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Synergistic Adsorptive Removal of Urea from Agricultural Effluents Using Ball Clay and Sepiolite Composite

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Abstract

Agriculture effluents have become a big problem since water is the basic component of all operation in agriculture practice. These effluents composed of agrochemicals such as fertilizer, pesticides, herbicides, crop residues are the pollutants of agricultural effluents. Lakes, rivers and streams often receives water run-off from farmlands. Nitrates and urea in the water bodies are toxic to aquatic lives by causing depletion of oxygen in water making it unfit for human and aquatic life. This research assessed the adsorptive removal of urea from agricultural effluent by means of thermally activated ball clay and sepiolite composite (TABCSC) and non-activated ball clay and sepiolite composite (NABCSC) as absorbent. The adsorption process was done at Varying amounts TABCSC (0.6g - 4.5g), pH range of 3 - 11, time (30 - 90 minutes) and temperature $(25 – 45 °C)$ as recommended by design expert version 13. TABCSC and NABCSC characterized by means of Fourier transformed infrared spectroscopy (FTIR) and scanning electron microscope (SEM) reveals the presence of large surface area, porosity as well as the functional groups: hydroxyl, carboxylic, hydrogen bonding and aldehyde group that aids adsorptive removal of urea. The highest adsorptive removal efficiency by TABCSC was found to be 99.23% (at pH = 7, temperature = $25 °C$, dosage = 0.6 g and time = 60 minutes) while that of NABCSC was at 93.23% (at pH = 11, temperature = $35 °C$, dosage = 0.6 g and time = 60 minutes). The adsorptive removal of urea was found to increase with increase in pH value and contact time. The adsorptive removal mechanism of Urea by TABCSC was more fitting to the second order kinetics (R^2 = 0.9770) while removal by NABCSC aligns with the pseudo first order kinetics (R^2 = 0.9770). The isotherm of the removal process conforms more to the Freundlich isotherm of TABCSC (R^2 = 0.9995) and NABCSC (R^2 = 0.9671) respectively.
Keywords: Urea; Ball clay; Sepiolite; Composite; Adsorptive capacity and efficiency.
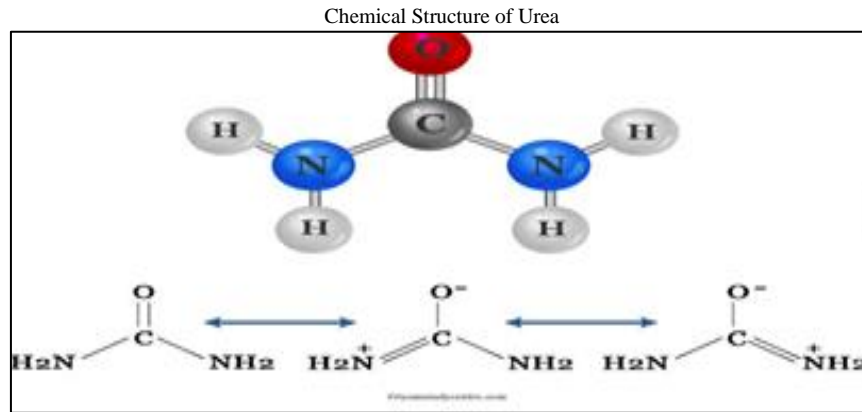
1. Introduction

Urea an organic compound known as carbamide has utilized in agriculture because of its high content of nitrogen among all forms of solid nitrogenous fertilizers. Statistically, worldwide use of urea fertilizer increased more than 100-fold, accounting for more than 50% of the global nitrogen fertilizer usage during the past few decades [1]. While the application fertilizer boosts the production of crops, making food affordable to even the low socio-economic classes, nutrient application that exceeds plant needs is a potential pollutant of surface and groundwater [2]. The increased use of chemical-based fertilizer in agricultural revolution could result in continued rise in concentration of chemical pollutions in fresh water reservoir due to the water run-off from fields carrying agricultural chemicals such as herbicides (weed killers) and pesticides which exist as residues on and in the soil [3, 4].

When plants nutrients from organic or synthetic fertilizers, decayed plant residues and agricultural waste such as wastewater from diaries gets into fresh water, they speed up eutrophication of water bodies; the process through

which water body gradually age and become conducive for growth of microorganisms while unfit for aquatic lives [5]. The fundamental reason for the treatment of wastewater is to circumvent the effect of pollution of water sources and protect public health through safeguarding of water sources against the spread of diseases.

The treatments used in water purification include: physical treatment, chemical treatment and biological treatment. The selection of a particular treatment technique primarily depends on a variety of factors, like waste type and concentration, treatment objectives, effluent heterogeneity, required level of cleanup, as well as economic factors [6].

Urea is a charge-neutral molecule with one oxygen atom and two nitrogen atoms serving as hydrogen bond acceptors, and two amino functions providing a total of four hydrogen bonds for donation. The product is highly water soluble, hence found in agricultural effluent.

Chemical Structure of Urea

Water containing urea can be remediated by methods such as: Hydrolysis of urea, biological method using microbes; chemically by decomposition of urea with strong oxidants to produce nontoxic gases like nitrogen and carbon dioxide [7] or by catalytic decomposition of urea using Pt/SiO_2 catalyst [8]. Use of adsorbents like activated carbons, zeolites, ion-exchange resins, silica and porous polymers. The aim of this research is to assess the adsorptive removal efficiency of urea from agricultural effluent by means of ball clay and sepiolite composite as adsorbent.

Ball clays are kaolinitic clays with chemical formula $(Al_2O_3.2SiO_2.2H_2O)$ normally comprise of 20 - 80% kaolinite, 10 - 25% mica, 6 - 65% quartz, as well as organic matter trances. The product is formed from the weathering and is found to exhibit excellent adsorption capacity over a wide concentration range. Likewise, Sepiolite is an opaque, off-white, grey or creamy colored material of hydrous magnesium silicate with the chemical formula $Mg_4Si_6O_{15}(OH)_2\cdot 6H_2O$ [9].

The experimental design and number of experimental runs to be carried were gotten by means of Response Surface Methodology (RSM) a collection of statistical and mathematical techniques useful for developing, improving, and optimizing processes. It combines design of experiments, regression analysis and optimization methods in a general purpose strategy to optimize the expected value of a stochastic response [10]. At the same time, could recommend the optimum condition of the process. It also has important applications in the design, development, and formulation of new products, as well as in the improvement of existing product designs.

The field of response surface methodology consists of the experimental strategy for exploring the space of the process or independent variables, empirical statistical modeling to develop an appropriate approximating relationship between the yield and the process variables, and optimization methods for finding the values of the process variables that produce desirable values of the response. In general, the relationship is;

$$y = f(\xi_1, \xi_{2,} \dots \xi_k) + \varepsilon \qquad\qquad 1$$

where the form of the true response function f is unknown and perhaps very complicated, and ε is a term that represents other sources of variability not accounted for in f. Usually ε includes effects such as measurement error on the response, background noise, the effect of other variables, and so on.

There is a close connection between RSM and linear regression analysis. This relationship is described by the model;

$$y = \beta_o + \beta_1\chi_1 + \beta_2\chi_2 + \dots + \beta_k\chi_k + \varepsilon \qquad\qquad 2$$

The β's are a set of unknown parameters. To estimate the values of these parameters, we must collect data on the system we are studying. Because, in general, polynomial models are linear functions of the unknown β's, we refer to the technique as linear regression analysis. Response surface designs can be readily analyzed using statistical packages such as SAS, MINITAB, STATISTICA, or Design Expert [11].

2. Materials and Methods

2.1. Chemicals

Nessler Reagents (Reagent "A" code HI93700A-0 and Reagent "B" code HI93700B-0, Hydrogen chloride (HCl), Sodium hydroxide (NaOH), Sodium sulphate (Na_2SO_4), Catalyst mixture (Na_2SO_4 + $CuSO_4.5H_2O$),

Concentrated H_2SO_4, Boric acid, Sodium thiosulphate pentahydrate $Na_2SO_4.5H_2O$ and Mix indicator (methylene blue + red).

2.2. Sampling

Sepiolite and ball clay were obtained from Central drug house (P) Ltd. 7/28 Vardaan, Daryaganj, New Delhi-110002 (INDIA). Agricultural effluents were obtained from Rafin Kada Wukari, at 5 different points as presented in Table 1 after which, the 5 samples were homogenized in equal properties to obtain a composite sample.

Table-1. Sampling Points

Sample	Point coordinate
Sample A	7°706292 N, 9°891290E
Sample B	7°706108N, 9°891313E
Sample C	7°706597N, 9°891117E
Sample D	7°706249N, 9°891134E
Sample E	7°706965N, 9°890627E

Location: Rafinkada

2.3. Sample Preparation and Conditioning

166.618g of raw composite was calcined in a muffle furnace at 600°C for 1 h. It was then cooled, sealed in an air tight container and labeled as TABCSC for future use. The percentage yield was calculated using the mathematical formula below;

$$Percentage\ yield = \frac{calcined\ weight}{Raw\ material\ weight} \times 100 \qquad 3$$

Varying amounts of thermally activated composite (0.6g - 4.5g) as designed by the design expert software were weighed into 25 different 100 mL of agricultural effluents. The same process was carried out for Non-activated (raw) composite. Drop-wise addition of 0.1 M NaOH and 0.1 M HCl were used to adjust the pH of the solution with the aid of a pH meter until the desired pH (Range from 3-11 as proscribed by design expert) was obtained. The solutions were stirred at varying time (30 – 90 minutes) and varying temperature (25 - 45ºC) (as proscribed by design expert software) with the aid of mechanical shaker and a water bath respectively until equilibrium was achieved. The solution was then filtered. The various filtrates were subjected to urea analysis to determine the residual urea content.

2.4. Characterization of Ball Clay and Sepiolite

The FT-IR was carried using the KBr disk method [12]. Where a few crystals were mixed with KBr (Merck for spectroscopy) and pulverized in an agate mortar to form a homogenous powder from which, under a pressure of 7 tons, the appropriate pellet was prepared. All spectra were recorded from 4000 to 400 cm^{-1} using the Pelkin Elmer 3000 MX spectrometer. Scans were 32 per spectrum with a resolution of 4 cm^{-1}. The IR spectra were analyzed using the spectroscopic software Win-IR Pro Version 3.0 with a peak sensitivity of 2 cm^{-1}. Surface morphology of adsorbents (Ball Clay and Sepiolite) were determine by scanning electron microscopy.

2.5. Determination of Urea using Modified Kjeldahl Method

10 mL of sample filtrate each was measured into 500 mL Kjeldahl digestion flask. 15 mL mixture of salicylic + H_2SO_4 was added and thoroughly swirled, before it was allowed to stand overnight. 0.5g of $Na_2SO_4.5H_2O$ was added. The mixture in the flask was gently heated until frosting ceased. The flask was gently cooled and 2 g of catalyst mixture added and digested for 2h – 3h. After digestion was complete the samples were allowed to cool and transferred into a 100 mL volumetric flask and also made up to the mark with distilled water. 20 mL of the 2% Boric acid was measured into a 100 mL conical flask and was introduced to the bottom of a condenser of the Kjeldahl distillation set after the addition of 3 to 5 drops of mix indicator. 10 mL of the digest was measured using pipette into a distillation flask and also10 mL of 10N NaOH was added to liberate the Ammonical-N. The sample was distilled off and collected up to 50 mL combined volume in the conical flask (Green colour). The distillate was then titrated with 0.025N H_2SO_4 which had a color change of green to purple, which signaled its end point. Ammonical-N (NH_4-N) and Urea content were estimated using the equations 4 and 5.

Calculations

$$Ammonical\text{-}N\ (\%) = \frac{0.014 \times T - B \times N \times vol\ of\ Dg \times 100}{volume\ of\ sample \times Aliquote} \qquad 4$$

Urea is obtained by the following relations U = (%) = Ammonical–N × 2.14

$$Urea\ (mg.L^{-1}) = \frac{NH_4 - N \times 2.14}{10^4} \qquad 5$$

2.6. Data Analyses

The adsorption capacity (q_e) and adsorptive removal efficiency (R_e) were calculated using the concentration difference between the initial concentration and the equilibrium concentration displayed in equations 6 and 7. Where C_o = initial concentration of ammonium, C_e = equilibrium concentration of ammonium, M = mass of adsorbent (ball clay), V = solution volume and Re = adsorptive removal efficiency [13].

$$Adsorption\ capacity\ (q_e) = \frac{C_o - C_e}{M} \times V \qquad 6$$

$$\text{Removal efficiency (R}_e) = \frac{C_o - C_e}{C_o} \times 100 \qquad\qquad 7$$

To evaluate the adsorption kinetics of ammonium, the pseudo-first order kinetic model and pseudo-second-order kinetic model were employed as shown in equations 8 and 9 where K_1 and K_2 are constants of the equilibrium rate [14].

$$\text{Pseudo-first order kinetic model: } \log(q_m - q_t) = \log q_m - \frac{k_1}{2.303}t \qquad 8$$

$$\text{Pseudo-second order kinetic model: } \frac{t}{q_t} = \frac{1}{k_2 q_m^2} + \frac{1}{q_m}t \qquad 9$$

Where K_1 and q_m can be obtain from the plot of $\log(q_m - q_t)$ versus (t) which gives $\frac{k_1}{2.303}$ as slope and $\log q_e$ as intercept for the pseudo-first order kinetic model similarly for the pseudo second order, the kinetic constant k_2 and the theoretical q_m can be calculated from the plots of $(\frac{t}{q_t})$ versus (t).

To further analyze the adsorption mechanism, the Langmuir and Freundlich isotherm models were adopted [14].

$$\text{Langmuir: } \frac{C_e}{q_e} = \frac{1}{K_2 q_o} + \frac{C_e}{q_o} \qquad\qquad 10$$

A plot between C_e/q_e versus C_e will generate a straight line with a slope of $1/q_o$ and an intercept equals to $1/k_2 q_o$.

$$\text{Freundlich: } \ln q_e = \ln b + \frac{1}{n}\ln C_e \qquad\qquad 11$$

A plot of $\ln q_e$ versus $\ln C_e$ produces a straight line with a slope= $1/n$ and intercept = ln b.

3. Results and Discussion
3.1. Characterization of Adsorbents

To determine the surface morphology of the adsorbent, Scanning electron microscope (SEM - JEOL, JSM 7600 F) was used. Figure 1 showed the morphology of thermally activated ball clay (TABC) and not activated ball clay (NABC) at 8,000, 9,000 and 10, 000 magnifications respectively. The micrograph of TABC shows significant compact tubular crystals and mono-disperse particle size on the surface compared to NABC, which increases the surface active site of the adsorbent for adsorption [15].

Figure-1. Scanning Electronic Microscope of TABC (A) and NABC (B) At 8,000, 9,000 and 10,000 magnification
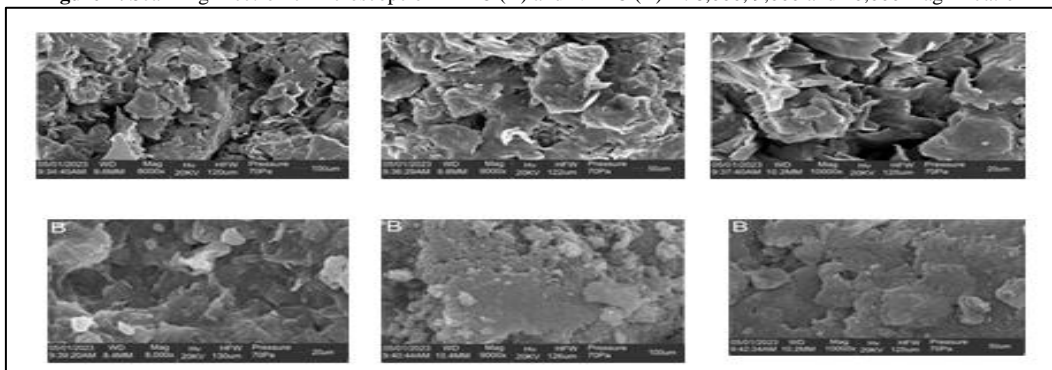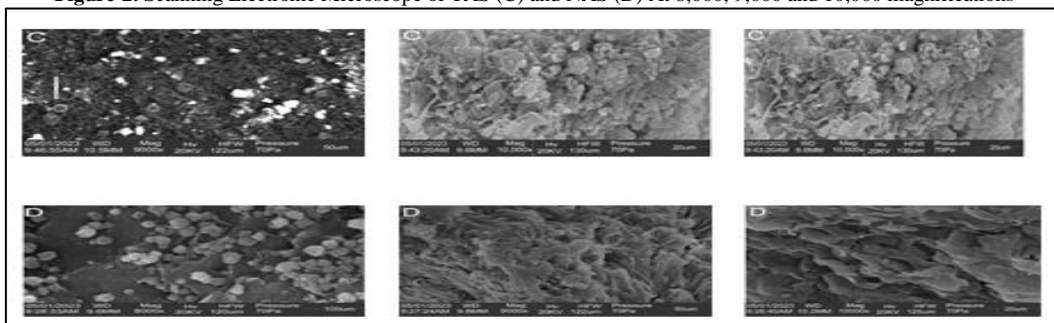

Figure 2 showed a similar feature smaller size of particles with fine porous structure in Nano-scale range. However, the non-activated sepiolite clay (NASC) exhibits more porosity and surface area compared to the thermally activated sepiolite clay (TASC), which enhanced adsorption capacity. Good adsorbents have specific properties such as large pores, availability of oxygen, hydrogen content and Hydroxyl group [16]

Figure-2. Scanning Electronic Microscope of TAS (C) and NAS (D) At 8,000, 9,000 and 10,000 magnifications

The FTIR spectrum is important in identification of surface functional groups, which plays a great role in adsorption mechanism, and capacity of an adsorbent [16].

The FT-IR analysis of TABC and NABC shown in Figure 3 indicates a peak at 3394.00 cm^{-1} within the frequency range of (3000-4000 cm^{-1}) due to stretching vibrations of O-H groups. The band at 3394 is connected with the internal -OH stretching from hydroxyl groups [17]. The bands at 1633.33 cm^{-1} and 1388.00 are attributed to -OH bend vibration [18]. The broad band at 1033.45 cm^{-1} is attributed to Si-O in-plane stretching vibration [19]. The

characteristic sharp bands at 912.26 cm^{-1} is assigned to the Al−O−H bending vibration (hydroxyl groups sitting on the alumina faces) [14]. The peak at 668.00 cm^{-1} are attributed to C-H bend. The peak at 535.00 cm^{-1} is attributed to C-l stretching. The peaks at 428.00 cm^{-1} and 360.22 cm^{-1} are attributed Al-O-Si octahedral vibration on the thermally activated ball clay [20].

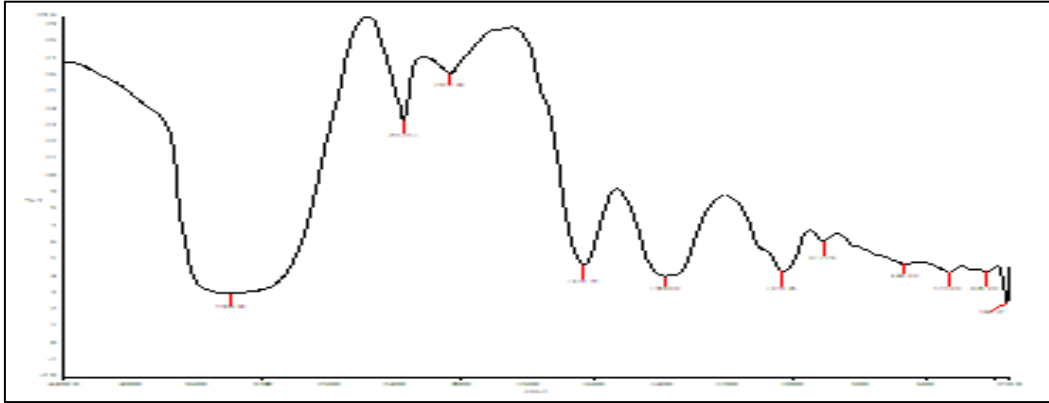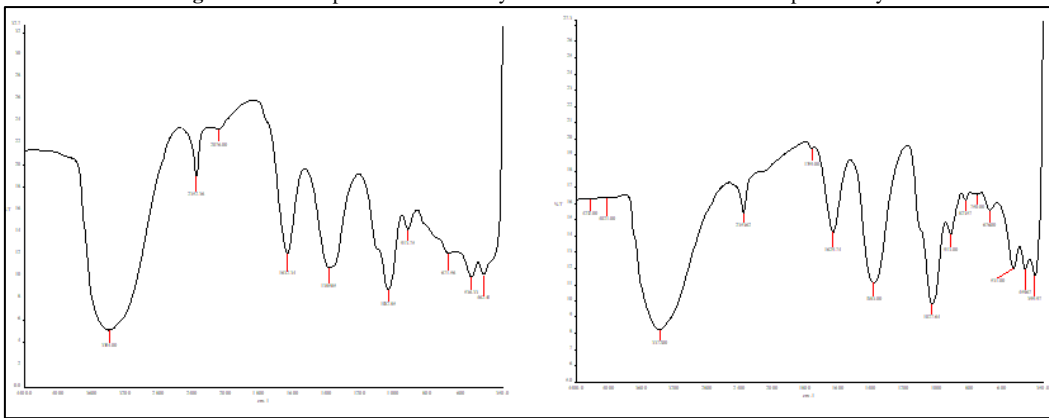**Figure-3.** FTIR Spectrum for Thermally Activated and Non Activated Ball Clay

Figure-4. FT-IR Spectra for Thermally Activated and Non Activated Sepiolite clay

3.2. Batch Adsorption Experiments

Base on design expert recommendation, 25 batches of experimental runs were carried out for urea removal from agriculture effluent within the varying conditions: temperature (25 - 45ºC), dosage of ball clay adsorbent (0.5g - 5g), varying pH (3 - 11) and contact time (30 - 90 minutes) with the corresponding residual urea content after adsorptive removal as displayed in Table 2. The optimum condition for the adsorptive removal of urea in the effluent by TABCSC was at pH of 7, temperature of 25°C, dosage of 0.6 g and contact time of 60 minutes while by NABCSC was achieved at a temperature of 35°C, dosage of 0.6g, pH of 11 and contact time of 60 minute and at a temperature of 45°C, dosage of 2.55g, pH of 7 and contact time of 90 minute with residual concentrations of 0.0077 mg/L and 0.0666 mg/L for TABCSC and NABCSC respectively.

Table-2. Optimization of Urea Adsorption Removal Condition and Residual concentrations of urea in aquaculture effluent at varying condition

Std	Run	Factor 1 A:Temperature ... oC	Factor 2 B:Dosage (D) g	Factor 3 C:pH	Factor 4 D:Time (t) Min	Response 1 TABCSC Conc o... mg/ml	Response 2 NABCSC Conc ... mg/ml
7	1	25	2.55	3	60	0.0677	0.0677
11	2	35	2.55	11	90	0.0677	0.068
2	3	45	2.55	7	30	0.0667	0.0677
20	4	35	2.55	11	30	0.0677	0.6103
13	5	35	4.5	7	90	0.0677	0.0677
24	6	45	2.55	11	60	0.0677	0.0677
3	7	35	2.55	3	30	0.0682	0.0677
10	8	35	0.6	7	30	0.0677	0.0677
22	9	35	0.6	7	90	0.0668	0.6103
14	10	25	2.55	7	30	0.0668	0.6103
9	11	35	2.55	3	90	0.0677	0.0677
12	12	35	2.55	3	60	0.0668	0.0677
6	13	25	0.6	7	60	0.0077	0.0677
5	14	35	0.6	11	60	0.0677	0.0666
4	15	45	2.55	7	90	0.0677	0.0666
25	16	45	2.55	7	60	0.0677	0.0686
21	17	45	4.5	3	60	0.0668	0.0677
15	18	35	0.6	7	60	0.0683	0.0677
8	19	35	4.5	3	60	0.0677	0.0682
16	20	35	4.5	11	60	0.0677	0.0682
17	21	25	0.6	11	60	0.0677	0.0675
23	22	45	2.55	7	90	0.0677	0.0677
19	23	35	2.55	3	60	0.339	0.0677
1	24	25	4.5	7	30	0.8814	0.339
18	25	35	2.55	7	60	0.6103	0.0677

TABCSC = Thermally activated ball clay and sepiolite composite, NABCSC = Non-activated ball clay and sepiolite composite, Conc. = Concentration

3.4. Adsorptive Removal Efficiency of Urea

The adsorptive removal efficiency of urea displayed in Table 3 revealed 11.86% to 99.23% removal efficiency by TABCSC and 38.97% to 93.34% by NABCSC. The optimum removal efficiencies were greater than the 82.4% removal of urea using natural zeolite while the 95.5% efficiency obtained using modified zeolite gave better result than NABSC [21]. However, the amounts of urea removed by 600 biochar - peroxymonosulfate and 900 biochar - peroxymonosulfate were 57% and 70%, respectively suggesting better adsorption by TABCSC and NABSC [22].

Table-3. Percentage Efficiency of Thermal and Non-Thermal Activated Ball Clay and Sepiolite Composite

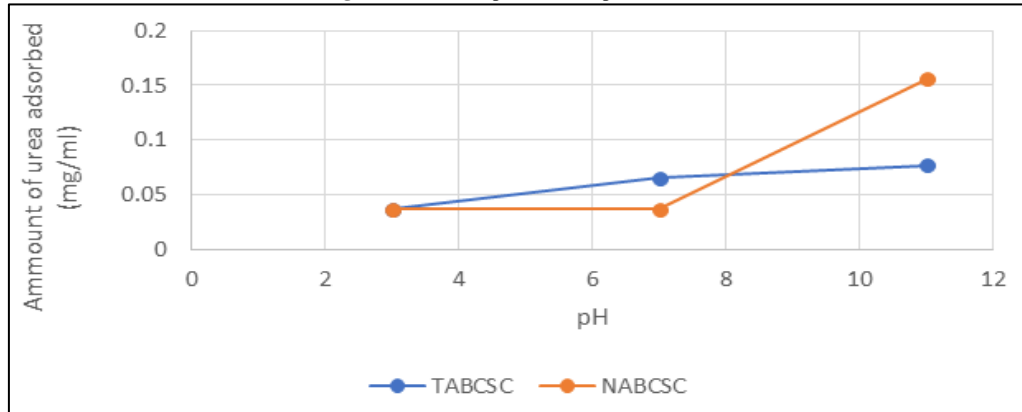| S/N	TABCSC Qe (mg/L)	TABCSC Re (%)	NABCSC Qe (mg/L)	NABCSC Re (%)
1	0.0365	93.23	0.0365	93.23
2	0.0365	93.23	0.0365	93.2
3	0.0366	93.33	0.0365	93.23
4	0.0365	93.23	0.01528	39.7
5	0.0207	93.23	0.0207	93.23
6	0.0365	93.23	0.03656	93.23
7	0.0365	93.18	0.0356	93.23
8	0.1553	93.23	0.1553	93.23
9	0.1555	93.23	0.0649	38.97
10	0.0365	93.32	0.0152	38.97+
11	0.0356	93.23	0.036	93.23
12	0.0365	93.32	0.365	93.23
13	0.1653	99.23*	0.155	93.23
14	0.1553	93.23	0.155	93.34*
15	0.0356	93.23	0.036	93.34*
16	0.0356	93.23	0.036	93.14
17	0.02073	93.32	0.0207	93.23
18	0.1552	93.17	0.1553	93.23
19	0.0207	93.23	0.0207	93.18
20	0.02071	93.23	0.0207	93.18
21	0.1553	93.23	0.01125	93.25
22	0.0356	93.23	0.0365	93.23
23	0.0259	66.1	0.0365	93.23
24	0.0026	11.86+	0.01468	66.1
25	0.0152	38.97	0.0365	93.23

Key: Qe =Equilibrium concentration, Re =Removal efficiency, * = Optimum, + = Minimum

3.4. Effect of pH on Adsorption of Urea

The optimum condition for the adsorptive removal of urea in the effluent by TABCSC was at pH 7, temperature of 25°C, dosage of 0.6 g and contact time of 60 minutes while by NABCSC was achieved at a temperature of 35°C, dosage of 0.6g, pH of 11 and contact time of 60 minute and at a temperature of 45°C, dosage of 2.55g, pH 7 and contact time of 90 minute with residual concentrations of 0.0077 mg/L and 0.0666 mg/L for TABCSC and NABCSC respectively.

From the result obtained, it was observed that optimum removal was achieved at pH 11, which may be due to increase in electrostatic attraction between the adsorbate and adsorbents. As shown in Figure 5; when the pH approaches alkaline at 11, there was an observed increase in mean amount of ammonia adsorbed from 0.036 mg/mL to 0.076 mg/mL for TABCSC while from 0.036 mg/mL to 0.15 mg/mL for NABCSC respectively due to attraction between the adsorbate - adsorbent surface [23].
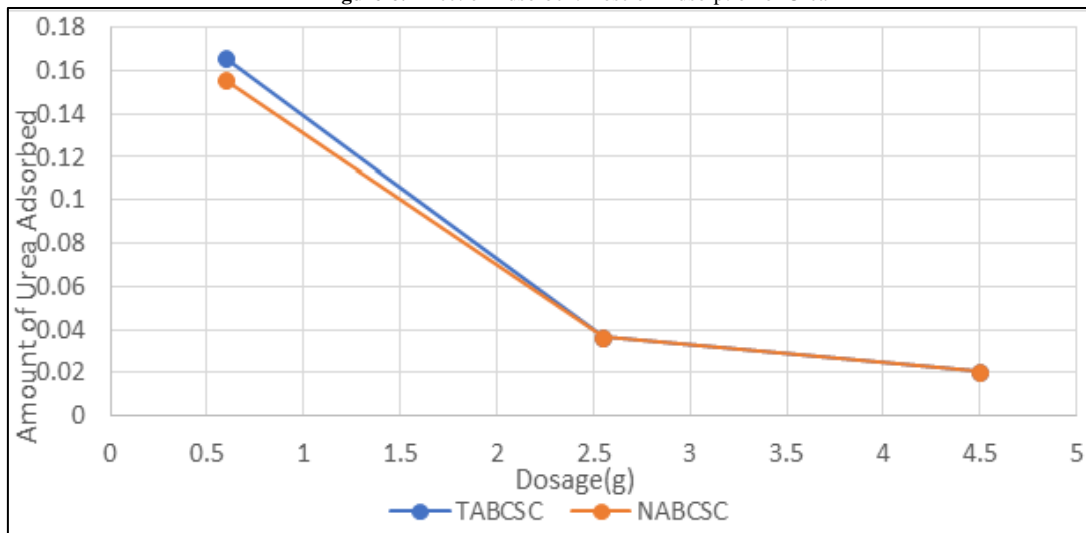
Figure-5. Effect of pH on Adsorption of Urea

3.5. Effect of Adsorbent Dosage on Urea Adsorption

The effect of adsorbent dosage on the removal of urea by TABSC and NABSC shows a decrease in removal on increasing of adsorbent dosage. As shown in Figure 6; when the adsorbent dosage was increase from 0.66 g to 4.50g the mean removal decrease from 0.16 g/mL to 0.020 mg/Ml for TABCSC while from 0.015 mg/mL to 0.020 mg/mL for NABCSC respectively.
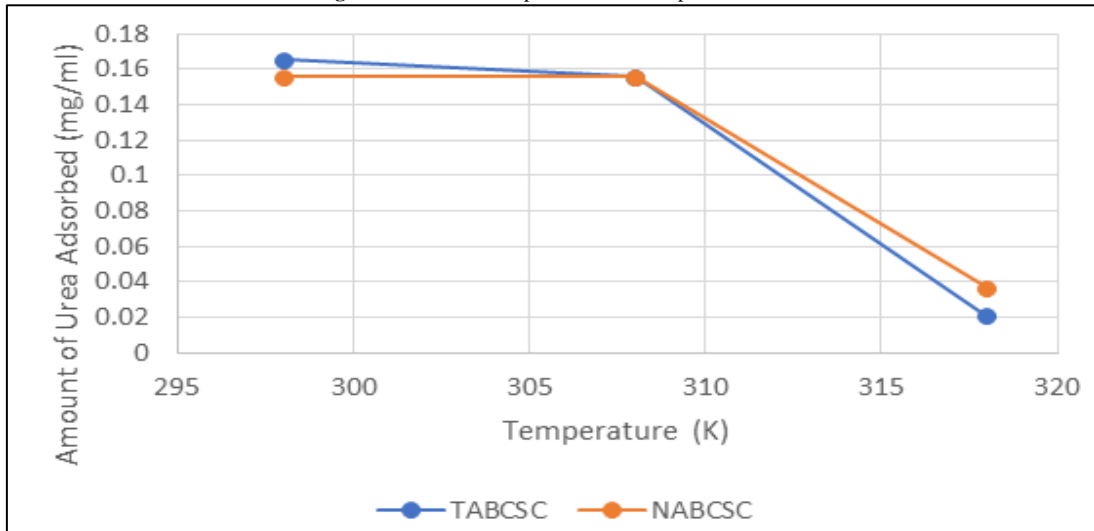
Figure-6. Effect of Adsorbent Dose on Adsorption of Urea

3.6. Effect of Temperature on Urea Adsorption

Figure 7 shows that as the temperature increases and the amount of urea adsorbed decreases by TABSC and NABSC respectively. When the temperature was increase from 298K to 318K the mean removal decrease from 0.16 g/mL to 0.020 mg/Ml for TABCSC while from 0.015 mg/mL to 0.036 mg/mL for NABCSC respectively. This may be attributed to increased entropy by urea molecules [24].
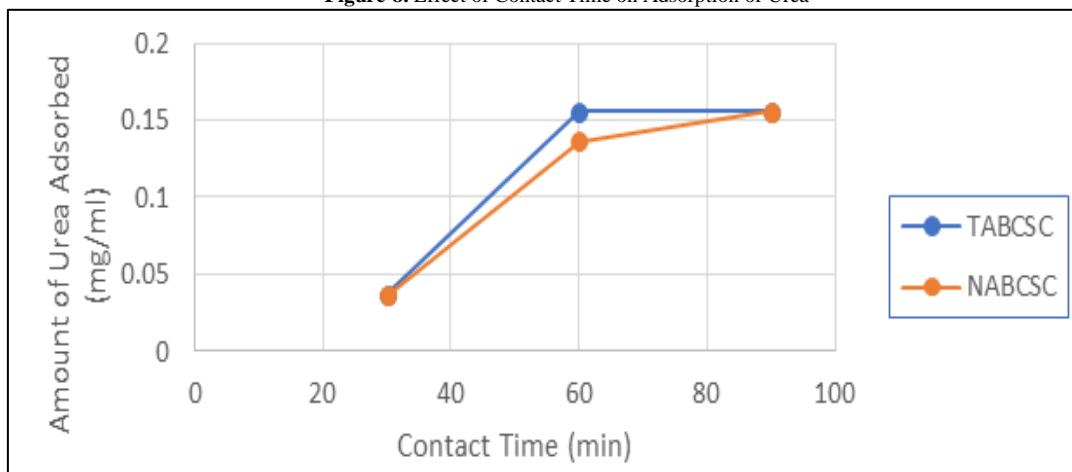
Figure-7. Effect of Temperature on Adsorption of Urea

3.7. Effect of Contact Time on Urea Adsorption

Effect of contact time on the mean amount of urea adsorbed is demonstrated in Figure 8 revealing that as the temperature increases and the amount of urea adsorbed increases by TABSC and NABSC respectively. For instance when the contact time between the adsorbate and adsorbent was increased from 30 to 90 minutes the mean amount of urea adsorbed increases from 0.036 g/mL to 0.155 mg/mL for both TABCSC and NABCSC respectively. Adsorption rate appeared to be very fast in the first 30 minutes, which could be explained to high number of adsorption sites from the start [15]. As the time increased, the adsorption sites became gradually saturated until equilibrium was attained at 90 minutes [25].

Figure-8. Effect of Contact Time on Adsorption of Urea

3.9. Adsorption Kinetic Model

Kinetics data's obtained from the effect of contact time on adsorption of urea when fitted into the kinetic models are shown in Table 4. The results revealed that both first and second order kinetic model could describe the mechanism of urea adsorption by TABSC and NABSC. However, from their correlation coefficient R^2, it was observed that the adsorptive removal mechanism of Urea by TABCSC was more fitting to the second order kinetics ($R^2 = 0.9770$) while removal by NABCSC aligns with the pseudo first order kinetics ($R^2 = 0.9770$). While the Blanchard pseudo-second order gave a better fittings for with R^2 values ranging from 0.9477 - 0.977 with the corresponding the pseudo-second order rate constant K_2 was in the range 0.0983 - 0.0985 g.mg^{-1}min^{-1} as compared with the Lagergren pseudo-first order which gave lower R^2 values ranging from 0.878- 0.977 and k_1 from 0.5355 to 0.7720 min^{-1}. The high value of R^2 for the second – order shows that the pseudo second order best describes the whole adsorption processes by TABSC indicating that chemisorption is predominant on all adsorbents as the rate determining step while pseudo first best describe removal by NABCSC indicating physisorption [26].

Table-4. Kinetic Parameters for Urea Adsorption on Adsorbents

Model	Parameters	TABSC	NABSC
First Order	K_1 (min^{-1})	0.5355	0.7720
	Qe (mg/g)	1.4397	1.3011
	R^2	0.8777	0.9770
	K_2 (min^{-1})	0.0983	0.0985
	Qe (mg/g)	1.5686	2.7365
Second Order	R^2	0.9770	0.9477

3.10. Adsorption Isotherms for Urea Removal

This Langmuir isotherm model is based on the assumption that adsorption occurs at homogeneous sites and forms a monolayer [27]. The theoretical values of Langmuir constants Q_m and K_L were calculated from the slope and intercept of a linear plot of 1/Qe versus 1/Ce respective. These values indicate the total number of binding sites that are available for adsorption [26]. From the values of the Langmuir isotherm calculated from the experimental data with the dimensionless constant called separation factor, R_L, the values were found to be all < 1 and > 0 indicating a favorable adsorption for all adsorbent [28]. The results of correlation coefficients R^2 on the adsorption of urea as described by both Langmuir and Freundlich isotherms in Table 5, the Freundlich gave the highest R^2 value than Langmuir during the adsorption process by TABSC and NABSC. This means that the Freundlich model best described the experimental data and can be concluded based on this model that the active sites on the adsorbents surface were homogeneously distributed and form a monolayer adsorption [29].

Freundlich isotherm assumes that adsorption takes place on heterogeneous surface of the adsorbent [27]. From the Freundlich equation stated earlier in equation 6, the K_F and n_F are obtained from slope and intercept of the plot of logQe versus logCe. For Freundlich model results in Table 5, the K_F value obtained for TABSC (1.0097), was less than NABSC (1.3179) which suggest TABSC to be more potent for adsorption of urea [28]. Adsorption is favorable for values > 1 and unfavorable for values < 1 for the adsorption intensity n_F [30]. This indicates that adsorption is favorable for urea. Adsorption is heterogeneous rather than homogeneous due to the higher R^2 values obtained from Freundlich isotherm and from the fact that the adsorbent was a composite of ball cay and sepiolite [27]. The isotherm parameter, 1/n values were 0.6795 and 0.7485 for TABSC and NABSC were both < 1 indicating a favorable adsorption processes [23].

Table-5. Isotherm Parameters for Urea Adsorption on Adsorbents

Model	Isotherm Parameters	TABSC	NABSC
Langmuir Isotherm	Qm (mg/g)	0.4775	0.4476
	K_L	0.703	0.9689
	R^2	0.9041	0.8608
	R_L	1.4223	1.0321
	K_F	1.0097	1.3179
Freundlich Isotherm	R^2	0.9995	0.9671
	1/n	0.6795	0.7485
	n_F	1.4717	1.3360

4. Conclusion

Thermally activated ball clay and sepiolite composite (TABSC) and Non-activated ball clay and sepiolite composite (NABSC) exhibited good physicochemical attributes as adsorbents. With excellent adsorption removal efficiency for urea, though the efficiency was affected by varying condition of pH, adsorbent dosage, temperature and contact time. The kinetics of urea removal was best described by the pseudo first order kinetics and second order kinetics for NABCSC and TABCSC while the isotherm of the removal process conforms more to the Freundlich isotherm. The use of thermally activated ball clay and sepiolite composite will help more in removing urea from agricultural effluent compared with the non-activated. However further studies can be carried out on the various modifications of the composite to find out the best modification for urea removal.

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