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Facile Method by Bentonite Treated with Heat and Acid to Enhance Pesticide Adsorption

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Abstract: In this work, simple conditions were applied to modify bentonite for the removal of pesticides from aqueous solution. Bentonite was modified in a single step as BA_{0.5} (with HCl 0.5 M) and BC₅₀₀ (calcined at 500 °C) and combined steps with different sequences (BA_{0.5}C₅₀₀ and BC₅₀₀A_{0.5}). These adsorbents were characterised by XRD, XRF, FT-IR, ²⁷Al MAS NMR, BET, NH₃-TPD, TGA, HPLC, particle size analysis and zeta potential. Single-component adsorption with atrazine, diuron, 2,4-D and paraquat was used in aqueous solution at various pesticide concentrations, contact times and pH levels. It was found that the sequence of the treatment significantly affected atrazine adsorption. BC₅₀₀A_{0.5} exhibited the highest efficiency for atrazine adsorption in a broad pH range of 3.0–9.0. Its adsorption at pH 6.0 was about 12 times greater than that of other adsorbents with an initial atrazine concentration of 50 mg L^{−1}, which indicates BC₅₀₀A_{0.5} specifically for the adsorption of atrazine. In addition, for the simultaneous adsorption of all four pesticides, BC₅₀₀A_{0.5} was found to remove the maximum total amount of the pesticides, indicating that it could be used as a good multifunctional adsorbent. All modified bentonites showed similar diuron adsorption better than that of unmodified bentonite. The greatest adsorption of 2,4-D prefers BA_{0.5}C₅₀₀, occurring at pH 2–4. In the case of paraquat adsorption, all adsorbents are good at absorbing paraquat, but bentonite had the highest rate of paraquat removal, whereas BA_{0.5}C₅₀₀ was found to have the lowest, and the adsorption increased with increasing pH. Furthermore, the adsorption process on the adsorbents fits well with the Langmuir isotherm and pseudo-second-order kinetics models, as the thermodynamic parameters showed a spontaneous and endothermic process.

Keywords: bentonite; pesticides; acid-activation; heat-treatment; modified clay

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1. Introduction

Toxic pesticides have a significant impact on human health as well as aquatic life. Currently, it is a topic of significant concern because of the increasing use of pesticides in agriculture and domestic activities [1–7]. Therefore, it is necessary to find ways to limit the agrochemical substances discharged into the environment as much as possible, while also acting to eventually eliminate them completely.

Adsorption is a simple and convenient method for the removal of compounds compared to other physical, chemical, or biological technologies. It also involves low investment in terms of both initial cost and land required. Various solid substrates offer good adsorptive properties, including zeolites, activated carbon, fly ash, mesoporous silica and clay minerals, which were applied in the removal of organic contaminants from water [2,8–14].

Bentonite clay minerals are available not only in Thailand, but their deposits are widespread all over the world. They are an important, low-cost source of montmorillonite and exhibit excellent adsorption capacities as well as high cation exchange capability (CEC) [15,16]. The major component of bentonite is montmorillonite, a dioctahedral smectite. Montmorillonite is a porous clay mineral consisting of a 2:1-layered structure, with alternating layers of exchangeable cations. The layers consist of octahedral alumina sheets

that are sandwiched by two tetrahedral silica sheets. Substituting Al^{3+} for Si^{4+} in the silica tetrahedral sheets and Mg^{2+} for Al^{3+} in the alumina octahedral sheets produced a net negative charge, which is usually balanced by adsorbed cations. These cations are easily replaced by either organic or inorganic cations, accounting for the unique hydrophilic, tumescent, and adsorption properties of montmorillonite [17,18]. As in previous reports, the type and concentration of the acid effect on modified clay were used for the removal of organic substance [19–22]. HCl acid is usually modified for this purpose according to its multifunctional groups such as silanol, so that it can be as efficient adsorbent. Furthermore, mild conditions can stabilise clay structure and the effect of heat used in the modification process was also promoted for the removal of organic compounds [23,24]. Acid and heat modification optimises the physical characteristics of bentonite for the removal of contaminants by causing structural and textural changes within the clay, thus enhancing the adsorption capacity. Acid and thermal treatments are low cost methods that require few chemicals and are simple to apply. Acid-activated bentonite is suitable for the removal or elimination of impurities; it increases both porous surface area and the numbers of silanol groups present in the clay, which are important for the adsorption of organic compounds [25,26]. Heat treatment significantly alters the surface properties of bentonite; it improves porosity by increasing mesopore volume, increases the number of surface adsorption sites, and increases the number of siloxane groups present while reducing the number of hydroxyl groups present [23,27–30]. In addition to these structural changes, both acid and heat treatments alter the textural properties of the clay and improve its dispersibility in water. As mentioned above, the use of heat and acid for treatments can promote pesticide adsorption performance. Thus, we are interested in using these treatments to modify bentonite by combining both treatments rather than solely with heat or acid, and we additionally consider the sequence of each treatment in the modification of bentonite in order to optimise active sites for the adsorption of different types of pesticides such as atrazine (basic), diuron (non-ionic), 2,4-D (acidic) and paraquat (cation) in aqueous media, including the investigation of the simultaneous adsorption of these pesticides to evaluate the potential of these adsorbents for application as multifunctional adsorbents. Isotherms, kinetic modelling and thermodynamic parameters of the adsorptions were investigated as well.

2. Material and Methods

2.1. Materials

Bentonite (B) was purchased from Thai Nippon Chemical Industry Co., Ltd. (Samut Sakhon, Thailand). Tables 1 and 4 list the chemical and physical properties of bentonite. Reagent grade atrazine (6-chloro-N2-ethyl-N4-(propan-2-yl)-1,3,5-triazine-2,4-diamine) (99.5% purity), diuron (3-(3,4-Dichlorophenyl)-1,1-dimethylurea) (99.6% purity), 2,4-D (2,4-dichlorophenoxy acetic acid) (99.9% purity) and paraquat (1,1'-Dimethyl-4,4'-bipyridinium dichloride) (98% purity) were obtained from Sigma-Aldrich.

2.2. Preparation of Modified Bentonite

Bentonite was sieved with a 63 μm mesh and dried overnight at 110 $^{\circ}\text{C}$ before being used in the modification. Single-step modified bentonite (modified by either acid or heat) and two-step-modified samples (modification with both acid and heat) were prepared using the following procedures:

Acid treatment: Bentonite (4 g) was activated by immersion in 100 mL HCl (37%) (AR grad, Sigma-Aldrich) at various concentrations ($x = 0.1\text{--}3\text{ M HCl}$) at 100 $^{\circ}\text{C}$ for 6 h (BA_x). Then, the mixture was centrifuged and washed with deionised-water (DI water) to ensure the removal of chloride ions, then dried in an oven overnight at 110 $^{\circ}\text{C}$. The BA_x samples were stored in a desiccator.

Heat treatment: Bentonite (4 g) was calcined at various temperatures ($y = 300\text{--}600\text{ }^{\circ}\text{C}$) for 12 h. (BC_y) was then cooled in a desiccator.

Combined acid and heat treatments: The obtained BA_x and BC_y samples were tested for atrazine, diuron, 2,4-D, and paraquat adsorption. The sample activated with 0.5 M HCl ($BA_{0.5}$) and the 500 °C heat-treated sample (BC_{500}) exhibited the best pesticide adsorption (data not shown). Therefore, the $BA_{0.5}$ and BC_{500} were selected for combined acid and heat treatment. The $BA_{0.5}C_{500}$ sample was prepared by the calcination of $BA_{0.5}$ (4 g) at 500 °C for 12 h. $BC_{500}A_{0.5}$ was prepared following the same procedure, however, using BC_{500} in place of bentonite.

2.3. Characterisation

The chemical compositions of the major elements in bentonite and modified bentonite were determined by energy dispersive XRF (EDS, Oxford Instrument ED 2000, Abingdon, UK) using an Rh X-ray tube with a vacuum medium. The CEC was determined by a 9080 CEC standard method (US EPA, OSWER), in which all adsorbed cations in a bentonite sample were replaced by a common ion, such as NH_4^+ , and then the amount of adsorbed common ion was determined. The interlayer spacing of the samples was determined by X-Ray diffraction patterns obtained from back-pressed powder samples recorded on a Bruker, D5005, Germany, Cu K α radiation, scanning from 3° to 50° at a rate of 0.05°/s at 35 mV and 35 mA. The framework and OH groups were confirmed by FT-IR spectroscopy (Spectrum GX, Perkin-Elmer, Waltham, MA, USA) as KBr pellets, over the range of 4000–400 cm^{-1} and near-IR diffuse reflection (DRIFT) in the range of 8000–4000 cm^{-1} . The DRIFT technique was especially appropriate in this region because no sample dilution was required. Specific surface and pore size distributions were evaluated by nitrogen gas adsorption at −196 °C using a BEL JAPAN, BELSORP-mini II, Japan instrument, with the Brunauer–Emmett–Teller (BET) method. All samples were characterised by solid-state ^{27}Al CP/MAS NMR (JEOL JNM-ECA600), with a static 11 T magnetic field at a spin rate of 11 kHz. The ^{27}Al CP/MAS NMR spectra were recorded at a frequency of 130 MHz. The NMR reference used was $Al(NO_3)_3 \cdot 9H_2O$ with a chemical shift of 0.00 ppm. The particle size distributions (PDS) of all samples were analysed by a Horiba laser-scattering particle-size-distribution analyser (LA-950), Japan. The active site was determined using NH_3 temperature-program desorption (TPD) apparatus (BEL Japan, model BELCAT-B, Osaka, Japan). Samples were pre-treated at 300 °C for 2 h and then exposed to a flow of NH_3 /He at 100 °C for 30 min. Weakly adsorbed NH_3 was removed by flushing with He gas at 100 °C for 30 min. The NH_3 TPD profile was obtained over the range of 100 °C–600 °C at a heating rate of 10 °C/min. Desorbed NH_3 was detected using a thermal conductivity detector. TGA curves were obtained by heating the sample in an alumina70 cell from 30 to 800 °C at a heating rate of 10 °C min^{-1} under air atmosphere using a thermogravimetric analyser (TGA-DSC, METTLER, Germany). Zeta potential measurements were performed using a Malvern, UK. Bentonite and modified bentonite slurries were homogenised using a Branson Sonifier, UK. Sonifier employs ultrasonic vibration to disperse the dry clay particle aggregates in suspensions. Before the sonication, the amount of clay powder and deionised (DI) water was kept constant at 10 wt.%. Dilution suspensions were prepared for the zeta potential measurement with a colloidal Dynamics Zeta Probe. The concentration employed was only 1 wt.% solids. The pH was increased to approximately 12 with 1 M NaOH before commencing the yield stress measurements. Concentrated HCl (1 M) was added dropwise to decrease the pH in a stepwise manner.

Atrazine, diuron, 2,4-D, and paraquat concentration were determined using UV–visible spectrophotometry at 223, 247, 283 and 257 nm, respectively (T80 + UV–Vis spectrophotometer PG instruments, Alma Park, Leicestershire, UK). The mixture solution of atrazine, diuron, 2,4-D and paraquat concentration were determined using HPLC (Hewlett Packard series 1100, Palo Alto, CA, USA). All experimental measurements were made in duplicate. The quantity of adsorbed atrazine, diuron, 2,4-D and paraquat by bentonite

and modified bentonite was calculated from the difference between the initial and final pesticide concentrations using the mass balance Equation (1):

$$q_e = \frac{V(C_i - C_e)}{M} \quad (1)$$

where q_e is the adsorbed pesticide remaining on adsorbents (mg g^{-1}) and C_i and C_e are the initial and final pesticide concentrations (mg L^{-1}), respectively. M is the mass of adsorbent (g), and V is the volume of the pesticide solution (L).

2.4. Batch Adsorption

All adsorbents were dried overnight at 110°C prior to commencing the adsorption study. Adsorption experiments were performed using a batch adsorption procedure with 20 mg of bentonite or modified bentonite added to 10 mL of pesticide solution, which was then kept in a shaker bath at 30°C for 24 h (equilibrium time ~ 12 h). The stock solution was prepared in methanol solutions; final methanol concentrations were less than 0.5% (v/v) to prevent co-solvent effects. Suspensions were centrifuged at 3500 rpm and then filtered. Each pesticide concentration in filtrates was determined by UV-Vis spectroscopy.

2.5. Effect of pH

The effect of pH on the adsorption of atrazine, diuron, 2,4-D, and paraquat by bentonite and modified bentonite was investigated over the pH range of 2.0–12.0. Pesticide solutions were prepared by dissolving the samples in distilled water. The adsorbents were exposed to the pesticide solution at a solid/liquid ratio of 20 mg/10 mL. The solution pH was adjusted by adding 0.1 or 0.01 M of HCl or NaOH solution, as appropriate. The mixture was placed in a shaker at 30°C until it reached equilibrium, then centrifuged to separate the filtrate from the solid phase. The filtrate was analysed for residual pesticide concentration. Duplicate tests were performed in all cases.

2.6. Simultaneous Adsorption of Various Pesticides in Solutions

The aqueous adsorbate solutions used in the adsorption study were: (i) a single-component (each pesticide); and (ii) a quaternary-component solution of atrazine, diuron, 2,4-D and paraquat. The initial concentration of each pesticide was 50 mg L^{-1} . The initial pH value was unadjusted (6.5 ± 0.5). The experiments were realised at room temperature using equal volumes of the pesticide solutions, $V = 10.0 \text{ mL}$. The mass of adsorbent in all adsorption studies was 20.0 mg. In the quaternary-component solution of the pesticides, the adsorption capacity of individual pesticides on bentonite and modified bentonite was investigated. The quaternary-component solution with 10 mL of each pesticide concentration 50 mg L^{-1} was added into 20 mg of adsorbent. The adsorption experiments were performed in a shaker and then kept in a shaker for 24 h. Suspensions were centrifuged at 3500 rpm and then filtered. Each pesticide concentration in filtrates was determined by UV-Vis spectroscopy. The quaternary-component solution containing all the investigated pesticides (atrazine, diuron, 2,4-D and paraquat) was determined by HPLC (Hewlett Packard series 1100) with a diode array detector and UV detector. The ZORBAX Eclipse ODS C18 column ($250 \text{ mm} \times 4.6 \text{ mm}$, particle size $5 \mu\text{m}$) was equipped with the HPLC system and the UV detector wavelength was set at 201, 223, 254 and 283 nm. Acetonitrile (A) and water pesticide (2% phosphoric acid) (B) were used as mobile phases. The gradient program of HPLC was as follows: 0–13 min 100% B; 3–15 min 60% A and 40% B; 15–18 min 100% (A) and 20–30 min 100% A. The flow rate was set at 0.9 mL min^{-1} .

2.7. Adsorption Isotherm

Adsorption isotherms for atrazine, diuron, 2,4-D and paraquat were acquired by batch equilibration using 20 mg of bentonite or modified bentonite in 10 mL of aqueous pesticide solution at various concentrations ($10\text{--}120 \text{ mg L}^{-1}$) at 6.0 ± 0.5 . The pH values were checked before and after adsorption measurement to ensure a small change of pH

values. After equilibration (12 h), solid and liquid phases were separated by centrifugation. Atrazine, diuron, 2,4-D, and paraquat concentration were determined spectrophotometrically by measuring absorbance at 223, 247, 283, and 257 nm, respectively. Data obtained from the adsorption tests were used to calculate the adsorption capacity, q_e (mg g^{-1}). The adsorption isotherms were evaluated by applying the Langmuir and Freundlich models.

2.8. Kinetic and Thermodynamics Adsorption Study

Kinetic adsorption experiments were performed at 30 °C by contacting the adsorbents with pesticide solutions at a solid/liquid ratio of 20 mg/10 mL. In the first phase of the study, the mixtures were shaken and the supernatants were collected at the following times: 2, 4, 6, 8, 10, 30, 60, 90, 120, 180, 240, 360, 720, 1080 and 1440 min. Afterward, supernatants were centrifuged and measured spectrophotometrically at 223, 247, 283 and 257 nm. All of the batch tests were performed in duplicate. Average values were used in the calculation. Deviations were less than 2%. In order to determine the adsorption properties at different temperatures, the above experiments were repeated at 303, 313 and 323 K. To evaluate the adsorption thermodynamics of pesticides onto the adsorbent, enthalpy (ΔH), entropy (ΔS) and free energy (ΔG) changes explained the thermodynamic data for adsorption process, which were calculated by Equations (4) and (5).

3. Results and Discussion

3.1. Characterisation of Bentonite and Modified Bentonite

3.1.1. XRF and CEC Analysis

Table 1 shows the effects of acid and heat treatment on the chemical and CEC properties of the adsorbents. Acid treatment has a significant effect on chemical composition. The weight percentage of oxide metal of Na^+ , Mg^{2+} , K^+ , Ca^{2+} , Fe^{3+} , and of Al^{3+} decreases significantly during treatment with acid in both single- and two-step modified samples, such as $\text{BA}_{0.5}$, $\text{BC}_{500}\text{A}_{0.5}$, and $\text{BA}_{0.5}\text{C}_{500}$ resulting from the effects of acid leaching. When comparing the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios of $\text{BC}_{500}\text{A}_{0.5}$ and $\text{BA}_{0.5}\text{C}_{500}$, it shows that $\text{BA}_{0.5}\text{C}_{500}$, treated with acid prior to heat treatment has a higher $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio (see Table 1), probably due to the calcined sample (BC_{500}) with larger mean particle sizes than unmodified bentonite before further treatment with acid (as mentioned in Topic 3.1.8). There are various methods available to determine CEC. Most approaches involve the complete exchange of naturally occurring cations in a clay mineral with a cationic species such as ammonium ion, followed by the removal of excess substitution ion and the determination of the amount retained in the clay interlayer [15]. It was found that CEC values for acid and heat-treated samples are lower than those for bentonite (see Table 1).

Table 1. Chemical composition and CEC values for bentonite and modified bentonite samples.

Sample	Chemical (%Weight)										$\text{SiO}_2/\text{Al}_2\text{O}_3$	CEC (cmol kg^{-1})	%LOI
	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	MnO	Fe_2O_3			
Bentonite (Na,Ca) _x (Al,Mg) ₂ $\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$	0.079	0.607	9.472	78.543	1.347	1.703	2.813	0.788	0.045	4.239	8.29	67.62	13.04
BC_{500}	0.058	0.760	9.426	78.914	1.308	1.693	2.750	0.805	0.044	4.021	8.37	47.21	4.98
$\text{BC}_{500}\text{A}_{0.5}$	ND	0.664	8.982	83.001	1.301	0.963	0.825	0.758	0.024	3.342	9.24	44.15	8.69
$\text{BA}_{0.5}$	ND	0.505	7.705	85.236	1.279	0.838	0.530	0.740	ND	2.957	11.06	43.45	9.43
$\text{BA}_{0.5}\text{C}_{500}$	ND	0.642	7.355	85.001	1.274	0.832	0.558	0.740	0.020	2.687	11.56	19.11	4.29

The decrease in CEC value with acid treatment results from cationic leaching, while low CEC values resulting from heat treatment may be explained by a charge reduction as the result of the migration of small radii cations into vacant octahedral sites and the formation of covalent bonds after heating [31]. Another explanation is that the cation becomes more strongly bound to the surface during calcination, so the exchange by NH_4^+ becomes more difficult. However, the extent of charge reduction depends on the nature of the cation and the heating temperature.

3.1.2. XRD Analysis

The swelling of bentonite is a consequence of its hydrated structure, in which cations are located in the interlayer space and solvated by water molecules adsorbed from the atmosphere [31]. XRD patterns of bentonite (34.8% montmorillonite) (Figure 1) show characteristic diffraction peaks at $2\theta = 6.3$, 19.8 and 34.9. Quartz (Q) and cristobalite (C) impurities are observed in the patterns. The d_{001} reflection at $2\theta = 6.30$ corresponds to d-spacing = 14.02 Å, which is an interlayer comprising the mono- and bi-layers of water molecules [32,33]. A decrease in d-spacing from calcination was caused by the removal of interlayer water and the migration of exchangeable cation [31]. Moreover, d-spacing decreases from the acid treatment result from the removal of some cations. BC_{500} shows d-spacing = 9.65 Å, while $BA_{0.5}$ shows $d_{001} = 13.00$ Å, as shown in Table 2, indicating that heat treatment significantly affects basal spacing. All adsorbents, except BC_{500} , show small changes in d-spacing after the pesticide adsorptions, excluding paraquat, suggesting that the pesticides probably bind to the active sites of the face and edge, whereas the pesticides adsorptions may also involve the interlayer space for BC_{500} . In the case of d-spacing for cationic pesticide (paraquat), it shows a similar value (12.05–12.38 Å), except $BA_{0.5}C_{500}$, suggesting that hydrated paraquat possibly exchanges in the interlayer space with a smaller size compared to interlayer water.

Figure 1. XRD patterns for bentonite (B), BC_{500} , $BC_{500}A_{0.5}$, $BA_{0.5}$, and $BA_{0.5}C_{500}$ adsorbents. (Q = quartz; M = montmorillonite; C = cristobalite.).

Table 2. The d-spacing (Å) of bentonite and modified bentonite changes upon atrazine, diuron, 2,4-D, and paraquat adsorption.

Samples	d-spacing (Å)				
	No Adsorption	Atrazine	Diuron	2,4-D	Paraquat
Bentonite	14.02	14.59	14.01	14.21	12.27
BC_{500}	9.65	12.38	12.29	12.90	12.05
$BA_{0.5}$	13.00	13.71	12.47	13.36	12.16
$BC_{500}A_{0.5}$	12.08	12.76	12.17	12.54	12.38
$BA_{0.5}C_{500}$	9.59	9.51	9.32	9.21	9.70

3.1.3. Thermogravimetric Analysis

The weight loss observed between 50 °C and 150 °C and between 150 °C and 400 °C is due to the evaporation of water adsorbed on the adsorbents and probably due to hydrated water bound tightly to cations, respectively. The amounts of water contained are shown in Table 3 and the supplementary information in Figure S1. This result shows that BC₅₀₀ and BA_{0.5}C₅₀₀ possess low hydrophilic properties due to low water content. Above 500 °C, the weight loss is traceable to the dehydration of some trapped water molecules in the interstices of the clay layers and due to dehydroxylation of the mineral, which is accompanied by a change in the crystal structure [34].

Table 3. Water content (%) in bentonite and modified bentonite.

Adsorbents	Weight Loss (%)	
	50–150 °C	150–400 °C
B	7.83	2.50
BA _{0.5}	5.56	2.01
BC ₅₀₀	1.03	1.41
BA _{0.5} C ₅₀₀	1.18	1.21
BC ₅₀₀ A _{0.5}	4.59	2.54

3.1.4. FT-IR Analysis

The middle-IR and near-IR spectra of adsorbents are shown in Figures 2 and 3, respectively. A characteristic bentonite stretching band at 3626 cm^{−1} is attributed to OH-di-octahedral smectite. These spectra confirm that the modified bentonite samples are still characteristic of bentonite. Bands at 3420 cm^{−1} and 1636 cm^{−1} correspond to the stretching and bending vibrations of hydrogen-bonded water molecules [35]. After calcination, the spectra show a decrease in the intensities of the Al–Al–OH band at 913–920 cm^{−1} and the Al–Mg–OH band at 840 cm^{−1} for BC₅₀₀ and BA_{0.5}C₅₀₀ samples, respectively, suggesting the occurrence of dehydroxylation during calcination and the partial leaching of octahedral Al cations in acid-treated samples [19,28]. Changes in the tetrahedral sheets are reflected in the position and shape of the Si–O stretching band [35]. There is a slight decrease in the tetrahedral Si–O band intensity at 1039 cm^{−1} for modified samples. We assigned this to Si–O vibrations within a three-dimensional amorphous phase formed during the acid and thermal treatments [35]. Two bands at 520 and 469 cm^{−1} correspond to bending vibrations of Al–O–Si and Si–O–Si, respectively. The band at 520 cm^{−1} is the most sensitive band in the presence of any remaining Al³⁺ species in the octahedral sheets and two samples of BA_{0.5} and BA_{0.5}C₅₀₀ obviously show those with a broader band. The band at 622 cm^{−1} results from coupled Al–O and Si–O out-of-plane vibrations [36].

NIR spectra were recorded to determine the Si–OH groups in the adsorbent (Figure 3). The bands at 4533 cm^{−1} and 7078 cm^{−1} are assigned to the combination mode and first overtones (2ν_{OH}) of structural OH groups, respectively, while the band at 5240 cm^{−1} corresponds to the combination mode of water molecules [26,28]. BA_{0.5}, BA_{0.5}C₅₀₀, and BC₅₀₀A_{0.5} shows a new band at 7319 cm^{−1} assigned to the first overtone for silanol (2ν_{Si–OH}), confirming the formation of Si–OH groups during treatment with acid [35].

Figure 2. Mid FT-IR spectra of bentonite (B), BC₅₀₀, BC₅₀₀A_{0.5}, BA_{0.5} and BA_{0.5}C₅₀₀ samples.

Figure 3. NIR FT-IR spectra of bentonite (B), BC₅₀₀, BC₅₀₀A_{0.5}, BA_{0.5} and BA_{0.5}C₅₀₀ samples.

3.1.5. Temperature-Programmed Desorption of Ammonium (NH₃-TPD)

The NH₃-TPD profile provides information on the strength and density of adsorbent surface acid sites. The NH₃-TPD profile of pristine bentonite shows three discrete desorption maximal peaks in the low-temperature region (50–200 °C), medium temperature region (200–420 °C), and high-temperature region (420–800 °C), which are attributed to weak,

medium, and strongly acidic sites, respectively [19]. Figure 4 shows NH_3 -TPD plots for bentonite and modified bentonite. All adsorbents exhibit a peak in the high-temperature region which corresponds to a strong acid site. We attribute this to the desorption of NH_3 from Al on the surface of the adsorbent. The greatest density ($3.071 \text{ mmol g}^{-1}$) for these acid sites is seen for $\text{BC}_{500}\text{A}_{0.5}$. The NH_3 -TPD profiles for acid-activated adsorbents show additional peaks in the mid-temperature region ($400\text{--}475^\circ\text{C}$) that can be ascribed to medium acidic Si-OH_2^+ sites [19].

Figure 4. NH_3 -TPD profiles for bentonite and modified bentonite.

3.1.6. NMR Analysis

Figure 5 shows ^{27}Al MAS NMR spectra for all adsorbents. A major peak at 3.73 ppm in the spectrum for bentonite arises from six-coordinate Al (Al(VI)), indicating that much of the aluminium is located in octahedral environments. It is notable that the octahedral peak is split into the acid treatment performed in the final step. The two minor peaks at 68.25 Al(IV)a and 55.76 Al(IV)b are attributed to the four-coordinate tetrahedral Al $\text{Q}^3(3\text{Si})$ and $\text{Q}^4(4\text{Si})$ core units, respectively [37,38]. This minor peak area decreases after modification with acid. The result suggests that four-coordinate tetrahedral Al is easily removed. In the case of calcination (BC_{500}), the observed decrease in Al(IV) peak may result from some Al in the bentonite tetrahedral sheets probably being substituted by other cations such as Mg^{2+} and Ca^{2+} due to cation migration, which corresponds to previous reports [28,39]. In summary, these arguments account for the disappearance of two minor peaks of tetrahedral Al. A small increase in Al(IV) peak high for $\text{BC}_{500}\text{A}_{0.5}$ may result from Al adopting a tetrahedral site. The NH_3 -TPD results indicate that the adsorbents contain Al Lewis-acid sites (three-coordinate Al), consistent with literature reports [37], although this is not apparent from ^{27}Al NMR spectra.

3.1.7. Textural Properties Study

Table 4 shows the specific surface area, pore surface area, pore volume, and zeta potential for all adsorbents. The BC_{500} sample shows little change in these properties. However, the samples treated with acid, either in a single step or in combination with heat treatment ($\text{BA}_{0.5}$, $\text{BA}_{0.5}\text{C}_{500}$ and $\text{BC}_{500}\text{A}_{0.5}$), see increases in specific surface area and pore volume; these increases may result from larger cations such as Na^+ , Mg^{2+} , K^+ , Ca^{2+} and Fe^{3+} , including Al^{3+} being replaced by very small H^+ cations based on the results of XRF (see Table 1) and FT-IR spectra (see Figure 2). Moreover, the zeta potential characterises the surface property of clay particles in suspension. The magnitude of this parameter is often used as a measure of the strength of the repulsive interactions between similarly charged particles. Table 4 shows the zeta potential of bentonite and modified bentonite suspension. In pH 7, the zeta potential is negative for B, BC_{500} , $\text{BC}_{500}\text{A}_{0.5}$, and $\text{BA}_{0.5}$ and positive for $\text{BA}_{0.5}\text{C}_{500}$. Nonetheless, the permanent negative charge is very high in bentonite. This is due to the high degree of isomorphous substitution, where the Al(III)

elements in the octahedral sheet are substituted by Fe(II) or Mg(II) in addition to some Si(IV) in the tetrahedral layer being substituted by Al(III) [40].

Figure 5. ^{27}Al MAS NMR spectra for bentonite and modified bentonite (Spinning side-bands are marked with asterisks).

Table 4. Surface area, mean pore diameter, and zeta potential of the bentonite and modified bentonite samples.

Main Characteristics	B	BC ₅₀₀	BC ₅₀₀ A _{0.5}	BA _{0.5}	BA _{0.5} C ₅₀₀
Specific surface area (m ² /g)	31.76	32.19	67.86	77.12	80.09
Pore surface area (m ² g ^{−1})	30.901	31.301	55.354	64.704	69.154
Pore volume (cm ³ g ^{−1})	0.1246	0.1247	0.1750	0.2281	0.2456
Zeta potential (mV)-pH 7	−35.5	−22.5	−5.55	−11.4	4.83

3.1.8. Particle Size Analysis

The particle size distributions are shown in the supplementary information in Figure S2. The mean particle sizes of B, BC₅₀₀, BC₅₀₀A_{0.5}, BA_{0.5} and BA_{0.5}C₅₀₀ are 7.15, 11.50, 8.71, 27.36, and 97.08 μm , respectively (as mentioned in the supplementary information in Table S1). The samples were treated first with acid, BA_{0.5}C₅₀₀ and BA_{0.5} showing bimodal particle-size distribution. The BA_{0.5} sample has the maxima at approximately 11 μm (74.73%) and 25 μm (25.27%) (Figure S2b). The large particle size seen for BA_{0.5} may be due to the formation of a stable aggregate via hydrogen bonding between silanol groups, while BA_{0.5}C₅₀₀ exhibits the maxima at approximately 13 μm (58.39%) and 229 μm (41.61%) (Figure S2c). The larger particle size may result from the occurrence of dehydroxylation between the aggregated particles due to calcination. On the other hand, the particle size distributions for BC₅₀₀A_{0.5} and BC₅₀₀ show only monomodal distributions, with maxima at about 9 and 11 μm , respectively (Figure S2d,e). The BC₅₀₀A_{0.5} particle size is smaller than that for BC₅₀₀ due to acid erosion.

3.2. Adsorption of Pesticides onto Bentonite and Modified Bentonite

3.2.1. The Effect of pH

The changes in pH of the solution affect the speciation of adsorbate species, adsorbent surface charge, and degree of pesticide ionisation [41,42]. Bentonite can adsorb pesticides through two different mechanisms including cation exchange and adsorption [43]. Both mechanisms are pH dependent because most silanol and aluminol groups are protonated on the surface of bentonite under acid conditions. Thus, bentonite surface exists in a typically positive charge at low pH and the charge decreases, eventually becoming negative as pH increases.

Figure 6a shows the effect of pH on cationic pesticide (paraquat; PQ^{2+}) adsorption by bentonite and modified bentonite. PQ^{2+} attaches to the active site through ion exchange, emerging mostly at the interlayer space of bentonite and the modified bentonite samples due to its small size, unlike the ion exchange of protonated atrazine (acidic form) that occurs very well at the face and edge of the adsorbents because of the large size of atrazine. The high adsorption of PQ^{2+} appears on bentonite and BC_{500} as shown in Figure 6a. The lowest adsorption of PQ^{2+} is on $BA_{0.5}C_{500}$. The high amount of adsorbed PQ^{2+} corresponds to the high value of CEC and negative zeta potential (see Tables 1 and 4). All adsorbents display the adsorption capacity of PQ^{2+} , which increases with an increase in the pH of the solution, as shown in Figure 6a. The adsorption value of PQ^{2+} increases drastically at high pH because the surface of the adsorbents becomes more negatively charged, possibly due to the $SiOH^-$ group on the surface changing to SiO^- that prefers to adsorb PQ^{2+} .

Figure 6. Cont.

Figure 6. Adsorption capacity of modified and unmodified bentonite for paraquat (a); 2,4-D (b); atrazine (c); and diuron (d) at various pH and at 50 ppm.

In contrast to the case of 2,4-D adsorption (Figure 6b), 2,4-D has a pK_a of 3.55; it can exist in both neutral and anionic form. At a pH of 3–6, an anionic form appears at around 22–99.5% in aqueous solution [44]. 2,4-D adsorption by $BA_{0.5}C_{500}$ is found to be the highest in the pH range of 2–6, due to the positively charged surface of $BA_{0.5}C_{500}$ (as in Table 4), preferring to absorb the anion form and including $BA_{0.5}C_{500}$ with the highest surface area. Thus, $BA_{0.5}C_{500}$ is an adsorbent suitable for 2,4-D. The lower adsorption capacity of 2,4-D with an increase in pH is probably due to the increased negative charge of the adsorbents.

Considering the case of atrazine adsorption by bentonite and modified bentonite shown in Figure 6c, atrazine is possibly in either protonated or neutral form depending on the solution pH. At pH values approaching a pK_a of atrazine ($pK_a = 1.7$), both protonated and neutral forms are present in the solution. Protonated atrazine preferentially adsorbs by cation exchange, while un-protonated form tends to adsorb on the active sites. According to the results of the adsorption in the range of pH 4–8, the neutral form of atrazine seems to be the most preferential to $BC_{500}A_{0.5}$. At pH 2.0, BC_{500} exhibits the greatest atrazine adsorption capacity. One explanation is that at pH 2, where atrazine exists in a neutral and protonated form, and the removal of atrazine would be through ion exchange and the adsorption mechanism. BC_{500} removes atrazine mainly through ion exchange due to its low surface area. Nonetheless, it has a lower CEC than bentonite, suggesting that the ion exchange process of cationic atrazine probably occurs efficiently at the edge and face of BC_{500} instead of at the interlayer spacing (like bentonite), in which a large molecule of

atrazine is difficult to penetrate, causing very low adsorption for bentonite. The result of calcination might cause more exchangeable cations moving to the edge and face of BC₅₀₀. Consequently, the cation exchange of atrazine is easier at these sites. In the case of adsorbents activated with acid (BA_{0.5}C₅₀₀, BA_{0.5}, and BC₅₀₀A_{0.5}), some partial cations are removed. Thus, these adsorbents show lower CEC values, causing a reduction in ion exchange.

However, these adsorbents contain high specific surface areas and a feature of Al Lewis-acid site, Si-OH and Si-OH₂⁺ groups, which are available for binding to both forms of atrazine. At pH 2, however, the adsorbent of BC₅₀₀A_{0.5} still shows a high adsorption capacity in spite of having a smaller specific surface area (Table 5), suggesting that atrazine binds to BC₅₀₀A_{0.5} through both ion exchange and the adsorption process. This may result from a small particle size with highly active sites at the edge and face of BC₅₀₀A_{0.5} which enhances the removal of atrazine. The feasible interaction of atrazine bound to the adsorbents is a formation of a Lewis acid-base complex from an Al Lewis-acid site and Lewis base from atrazine (lone pair of electron on nitrogen), including the formation of hydrogen bonds to Si-OH and Si-OH₂⁺ groups.

Table 5. Langmuir and Freundlich paraquat adsorption isotherm constants.

Samples	Langmuir			Freundlich		
	q _m (mg g ⁻¹)	K _L (L mg ⁻¹)	R ²	K _F (mg g ⁻¹). (L mg ⁻¹) ^{1/n}	n	R ²
B	4.76	18.77	0.9972	6.69	1.81	0.8977
BA _{0.5}	1.75	100.39	0.9966	3.54	1.56	0.9266
BC ₅₀₀	3.58	23.26	0.9983	5.12	1.71	0.9101
BA _{0.5} C ₅₀₀	0.85	52.63	0.9987	11.83	5.26	0.9726
BC ₅₀₀ A _{0.5}	2.11	43.90	0.9986	2.44	1.43	0.8715

The adsorptions of diuron are shown in Figure 6d. Diuron exists half in neutral form and half in cationic form at approximately pH 4 [45]. The diuron adsorption is high for all adsorbents at low pH arising through the ion exchange process and the adsorption decreases with increasing pH, possibly due to competition between excess OH⁻ and adsorbate to interact with active sites. However, the high adsorption of diuron with BC₅₀₀ and BA_{0.5}C₅₀₀ compared to the others may result from an increase in hydrophobicity (as mentioned in TG results) for both adsorbents to adsorb a more neutral form.

3.2.2. Simultaneous Adsorption of Various Pesticides in Solutions

The results of each pesticide adsorption (single-component) and simultaneous adsorptions of the four pesticides (quaternary-component) from aqueous solution onto all adsorbents at ambient temperature and at initial pH of solution (6.5 ± 0.5) without pH adjustment are shown in Figures 7 and 8, respectively. All adsorbents can remove PQ²⁺ from both single and quaternary-component systems. In the quaternary-component system, the adsorption of PQ²⁺ was slightly reduced compared with single-component due to the PQ²⁺ adsorption occurring mainly inside the interlayer space of the adsorbents. Accordingly, the other pesticides (atrazine diuron and 2,4-D) in the quaternary-component do not affect the adsorption of PQ²⁺ in the interlayer space of the adsorbents. The 2,4-D adsorption is decreased, except for BA_{0.5}C₅₀₀ with the same adsorption capacity as in a single component, possibly due to the positive zeta potential of BA_{0.5}C₅₀₀ surface (see Table 4) which provides an electrostatic attraction from the positively charged surface and 2,4-D (anion pesticide). Atrazine still prefers BC₅₀₀A_{0.5} in quaternary-component, but the adsorption capacity is lower than that in a single-component due to the limited number of active sites (as mentioned in Topic 2.6). In contrast to diuron (non-polar pesticide), it was found that the adsorption of diuron in the quaternary-component was higher than that in the single-component. This could be explained by the simultaneous adsorption; PQ²⁺ adsorbed at the surface of the adsorbents can act as an additional active site, which

is competent to attach diuron through the interaction between dipole ($C=O$ of diuron) and cation (PQ^{2+}). Therefore, the presence of PQ^{2+} in quaternary-component enhances diuron adsorption. The maximum total values of the simultaneous adsorption of various pesticides from aqueous solution belong to $BC_{500}A_{0.5}$, indicating that $BC_{500}A_{0.5}$ is the most suitable for the simultaneous removal of different types of pesticides. Hence, it could be regarded as an effectively multifunctional adsorbent.

Figure 7. Adsorption of single-component pesticide with a concentration of 50 mg L^{-1} at $\text{pH } 6.5 \pm 0.5$ onto bentonite and modified bentonite.

Figure 8. Adsorption of quaternary-component pesticides (with each pesticide 50 mg L^{-1}) at $\text{pH } 6.5 \pm 0.5$ onto bentonite and modified bentonite.

3.3. Adsorption Isotherms

Pesticide adsorption data were evaluated with Langmuir and Freundlich isotherm models. The Langmuir isotherm was used to determine the monolayer and homogeneous adsorption on a surface [33]. The Freundlich isotherm is an empirical equation that assumes the adsorption surface is heterogeneous during the course of the adsorption process or multilayer sorption [46].

Linear forms of the Langmuir and Freundlich adsorption isotherms shown in Equations (2) and (3), respectively, were applied to quantitatively evaluate sorption performance:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m K_L} \quad (2)$$

where C_e is the equilibrium concentration of the pesticide in a bulk solution (mg L^{-1}), q_e is the amount of pesticide adsorbed per unit mass of adsorbent at equilibrium (mg g^{-1}), q_m is the maximum adsorption capacity (mg g^{-1}), and K_L is the Langmuir constant (L mg^{-1}):

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (3)$$

where K_F (units: $(\text{mg g}^{-1})(\text{L mg}^{-1})^{1/n}$) is the Freundlich constant, a characteristic of the system. The constant is indicative of the relative adsorption capacity of adsorption, while the term $1/n$ represents adsorption intensity. The detailed parameters of these different isotherm equations are also listed in Tables 5–8. All correlation coefficients (R^2) exceed 0.9, suggesting that all models fit the experimental results well.

The atrazine adsorption at pH 6 fits the Langmuir model better than the Freundlich model and the calculated maximum monolayer (q_m) of adsorbed atrazine on $\text{BC}_{500}\text{A}_{0.5}$ is higher than the other adsorbents. Moreover, neutral diuron adsorption at pH 6 shows the best fit to the Langmuir model compared to the Freundlich isotherm model for BC_{500} , $\text{BA}_{0.5}\text{C}_{500}$, and $\text{BC}_{500}\text{A}_{0.5}$. Moreover, diuron at pH 6 was preferentially adsorbed on bentonite and the modified bentonite surfaces via monolayer adsorption. In the case of bentonite and $\text{BA}_{0.5}$ for diuron adsorption at pH 6, it is fit both for the Langmuir and the Freundlich isotherm models. In the case of anion and cation, pesticides would be described with 2,4-D and paraquat pesticide, respectively. The data for 2,4-D adsorption at pH 6 the adsorption is only anion 2,4-D. The R^2 value confirms the adsorption equilibrium data fitted well with the Langmuir model. The q_m of 2,4-D adsorbed on $\text{BA}_{0.5}\text{C}_{500}$ is higher than that on the other adsorbents in this experiment. Moreover, the adsorption isotherm for the removal of paraquat from aqueous solution, the R^2 values from the Langmuir isotherm of all adsorbents are close to 1, indicating that the surface of each adsorbent is unique for paraquat adsorption in monolayer adsorption.

We selected the adsorbent that is capable of adsorbing the maximum amount of each pesticide to study the adsorption isotherms. The adsorption isotherms of bentonite and the selected modified bentonite at 303, 313, and 323 K are shown in the supplementary information in Figure S3 and Tables 9–12. The results indicate that atrazine, diuron and 2,4-D adsorptions increase with higher temperatures, being the cause of increased pesticide diffusion rates onto the active sites of the adsorbents, but with little significant effect for paraquat adsorption.

Table 6. Langmuir and Freundlich 2,4-D adsorption isotherm constants.

Samples	Langmuir			Freundlich		
	q_m	K_L	R^2	K_F	n	R^2
	(mg g^{-1})	(L mg^{-1})		(mg g^{-1}). (L mg^{-1}) $^{1/n}$		
B	0.32	12.19	0.9968	1.26	4.32	0.9701
BA _{0.5}	0.31	14.74	0.9976	0.96	3.06	0.9906
BC ₅₀₀	0.28	15.24	0.9972	1.17	3.06	0.9479
BA _{0.5} C ₅₀₀	0.39	16.57	0.9925	0.58	1.80	0.9842
BC ₅₀₀ A _{0.5}	0.31	14.74	0.9986	1.22	3.70	0.9946

Table 7. Langmuir and Freundlich atrazine adsorption isotherm constants.

Samples	Langmuir			Freundlich		
	q_m	K_L	R^2	K_F	n	R^2
	(mg g^{-1})	(L mg^{-1})		(mg g^{-1}). (L mg^{-1}) $^{1/n}$		
B	3.18	1.01	0.9970	0.38	2.52	0.9822
BA _{0.5}	6.37	0.52	0.9993	0.28	1.99	0.9563
BC ₅₀₀	4.52	2.05	0.9920	0.36	2.38	0.9795
BA _{0.5} C ₅₀₀	5.22	0.53	0.9982	0.31	2.14	0.9651
BC ₅₀₀ A _{0.5}	15.87	3.64	0.9970	0.31	2.04	0.9902

Table 8. Langmuir and Freundlich diuron adsorption isotherm constants.

Samples	Langmuir			Freundlich		
	q_m	K_L	R^2	K_F	n	R^2
	(mg g^{-1})	(L mg^{-1})		(mg g^{-1}). (L mg^{-1}) $^{1/n}$		
B	0.17	31.71	0.9820	0.39	1.87	0.9703
BA _{0.5}	0.88	8.01	0.9327	2.08	3.61	0.9668
BC ₅₀₀	1.92	5.05	0.9541	4.01	5.08	0.8312
BA _{0.5} C ₅₀₀	1.24	7.41	0.9715	3.01	4.04	0.8983
BC ₅₀₀ A _{0.5}	1.19	6.38	0.9262	2.82	4.55	0.8886

The maximum adsorption monolayer capacity (q_m) and the Langmuir constant (K_L), calculated from the slope and intercept of the linear plot, are shown in Tables 9–12.

Table 9. Parameters for adsorption of atrazine on bentonite and BC₅₀₀A_{0.5}.

Samples	Temperature (K)	Langmuir Isotherm		
		q_m (mg g^{-1})	K_L (M^{-1})	R^2
Bentonite	303	3.38	6.15	0.9915
	313	3.89	5.53	0.9964
	323	4.19	6.65	0.9990
BC ₅₀₀ A _{0.5}	303	16.64	452.14	0.9992
	313	17.15	632.94	0.9995
	323	18.35	955.66	0.9986

Table 10. Parameters for adsorption of diuron on bentonite and BC₅₀₀.

Samples	Temperature (K)	Langmuir Isotherm		
		q _m (mg g ⁻¹)	K _L (M ⁻¹)	R ²
Bentonite	303	5.12	0.83	0.9580
	313	5.10	1.06	0.9920
	323	5.45	1.30	0.9608
BC ₅₀₀	303	10.34	11.85	0.8725
	313	11.27	13.87	0.8531
	323	11.95	14.86	0.8935

Table 11. Parameters for adsorption of 2,4-D on bentonite and BA_{0.5}C₅₀₀.

Samples	Temperature (K)	Langmuir Isotherm		
		q _m (mg g ⁻¹)	K _L (M ⁻¹)	R ²
Bentonite	303	4.07	1.29	0.9829
	313	4.50	1.17	0.9618
	323	4.40	1.85	0.9643
BA _{0.5} C ₅₀₀	303	7.37	2.66	0.9662
	313	8.55	8.64	0.9990
	323	8.66	10.45	0.9981

Table 12. Parameters for adsorption of paraquat on bentonite and BC₅₀₀.

Samples	Temperature (K)	Langmuir Isotherm		
		q _m (mg g ⁻¹)	K _L (M ⁻¹)	R ²
Bentonite	303	94.34	480.83	0.9966
	313	92.59	563.90	0.9970
	323	87.72	4023.82	0.9697
BC ₅₀₀	303	92.59	328.58	0.9959
	313	84.03	1446.36	0.9671
	323	84.03	1446.36	0.9671

Enthalpy (ΔH), entropy (ΔS) and free energy (ΔG) changes explain the thermodynamic data for the adsorption process, which were calculated by

$$\Delta G^\circ = -RT \ln K_L \quad (4)$$

where R is the gas constant (8.314 J mol⁻¹ K⁻¹); T is temperature (K) and K_L is adsorption constant in the Langmuir isotherm. The values of ΔH° and ΔS° can be calculated from the slope and intercept of the linear variation of $\ln K_L$ with reciprocal of temperature (1/T) as in the following equation:

$$\ln K_L = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (5)$$

The thermodynamic parameters of the system: Gibbs free energy change (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°), are shown in the supplementary information in Tables S2–S5; the free energy values at temperatures 303 K, 313 K and 323 K in the adsorption of pesticides are negative in all cases, demonstrating the spontaneous nature of the process. ΔH° values are positive for all of the pesticides, showing the endothermic nature of the adsorption process. ΔS° values are also reported; positive values suggest that the organisation of the adsorbate in the solid–solution interface becomes more random.

3.4. Kinetic Experiments

Kinetics studies on the adsorption of pesticide onto bentonite and modified bentonites were performed. The results are shown in Figure 9. Measurements were made using 20 mg adsorbent at 30 °C, with atrazine concentrations of 50 mg L⁻¹. All adsorbents exhibited a high affinity for atrazine during the first 50 min, and equilibrium was reached within 200 min.

Figure 9. Pseudo-second order plots of atrazine (a); diuron (b); 2,4-D (c); and paraquat (d) adsorption onto bentonite and modified bentonites.

Pseudo-first and pseudo-second-order models were employed to correlate the kinetics data. A pseudo-first-order kinetics adsorption model was suggested for the sorption of solid/liquid systems and is expressed in an integrated and linear form in Equation (6) [47]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (6)$$

where k_1 is the adsorption rate constant (min⁻¹), q_e and q_t are the atrazine adsorption loadings (mg g⁻¹) at equilibrium and at time t (min), respectively. If the pseudo-first-order kinetics is applicable, a plot of $\log(q_e - q_t)$ versus t should provide a straight line, from which k_1 and the predicted value for q_e can be determined from the slope and intercept of the plot.

The pseudo-second-order kinetics model is expressed by Equation (7) [48]:

$$\frac{t}{q_t} = \frac{1}{q_e} t + \frac{1}{k_2 q_e^2} \quad (7)$$

where k_2 (g mg⁻¹ min⁻¹) is the pseudo-second-order adsorption rate constant. A plot of t/q_t against (Figure 9) yields a straight line, from which the rate constant k_2 and q_e can be calculated. The pseudo-second-order model is based on the assumption that the rate-limiting step may be chemisorption, which involves valence forces by electron sharing or electron exchange between the adsorbent and the adsorbate. Tables S6–S9 in

the supplementary information shows maximum adsorption capacities of q_e , k_1 , k_2 and the correlation coefficient R^2 , calculated from the pseudo-first and pseudo-second-order models. The maximum adsorption capacity, q_e , calculated from the pseudo-second-order equation, is in accordance with the experimentally determined values. The R^2 values for the pseudo-second-order are greater than those in the pseudo-first-order model. These results suggest that adsorption follows the pseudo-second-order model. The indication is that the adsorption of pesticides occurs by a chemisorption mechanism between pesticide and adsorbent by inner-sphere complexes.

The Langmuir maximum adsorption capacity for the pesticides obtained from this work was compared with other reports from the literature. Table 13 confirms that the efficiency of bentonite and modified bentonite is similar to that of the other adsorbents, but the adsorbent of $BC_{500}A_{0.5}$ is the best for atrazine removal due to the smallest particle size and the highly active region of Al Lewis-acid site which is available for easily bound atrazine via a Lewis acid-base complex. Therefore, the fixation of atrazine in $BC_{500}A_{0.5}$ is more promoted than zeoliteX, biochars (SBB) and iron nanoparticles (INPs). While ion exchange is a primary process in removing cationic pesticide (paraquat), bentonite is therefore more efficient than diatomaceous earth. For diuron adsorption, BC_{500} is considered a preferred diuron for hydrophobic interaction that BC_{500} provides high hydrophobic space. Consequently, it shows a similar result to using activated carbon.

Table 13. Comparison of q_m values from the Langmuir isotherm model of adsorbents and modified adsorbents for the removal of pesticides.

Pesticide	Absorbents	q_m	pH	Reference
Atrazine	Zeolite-X	$q_m = 11.86 \text{ mg g}^{-1}$	Not adjust	[2]
	Biochars (SBB)	$q_m = 3.05 \text{ mg g}^{-1}$		[46]
	carbon nanotubes (MWCNTs-O)	$q_e = 17.35 \text{ mg g}^{-1}$	6	[9]
	Iron nanoparticles (INPs)	$q_m = 11.76 \text{ } \mu\text{g g}^{-1}$	4.5	[49]
	Combination with Heat 500 °C and activated 0.5 HCl on Bentonite ($BC_{500}A_{0.5}$)	$q_m = 15.87 \text{ mg g}^{-1}$	6.5	This work
Diuron	Activated carbon	$q_m = 0.97 \text{ mmol g}^{-1}$		[50]
	CTA-TixHy-montm	$q_{e, \text{exp}} = 3.08 \text{ mg g}^{-1}$		[45]
	Heat treatment (500 °C) of bentonite (BC_{500})	$q_m = 1.92 \text{ mg g}^{-1}$	6.5	This work
2,4-D	Graphene (FGN)	$q_e = 19.95 \text{ mg g}^{-1}$		[51]
	Combination with Heat 500 °C and activated 0.5 HCl on Bentonite ($BA_{0.5}C_{500}$)	$q_m = 0.39$ $q_{e, \text{exp}} = 6.25 \text{ mg g}^{-1}$	6.5	This work
Paraquat	Treated diatomaceous earth	$q_m = 17.54 \text{ mg g}^{-1}$		[52]
	Bentonite	$q_m = 94.34 \text{ mg g}^{-1}$	6.5	This work

4. Conclusions

Bentonite was modified by either acid, heat, or both for the removal of different types of pesticides from an aqueous solution. It was found that $BC_{500}A_{0.5}$ is the best and specific to atrazine adsorption with a very large amount compared to other adsorbents as a result of its small particle size with high edges and faces containing a high number of active sites (Al Lewis-acid sites, Si-OH, and Si-OH₂⁺ groups). It is remarkable that $BC_{500}A_{0.5}$ is highly specific in the adsorption of atrazine mainly due to participation and strong interaction between a lone pair electron on the nitrogen of the pesticide to Al Lewis-acid site of the adsorbent and additional moderate interaction is hydrogen bond formation of amine groups to Si-OH and Si-OH₂⁺ groups. BC_{500} shows higher diuron adsorption than the others adsorbent due to its high hydrophobicity in siloxanes; consequently, the interaction of BC_{500} and diuron maybe mainly hydrophobic. Additionally, $BA_{0.5}C_{500}$ is suitable for 2,4-D. The 2,4-D-adsorption may be induced by the positive zeta potential

compensation indicating an interaction of anionic 2,4-D and the positively charged surface of the adsorbent.

Finally, it seems apparent that high paraquat adsorption capacity was found for all adsorbents. However, bentonite is the most favourite for paraquat as a result of the main removal of paraquat through ion exchange which is easily occurring due to a small size of paraquat and bentonite presents a high value of CEC, whereas $BA_{0.5}C_{500}$ showed the lowest capacity because of $BA_{0.5}C_{500}$ with low CEC and swelling. $BC_{500}A_{0.5}$ was recently developed by combining steps of bentonite for simultaneous pesticide removal from an aqueous solution, because it could remove a higher total amount of pesticides than the other adsorbents, indicating that it could be used as a good multifunctional adsorbent. The adsorption of all pesticides fits well with the Langmuir adsorption model compared to the Freundlich model, and the adsorption kinetics follow a pseudo-second order (chemisorption). The thermodynamic parameters of the pesticide adsorption, such as Gibbs free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were also calculated, and the parameter values are reported in spontaneous and endothermic processes. This research demonstrated that the treatment of bentonite with a sequence of the combination of heat and acid provides a high potential adsorbent for pesticide removal. It also offers a low cost and convenient method when compared with other technics.

Based on the use of artificially prepared pesticide solution in this work the effect of ionic strength on the adsorption was neglected. However, in future work, adsorptions in wastewater effect of ionic strength will be considered.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/app11115147/s1>, Figure S1: TGA/DTG for bentonite (a), $BA_{0.5}$ (b), BC_{500} (c), $BA_{0.5}C_{500}$ (d) and $BC_{500}A_{0.5}$ (e); Figure S2: Particle size distributions for bentonite (a), $BA_{0.5}$ (b), $BA_{0.5}C_{500}$ (c), BC_{500} (d), and $BC_{500}A_{0.5}$ (e). Figure S3: Adsorption isotherm of pesticide on bentonite and modified bentonite at 303, 313 and 323 K. Table S1: Measurement of particle size distribution. Table S2: Thermodynamic parameters for adsorption of atrazine on bentonite and $BC_{500}A_{0.5}$. Table S3: Thermodynamic parameters for adsorption of diuron on bentonite and BC_{500} . Table S4: Thermodynamic parameters for adsorption of 2,4-D on bentonite and $BA_{0.5}C_{500}$. Table S5: Thermodynamic parameters for adsorption of paraquat on bentonite and BC_{500} . Table S6: Kinetic model parameters obtained for the adsorption of atrazine onto bentonite and modified bentonite adsorbents. Table S7: Kinetic model parameters obtained for the adsorption of diuron onto bentonite and modified bentonite adsorbents. Table S8: Kinetic model parameters obtained for the adsorption of 2,4-D onto bentonite and modified bentonite adsorbents. Table S9: Kinetic model parameters obtained for the adsorption of paraquat onto bentonite and modified bentonite adsorbents.

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