was then manually agitated. The pH values of the supernatant liquid were noted. The difference between the initial and final pH (pH_f) values ($\Delta\text{pH} = \text{pH}_0 - \text{pH}_f$) was plotted against the pH₀. The point of intersection of the resulting curve is at which ΔpH_0 gave the PZC. The particular chemical and physical properties that have been shown by previous works in the literature using the X-ray

diffraction analysis indicate that the RHA mainly consists of amorphous materials [15].

2.2. Chemicals and Reagents

Chemicals used for all the experiments are of analytical grades. Distilled-deionized water was used in all experiments and preparation of reagents.

2.2.1. Buffer preparation

Different pH buffers were used over a range of 3-8 to study the effect of pH on the removal efficiency of the adsorbent. For maximum range of pH, the initial pH (pH_0) of the adsorbate solution was adjusted using 1 M (36.5 g/L) HCl or 1 M (40 g/L) NaOH aqueous solution without any further adjustment during the sorption process except the effect of pH experiments. Laboratory pH meter (Hanna, pH 211 microprocessor) was used for measurement of pH during the experiments.

2.2.2. Preparation of metal solutions

Metal ions solutions were prepared by dissolving analytical grade $Cd(NO_3)_2 \cdot 3H_2O$ and $Pb(NO_3)_2$ (Merck, Germany) in distilled-deionized water to obtain 1000 mg/L of solution. The stock solutions were diluted to the required concentrations for the experiments. The pH of the solution was measured and observed as 5.5, and no chemicals were added to change pH except for the pH experiments.

Metal ion concentrations were determined using Perkin Elmer A Analyst 200(USA) Atomic Absorption Spectrophotometer (with deuterium arc background correction). The instrument operating conditions (i.e., wavelength and slit width) were set according to the operating manual. Each sample was read in triplicate to get the average concentration and was corrected for the volume of acid used in sample preparation.

2.2.3. Preparation of anionic surfactant micelles

Sodium dodecyl sulfate ($C_{12}H_{25}SO_3Na$, SDS) was purchased from Merck Chemical Company as certified grade. Various concentrations of the surfactant solution were prepared accordingly by dissolving appropriately weighed amounts in distilled-deionized water. SDS solutions (0.25-1.5%, w/v) were prepared at concentrations above the critical micelle concentration (CMC) (0.1728 - 0.2304 %, w/v) to ensure the complete micelles formation.

2.3. Batch Adsorption Experiments

Batch adsorption tests were conducted by mixing varying known weights of rice husk ash (RHA), fixed and varied concentration of surfactant, SDS (0.25 – 1.5%, w/v) and solutions of known

metal-ions concentration (in the range 10-100 mg/L). The mixture was shaken on a mechanical shaker and 5 mL portion of the solution was withdrawn from the reaction flask at known time intervals. The sample was then filtered using Whatman No.42 filter paper to remove any fine particles and analyzed for the metal ions. Series of experiments were conducted to determine the effects of combined doses of rice husk ash amount and surfactant concentration, initial metal ion concentration, contact time, effect of solution pH and equilibrium isotherms. The metal solutions initial pH (pH_0) was at 5.5 (except for effect of pH experiments) and all the experiments were conducted at room temperature at 25 °C (except for effect of temperature experiments). The metal removal rate (R) was calculated from Equation 1[16].

$$R = \frac{C_i - C_e}{C_i} \times 100 \quad (1)$$

Where, C_i and C_e are initial and equilibrium metal concentrations respectively. The metal uptake capacity, q of RHA in the presence of surfactant micelles was calculated from the difference between the initial and equilibrium concentrations as shown in Equation 2.

$$q = \frac{(C_i - C_e)V}{M} \quad (2)$$

Where, q (mg/g) is the adsorbed metal quantity per gram of RHA at any time, M (g) is the adsorbent dose; V (L) is the solution volume.

2.4. Adsorption isotherm experiments

For single metal-ion-RHA- DS^- systems, initial metal ion concentration was varied from 10 to 100 mg/L. In binary metal ion mixture-RHA- DS^- systems, for each initial concentration of Cd^{2+} and Pb^{2+} solution; 10, 20, 30, 50 and 100 mg/L of either Cd^{2+} or Pb^{2+} solutions were varied in the range of 10-100 mg/L (10, 20, 30, 50 and 100 mg/L). In all cases, the (pH_0) of solution was maintained at 5.5 for Cd^{2+} and Pb^{2+} .

2.5. Theory of Adsorption Behavior of Heavy Metals on Anionic Surfactant Micelles

Polar moiety with negative charge and non-polar moiety with neutral charge are present in anionic surfactant molecules. A surfactant molecule forms micelles by aggregation with other surfactant molecules at surfactant concentration greater than the critical micelle concentration (CMC).

These micelles' surfaces are surrounded by negative charges. Columbic attraction results in binding of metal ions to the surface of these micelles. The behaviour of surfactants at interfaces is determined by a number of forces, which include electrostatic attraction, covalent bonding, hydrogen bonding, hydrophobic bonding and solvation of various species [17].

3. Results and Discussion

3.1. Absorbent and Its Characteristics (RHA)

The results of the physicochemical characterization of the RHA are presented in Table 1. The pH solution of the RHA was 7.5 while specific surface area was 177 m²/g and bulk density was 0.386 g/cm³. The results of the proximate chemical composition revealed very high amount of inorganic ash and the predominance of silicon dioxide (silica) amongst other selected oxides determined (Table 2). The point zero charge (PZC) of the RHA was determined to assess the role of the RHA in the removal of the metal ions from aqueous medium and to ascertain the influence of pH on the metal ions removal. Interaction of cations with the surface of a material is favored at pH > pH_{PZC}, while the interaction of anions is favored at pH < pH_{PZC} [14].

Table 1. Proximate physicochemical characteristics of RHA

Physicochemical characteristics	Values
pH _{solution}	7.5
Bulk density(g/cm ³)	0.386
Point zero charge (PZC)	8.0
Particle size distribution (μm)(%)	
<63*	54.50
90-63	16.54
90-125	12.82
>125	16.14
Volatile matter (%)	4.14
Moisture (%)	2.10
Specific surface area* (m ² /g)	177

Table 2. Chemical Composition of RHA

Chemical Composition	Value
SiO ₂	96.34
K ₂ O	2.31
MgO	0.45
Fe ₂ O ₃	0.20
Al ₂ O ₃	0.41
CaO	0.41

The result of the zero point of charge of the RHA ($\text{pH}_{\text{PZC}} 8.0$) is presented in Fig. 1. A value of 8.3 has been reported as the point zero charge of RHA [10].

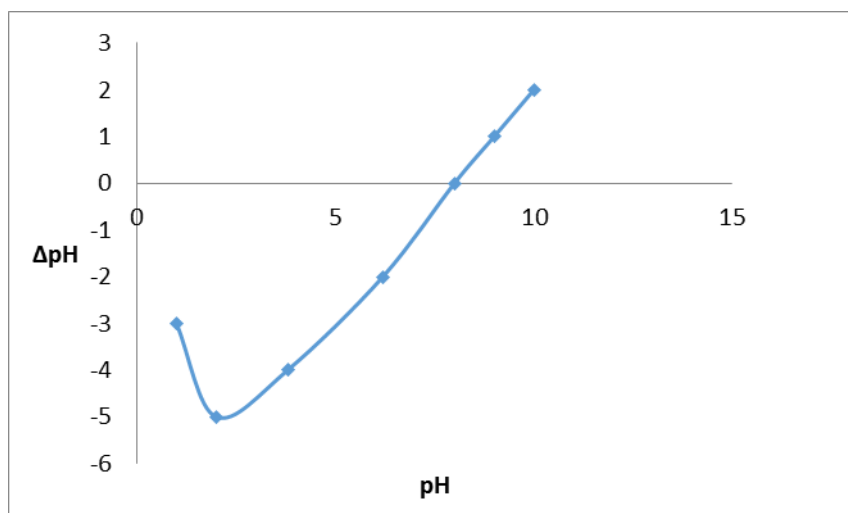


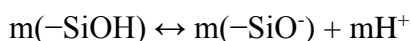
Fig. 1. Determination of point of zero charge (PZC) of the RHA surface

3.2. Adsorption Experiment

Different batch experiments were conducted to study the effect of anionic surfactant micelles on the removal of metal ions by rice husk ash from aqueous bulk solution. The ability of SDS micelles to aid or increase the adsorptive capacity of RHA was also investigated. The probable interactions between the SDS micelles, RHA, RHA-SDS and the M (metal ions) are delineated below:

$M^+ \text{-} DS^-$ interaction: Columbic interaction takes place between metal ions and surfactant micelles surrounded by negative charges, and as such, metal ions will be adsorbed on the micelles surface. It has been reported that anionic micelles have a higher affinity for divalent species [18]. This is an advantage in the preferential adsorption of divalent metal ions in the presence of monovalent metal ions.

$M^+ \text{-} RHA$ interaction: M^+ -RHA interaction could result in metal ions getting adsorbed on the surface of the RHA. The adsorption of metal ions on hydrous oxide surface can be explained on the basis of surface complex formation model. The hydrolysis of silicon dioxide produces hydrous oxide surface group $-\text{SiOH}$ (silanol group). Silica surface formed has weak acidity ($\text{pK}_a = 6\text{-}8$) [17]. Silica being the predominant component of RHA, the sorption process could proceed by cations exchange reaction through substitution with protons from the silanol groups. Interaction may be represented thus [19]:



Overall reaction:



M⁺-RHA-DS⁻ interaction: As a result of the spheres of negatively charged molecules contribution from the surfactant micelles and the complete solubilization of the adsorbent species in the aqua system, intra-particle contact between the metal ions and the RHA is enhanced, thereby increasing the solid phase concentration of the metal ions and promotes sweeping adsorption of the metal ions. The DS⁻ molecules characteristic feature is their tendency to adsorb at the surface/interphase mostly in an oriented fashion [18]. The organized micelles could be of importance in the adsorption kinetics and equilibria of the metal ions and RHA interaction.

3.2.1. Effect of RHA dose alone as adsorbent, m_s

Various doses of RHA alone were studied to ascertain the effect of varying the doses of the adsorbent on the uptake of Cd²⁺ and Pb²⁺ ions from aqueous solutions. Increasing the adsorbent dose, m_s , from 1 to 10 g resulted in an increasing trend for the percentage adsorption of Cd²⁺ and Pb²⁺. The metal ions removal efficiency increased from 11.4% to 57.7% for Pb²⁺ adsorption and 12.5% to 64.0% for Cd²⁺ adsorption. Similar trends have been reported in the literature [10, 20]. The increase in metal ions removal with increasing adsorbent dosages can be attributed to the availability of more surface area and adsorption sites. However, it was observed that at adsorbent doses of $m_s > 8.0$ g, the metal ions removal capacity of RHA remained constant (Fig. 2). This can be attributed to the fact that equilibrium has been established and the surface is saturated.

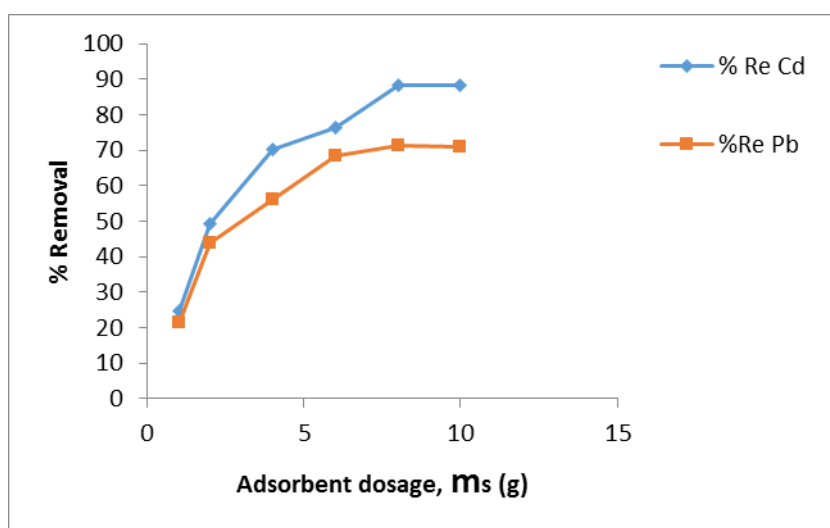


Fig. 2. Effect of adsorbent dose on the removal of Pb²⁺ and Cd²⁺ by RHA from aqueous media

3.2.2. Effect of RHA/SDS combination

In comparison with results obtained for Pb^{2+} and Cd^{2+} ions using RHA alone, an improvement in the value of the percentage metal ions removal was recorded when the metal ions were adsorbed in the aqueous SDS solutions. 8.0 g of colloidal RHA particles in 0.5% w/v SDS solution was used to investigate the removal efficiency of the combination. Maximum removal efficiencies of the metals ions attained were 71.8 and 88.9 % for Pb^{2+} and Cd^{2+} respectively. There was an increase in the adsorption/removal of Cd^{2+} aqueous solution than that observed for Pb^{2+} in the presence of SDS micelles. It is clear that counter ions bind to surfactant micelle surface due to columbic attraction and the adsorption behavior of metal ions on micelles is related to both aqueous ionic strength because of competitive adsorption between metals and the hydrate radius of metals [18]. The optimum surfactant concentration was also studied to determine the micellar concentration that yields optimum removal of the metal ions in combination with RHA. SDS concentration was varied within the range of 0.25 – 1.0 % w/v. The results obtained shows that the initial adsorption rate and metal ions removal capacity (RHA/SDS) increased steadily with the surfactant concentration as shown in Fig 3. The optimum surfactant concentration used for further investigation was 0.5% w/v and above this concentration there was no significant difference in the equilibrium adsorption capacity (q) of the RHA/SDS for the metal ions.

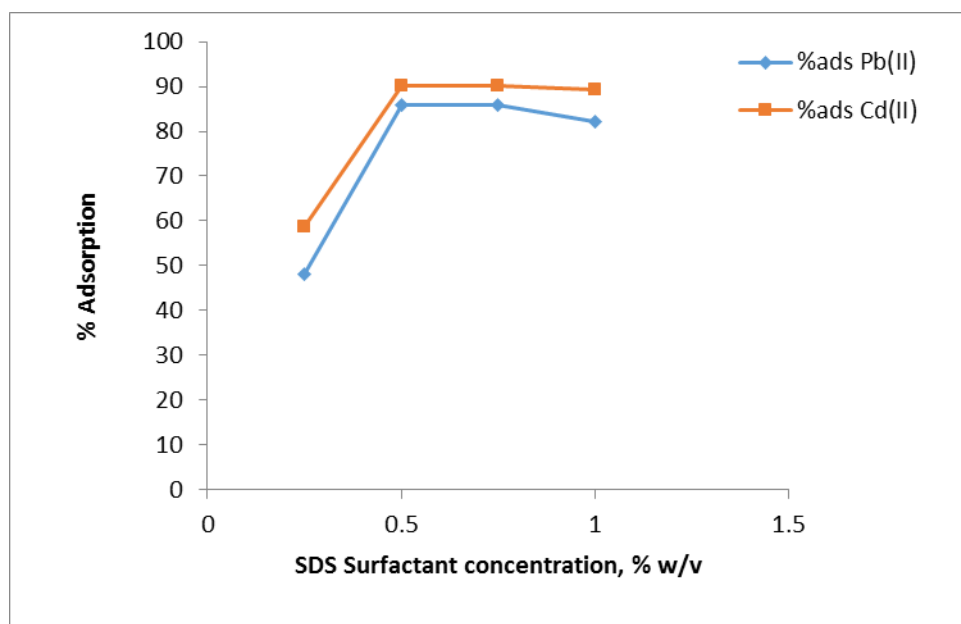


Fig. 3. Effect of anionic surfactant concentration on the adsorption of Pb^{2+} and Cd^{2+} ions

3.3. Process Optimization

3.3.1. Effect of pH

Adsorption processes are highly pH dependent. The pH of solutions influences the adsorbent

surface charge and the extent of ionization of the metal species being adsorbed or removed. The influence of pH as reported by Vimal et al [10], is a balance of competitive forces: H^+ and OH^- ions with the metal hydrolysis products (metal ions) for the active sites on adsorbents. At low pH (<3) protonation takes place on the adsorbent surface and hence adsorbs anions favorably, whereas, the surface is active for cations /metal ions adsorption at higher pH due to the deposition of OH^- ions [16]. However, as pH increases the possibility of formation of insoluble hydrolyzed species such as metal hydroxides also take place by co-precipitation, which is undesirable.

In order to optimize the effect of pH on the removal of metal ions from aqueous solutions, the experiments were conducted at the established optimum adsorbent dose of RHA and the SDS micellar solution concentration. The pH was varied between 3 and 8. This range was chosen because it has been reported that charge variability on silica surfaces (the principal RHA component) is pH dependent with isoelectric point occurring at approximately pH 2 (pure silica) and the charge becomes negative between pH 6 and 11[17]. Due to the fact that, Studies were limited to the range of pH 3 and 8 as higher pH leads to metal precipitation. Three different initial concentrations of metal ions were used (10, 50 and 100 mg/L). It was observed that the percentage removal of Pb^{2+} and Cd^{2+} ions for aqueous solutions was appreciable at pH between 6 and 8, though the optimum percentage Pb^{2+} and Cd^{2+} ions removal occurred at pH 8 (Fig. 4). This could be explained on the basis of surface charge density of the silanol groups and other functional groups such as hydroxyl, carboxyl, amino and others present at the surface the RHA [21].

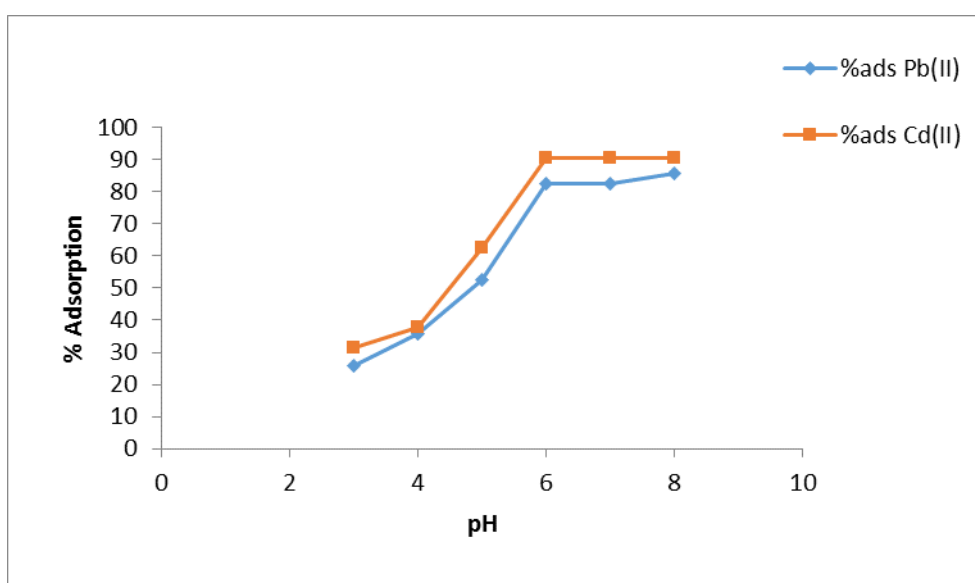


Fig. 4. Determination of the effect of pH on the adsorption of Pb^{2+} and Cd^{2+} ions

The measurement of the point of zero charge (PZC) of the RHA showed that the PZC occurs at about pH 8.0 (Fig. 1). From the results of the PZC it could be inferred that metal ions would be

chemically adsorbed onto RHA at pH values greater than the pH of PZC. For $\text{pH} > 8$, the adsorption seems to be due to the net result of ion exchange and surface complexation.

3.3.2 Effect of initial metal ion concentration (C_0)

The effect of the initial concentration of the metal ions on the adsorption capacity of the studied metal ions onto RHA/SDS was studied. Increasing the initial metal ion concentration in aqueous solution increased the amount of both metal ions adsorbed (Fig. 5). This has been attributed to the increasing driving force of metal ions towards active sites on the adsorbent. Maximum metal ions removal was observed at an initial concentration of 100 mg/L.

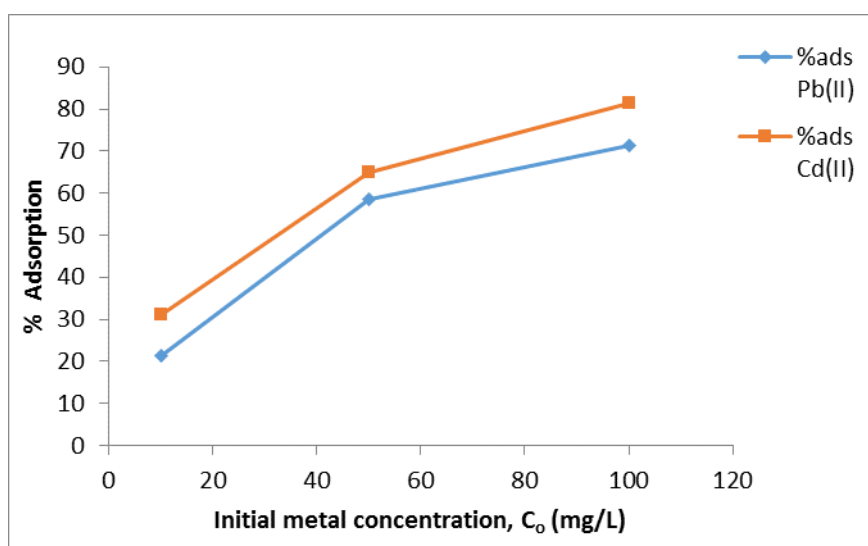


Fig. 5. Effect of initial metal ion concentration on the removal of Pb^{2+} and Cd^{2+} by RHA/SDS from aqueous solution

3.3.3 Effect of contact time

Metal ions solutions of 100 mg/L were kept in contact with the adsorbents (in aqueous SDS solution) for 24 hours. These were checked intermittently at given time intervals. Metal removal was found to be at the maximum in 120 minutes contact time and the removal difference was found not to be greater than 0.5 % after 24 hours contact time. Accordingly, all batch experiments were conducted with a contact time of 120 minutes under thorough agitation. Fig. 6 shows the metal ions adsorption (%). The rates of the Pb^{2+} and Cd^{2+} ions removal were very rapid during the initial 30 minutes, and thereafter, the rate of metal ion removal decreased. The change in the residual concentrations of the metal ions unadsorbed after measurement showed no significant difference. For 300 minutes contact time, it was observed that there was total attenuation of the adsorption process. It can be concluded that during the initial adsorption process stage, large number of vacant active sites are available for adsorption. After lapse of some time, the remaining sites become difficult to occupy due to repulsive

forces between the solute molecules on the solid surface and bulk phase. This is a probable reason for the adsorption process to become slow during the later periods.

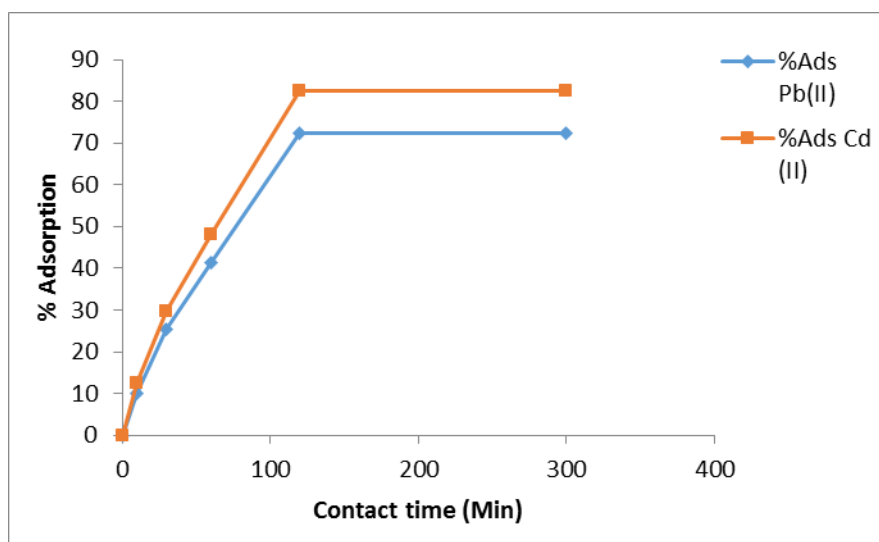


Fig. 6. Effect of contact time on the removal of Pb^{2+} and Cd^{2+} by RHA/SDS from aqueous solution

From the results, the 120 minutes (2 hours) equilibration time achieved in this study could be attributed to the presence of the anionic micelles. Longer equilibration time for adsorption of metal ions onto RHA has been reported; Vimal et al reported an equilibration time of 180 minutes (3 hrs) for the adsorption of Cd^{2+} , Zn^{2+} and Ni^{2+} onto RHA; El-said et al has reported an equilibration of 120 minutes for the adsorption of cadmium and mercury ions from aqueous solution by RHA [10][20].

3.4. Adsorption Isotherms

The adsorption isotherms of Pb^{2+} and Cd^{2+} ions onto RHA (in the presence of anionic micelles) were plotted from determined and calculated parameters. Adsorption isotherms give the relationship between adsorption capacity and concentration of the remaining adsorbate at constant temperature. In this study, equilibrium sorption data were fitted into Langmuir and Freundlich isotherm equations.

3.4.1. Langmuir isotherm

Figs. 7 and 8 illustrate the plots of Cd^{2+} and Pb^{2+} ions where a straight line could be well observed between $1/q_e$ and $1/C_e$. This is an indication that the experimental data followed the Langmuir's isotherm. Monolayer adsorption capacity, Q^0 (mg/g), the constant related to the energy of adsorption, b (Lg^{-1}), dimensionless separation factor, R_L and the correlation coefficients, R^2 were calculated from these plots and the results are summarized in Table 3. The Langmuir parameters i.e. Q^0 increased with temperature (Table 4). High temperatures increased the kinetic energy of the metal, thus, enhancing the mobility of the metal ions. This leads to a higher chance of the metals being adsorbed

onto the adsorbent and an increase in its adsorption capacity.

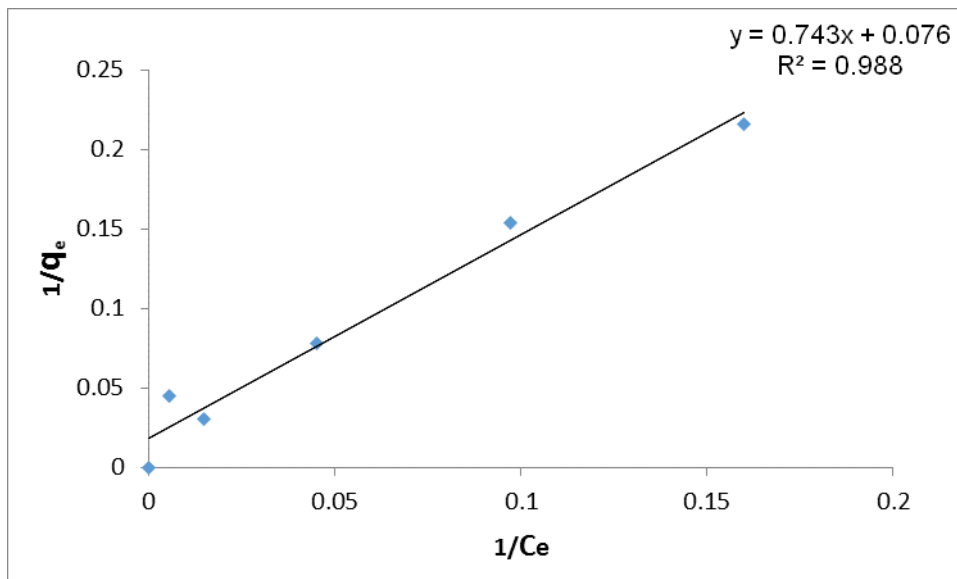


Fig. 7. Langmuir isotherm for Cd²⁺ adsorption by RHA /SDS

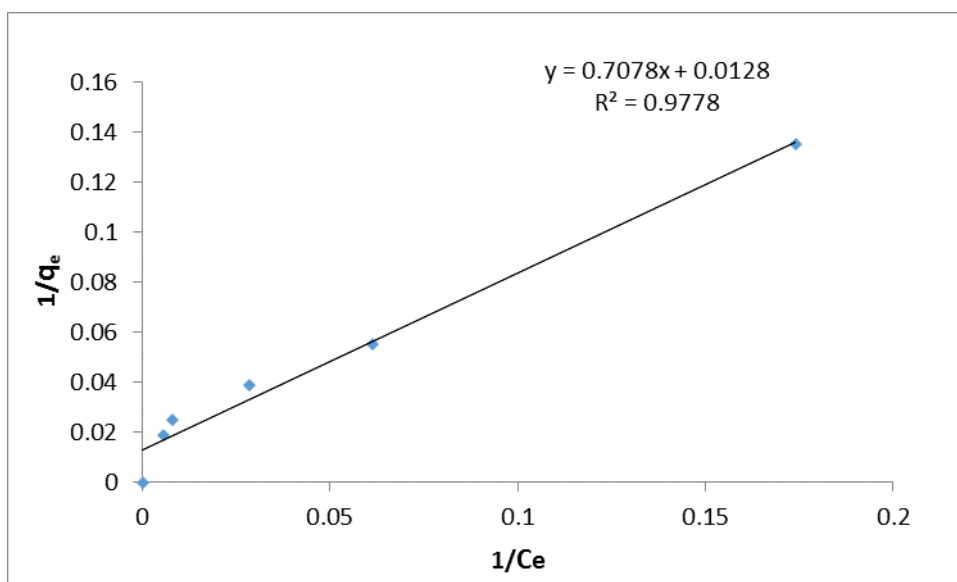


Fig. 8. Langmuir isotherm for Pb²⁺ adsorption by RHA/SDS

3.4.2. Freudlich isotherm

Figs 9 and 10 illustrate the plots of Cd²⁺ and Pb²⁺ ions adsorption isotherms, these adsorption isotherms incorporate the adsorption capacity and intensity, and also C_e and q_e which are the remaining concentration of adsorbate after equilibrium and the amount adsorbed at equilibrium respectively. The Freundlich constants (1/n and K_F) were calculated from the slope and intercept of the plots (Table 3). Where K_F is a constant indicative of relative adsorption capacity (mg/g) and 1/n is the intensity of adsorption.

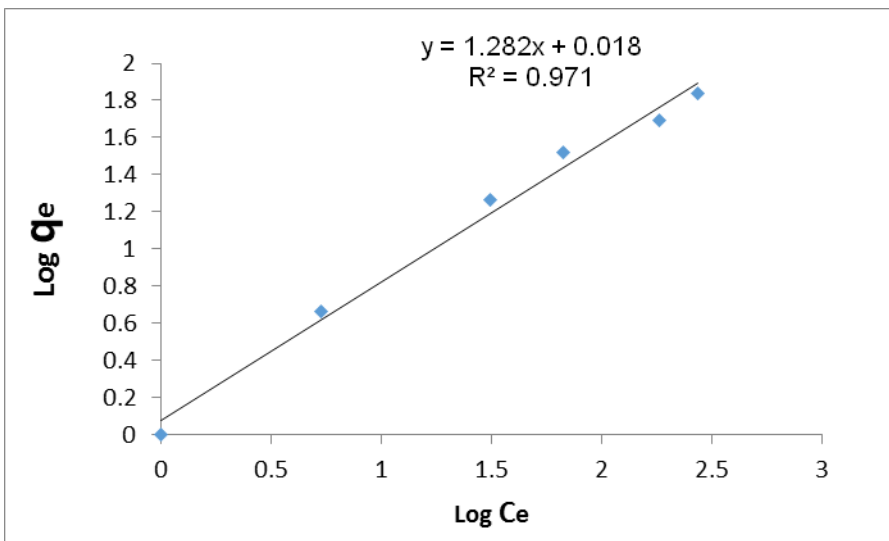


Fig. 9. Freundlich isotherm for Cd²⁺ adsorption by RHA/SDS

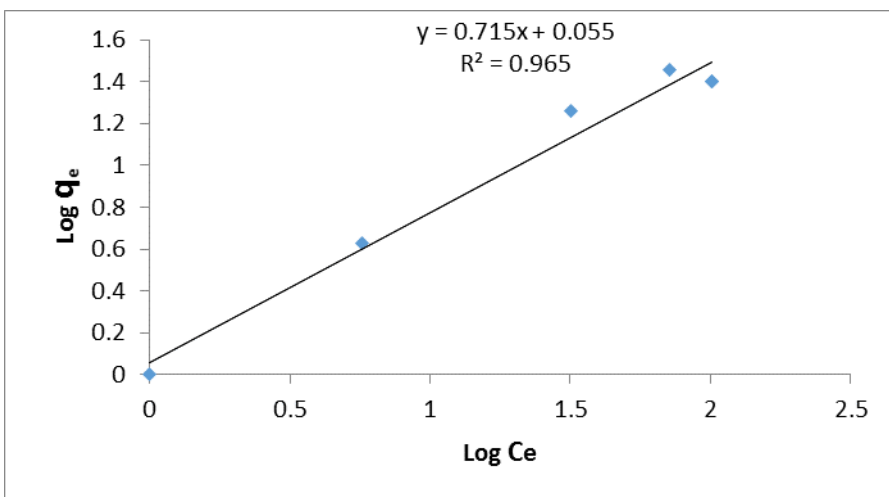


Fig. 10. Freundlich isotherm for Pb²⁺ adsorption by RHA/SDS

The values of $1/n < 1$ at different temperatures (25, 40 and 60°C) confirmed a favorable adsorption onto the adsorbent in aqueous SDS solution. The results indicated that the RHA/SDS showed more adsorption affinity for Cd²⁺ ion. Furthermore, Cd²⁺ adsorption was found to have higher b value than Pb²⁺ at all the temperature values studied (Table 4), indicating higher efficiency of removal for Cd²⁺ than Pb²⁺. The Langmuir isotherms were found to be more suitable as the data fitted well into the Langmuir equation and higher correlation coefficient, R² values were equally obtained in Langmuir isotherms (Tables 3 and 4).

Table 3. Langmuir and Freundlich isotherms parameters value (@ 25°C)

	Langmuir				Freudlich		
	Q ^o (mg/g)	b	R ²	R _L	K _F (mg/g)	1/n	R ²
Pb²⁺	101.01	0.065	0.977	0.135	7.61	0.423	0.965
Cd²⁺	103.10	0.082	0.988	0.098	8.59	0.625	0.971

3.4.3. Effect of temperature on metal uptake

The adsorption of Pb²⁺ and Cd²⁺ onto RHA in the presence of the anionic micelles was favored at higher temperatures as shown in Table 4. This indicated that chemical adsorption could potentially be the nature of the adsorption of Pb²⁺ and Cd²⁺ onto the RHA/SDS. The results demonstrated that an increase in the temperature from 25 to 60°C led to an increase in the adsorption capacity. Higher removal levels for Pb²⁺ and Cd²⁺ were observed at higher temperature range. This was probably due to the increasing tendency of adsorbate ions to adsorb from the solution to the interface with increasing temperature. The increase of the equilibrium uptake at increased temperature indicated that the adsorption of Pb²⁺ and Cd²⁺ ions to the RHA/SDS was potentially endothermic [22].

Table 4. Effect of varying temperatures on metal ions of Pb and Cd adsorption by RHA/SDS

	Temp. (°C)	Langmuir			Freudlich		
		Q ^o (mg/g)	b(L/mg)	R ²	K _F (mg/g)	1/n	R ²
Pb²⁺	25	101.01	0.065	0.977	0.74	0.42	0.965
	40	105.34	0.110	0.965	0.20	0.22	0.889
	60	108.57	0.190	0.992	0.40	0.52	0.977
Cd²⁺	25	103.10	0.082	0.988	0.59	0.625	0.971
	40	108.80	0.254	0.976	0.63	0.712	0.976
	60	111.32	0.455	0.997	0.78	0.812	0.990

3.4.4. Effect of binary metal ion

The simultaneous adsorption of Pb²⁺ and Cd²⁺ ions from binary mixtures were studied at optimized adsorption conditions. The results are presented in Figs 11 and 12. The concentration of the primary metal ion was held constant (100 mg/L) while the secondary metal ion was varied between 10 and 100 mg/L. The equilibrium uptake/removal percentage of Pb²⁺ ion decreased with increasing Cd²⁺ ion concentration (Fig. 11). Similar trend was observed for that of Cd²⁺ removal from aqueous solution

(Fig. 12). However, the percentage removal of Cd^{2+} from the binary aqueous mixtures of the metal ions was higher than that observed for the Pb^{2+} ion. The effects of the presence of a metal ion(s) on the adsorption of another metal ion(s) in multi-component systems are usually represented by the ratio of the sorption capacity for one metal in the presence of other metal ion, Q^{mix} , to the sorption capacity for the same metal when it is present alone in the solution, Q^0 [16]. It has been demonstrated that Q^{mix} , the total adsorption capacity for metal ions in binary solution, would become less than the individual metal ion adsorption capacity (Q^0) in single system if the metal ions interaction in the binary system is antagonistic [23].

From the results presented in Table 5, the Q^{mix} of both Pb^{2+} and Cd^{2+} values on the experiments were less than the Q^0_{Pb} and Q^0_{Cd} . Generally, both metal ions compete for the adsorption sites on the RHA. The higher percentage removal of Cd^{2+} ion shows a stronger affinity for the adsorption of Cd^{2+} ion onto the RHA adsorbent surface than for Pb^{2+} ion. El-Said et al, have reported that RHA has a stronger affinity for Cd^{2+} ion in the presence of other divalent metal ions [20]. It was however observed in this study that the level of antagonistic sorption attributes of both metal ions were seen to be reduced in the micellar mediated sorption of Pb^{2+} and Cd^{2+} ions from their aqueous binary mixtures. This can be attributed to the adsorption capacity and binding of the anionic micelles to the positively charged metal ions, thereby introducing synergistic removal of the metal ions from aqueous solutions.

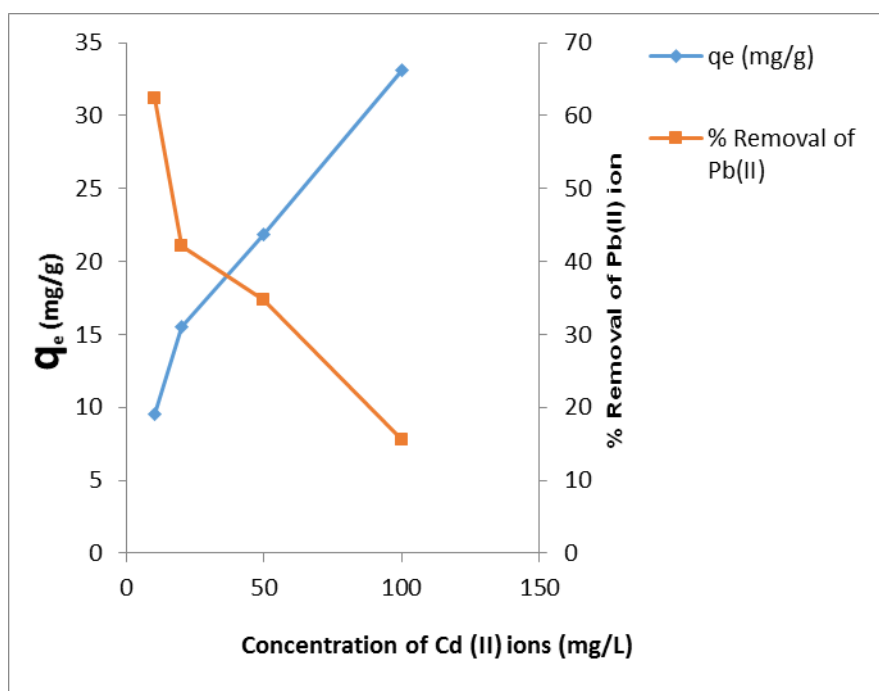


Fig. 11. Determination of the effect of the presence of Cd^{2+} on Pb^{2+} adsorption onto RHA-DS⁻

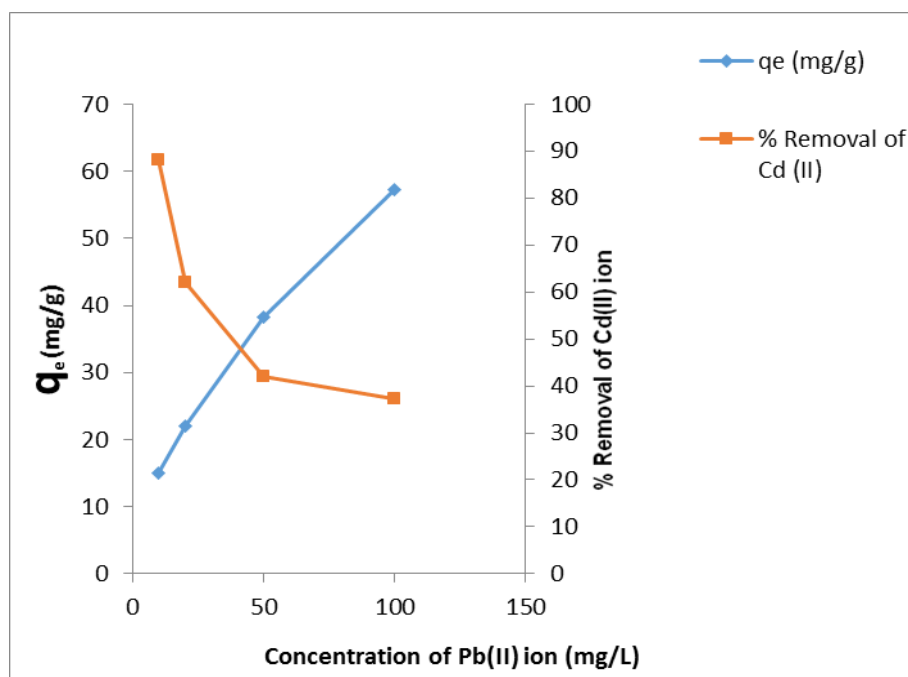


Fig. 12. Determination of the effect of the presence of Pb²⁺ on Cd²⁺ adsorption onto RHA-DS⁻

Table 5. Effect of binary metal ions adsorption on the adsorptive capacity of RHA.

*Binary solution	Q ^o of Cd ²⁺ single system	Binary System		
		Q ^m Cd ²⁺	Q ^m Pb ²⁺	Q ^{mix} (total)
Cd ²⁺ with Pb ²⁺	103.1	57.2	21.3	78.5

*Binary solution	Q ^o of Pb ²⁺ single system	Binary System		
		Q ^m Pb ²⁺	Q ^m Cd ²⁺	Q ^{mix} (total)
Pb ²⁺ with Cd ²⁺	101.01	33.1	15.0	48.1

4. Conclusion

This research work, adds to the increasing interest in the pursuit of heavy metals removal from wastewater and water bodies contaminated with toxic heavy metals. The use of low cost adsorbent material and the enhanced sorption process of lead and cadmium ions by the combination of anionic surfactant and rice husk ash are described in this study. The removal of lead and cadmium ions in single and binary solutions were found to be dependent on pH of solution, initial metal ions concentration, contact time, adsorbent (RHA) dosage and surfactant (SDS) concentration. The

monolayer and adsorptive capacities for both metal ions were found to increase with increase in temperature range studied (25-60°C). The equilibrium data were fitted into Langmuir and Freundlich models. Langmuir isotherms gave a better model. Adsorptive removal of the metal ions in binary mixtures were found to be antagonistic, this was however minimal in the presence of the anionic surfactant micelles. The process herein, is cost effective and attractive, which might help to reduce the disposal problems posed by the abundance of the rice husk and the ash generated. It is found in this study that combining rice husk ash and anionic surfactant of sodium dodecyl sulfate (SDS) significantly improves the adsorptive capacity of the rice husk ash, with an improvement in sorption time for both metal ions. Thus a potent, efficient and low cost alternative is added to the arrays of adsorption processes by natural adsorbents currently used in heavy metal removal from aqueous systems.

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