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Magnetic Wakame-Based Biochar/Ni Composites with Enhanced Adsorption Performance for Diesel

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ABSTRACT

In this study, the magnetic wakame biochar/Ni composites were prepared with three activating reagents of H_3PO_4 , $ZnCl_2$ and KOH by one-step pyrolysis activation, characterized by BET, SEM, TEM, FI-IR, XRD, Raman, and elemental analyzer, and their adsorption performance for diesel were also analyzed. The results showed that wakame biochar/Ni composites had larger specific surface area, abundant porous structure, and various reactive groups, rendering its enhancement of adsorption efficiency. The adsorption experiments indicated that the maximum adsorption capacities for diesel using WBPA 0.5, WBHZ 0.5 and WBPH 0.5 were 4.11, 8.83, and 13.47 g/g, respectively. The Langmuir model was more suitable for the adsorption isotherms process, and the Pseudo-second-order model could better describe the adsorption kinetic experimental. And the magnetic wakame biochar/Ni composites presented good stability and recyclability. This study provides a novel pattern for the high-value utilization of wakame, having huge potential in the treatment of oily wastewater.

KEYWORDS

Wakame; magnetic biochar/Ni composites; activating reagents; diesel adsorption

1 Introduction

With the rapid development of economy and industrialization, the production and consumption of petroleum products are increasing worldwide, and as a side effect of transportation, exploration and related processes, oil spill is unfortunately increasing accordingly [1,2]. Water resources and petroleum resources are indispensable in human life and industrial development, but the harm and pollution caused by oily pollutants to water resources are becoming seriously [3–5]. Oily pollutants mainly include alkane and naphthene, crude oil components of aromatic and asphaltene [6]. It is well known that aromatic compounds have strong toxicity and poor biodegradability (such as polyaromatic hydrocarbons), and complex hydrocarbons such as polycyclic isoprenoids are persistent in the environment (such as terpenes)



[7,8]. These oily pollutants cause serious problems to the animals and plants in the water and residents nearby, seriously threatening their health and quality of life [9], and may cause chronic rhinosinusitis and airway disorders [10], lung diseases, cancer and skin diseases [11]. Therefore, the removal and recovery of oily pollutants in water has attracted widespread attention in the research field.

Up to date, there is a variety of methods available for the treatment of oily wastewater, mainly including physical, chemical and biological method [12]. Physical method commonly employs oil booms, skimmers or sorbents to remove oil from water [13], oil dispersant as a chemical method is often used in the treatment of oily waste [14] and biological method uses petroleum-degrading microorganism to eliminate oil pollutants [15]. Among these, the treatment of oily wastewater by sorbent has been considered as an economically feasible, effective, facile-operating and no secondary pollution method [16,17], and there has been various sorbents employed to remove oil pollutant from water, such as activated carbon [18], kaolin [19], silica [20], fly ash [21], etc. However, most sorbents for the treatment of oily wastewater have been confronted with the challenges of low efficiency and poor reutilization.

In recent years, with the increasingly prominent energy crisis, the preparation of biochar materials from cheap, readily available, and renewable biomass in nature has attracted increasing attention [22,23]. The biomass materials for the preparation of biochar have been ranged from the first-generation agricultural wastes (such as straw, corn cob, bagasse) [24] to the second-generation forestry wastes (such as lignocellulose) [25]. At present, it has been transferred from land to lake and ocean, especially microalgae and macroalgae with high biomass and short growth cycle [26], have become the third generation of biomass carbon sources. And algal biochar, as a new kind of biomass carbon-based material, has been used in various fields, such as in the soil remediation [27], wastewater treatment [28] and lithium battery and sensor [29,30]. Generally, biochar could be prepared with various methods, including pyrolysis, hydrothermal carbonization, flash carbonization, and gasification [31], and activation is a crucial step in the preparation of biochar, which can form porous structure, enlarge specific surface area, increase surface active groups and change surface hydrophilicity or hydrophobicity, rendering the improvement of the physicochemical properties [32]. And physical activation and chemical activation are the common methods applied in the activation process, among which, chemical activation is a series of cross-linking or polycondensation reactions between chemical reagents (acid, alkali, and oxidation) with carbon materials to create abundant porous structures, possessing short activation time, low activation temperature and high productive rate, and so on [33]. However, there are still some practical problems to overcome in the application of biochar, it is difficult to separate and recovery effectively due to its small particles, which limits its large-scale application. Recently, magnetic separation technique has been introduced in the preparation of biochar, transition metals (Fe, Ni, etc.) or their oxides have been employed to prepare magnetic biochar [34,35], which can simply and rapidly realize the separation and recovery of biochar in a magnetic field.

In this study, a series of novel magnetic biochar/Ni composites derived from wakame were synthesized with three different activators (KOH, ZnCl_2 and H_3PO_4) by a facile and effective impregnation-pyrolysis method. The as-prepared samples were characterized by BET, SEM, TEM, FT-IR, XRD, Raman, and elemental compositions were also analyzed. Moreover, the adsorption performances for diesel wastewater using as-prepared samples were investigated by batch adsorption experiments, and the adsorption isotherms, kinetics and thermodynamics of as-prepared samples for diesel were also studied to further analyze its adsorption mechanism. Then, the magnetic recovery cycle experiments of as-prepared samples were carried out in an extra magnetic field. This study would provide a novel promising bio-absorbent prepared by macroalgae in the treatment of oily wastewater.

2 Materials and Methods

2.1 Materials

The wakame used in this study was purchased from Yantai City, Shandong Province, China. The wakame was washed and soaked in tap water several times to remove the salt in the wakame, and dried

at 85°C. Diesel (Sinopec), Potassium hydroxide (KOH), zinc chloride (ZnCl_2), phosphorus pentoxide (P_2O_5) and nickel chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$) were all purchased from Shanghai Sinopharm Chemical Reagent Co., Ltd., China. All reagents used in the experiment are of analytical grade and no further purification is required.

2.2 Preparation of Magnetic Biochar/Ni Composites

According to our previous work [36], 5.0 g of wakame powder were added to 50 mL 0.5 mol/L NiCl_2 solution, stirred by ultrasonic for 4 h, stood for overnight and filtered, and the underlayer precipitation was taken and dried. And then, mix 50 mL of activators (KOH, ZnCl_2 and H_3PO_4) with the pretreated wakame powder above, where the mass ratio of activator to wakame: activator/wakame (w/w) = 0.5:1 or 1:1, respectively, which were stirred at 80°C for 2 h, filtered and dried in an oven at 105°C for 12 h. The dried sample was transferred to a tube furnace, heated to 800°C at a rate of 10 °C/min under nitrogen atmosphere condition (with a flow rate of 100 mL/min), and kept at 800°C for 2 h. After cooling, the obtained magnetic wakame biochar was washed with deionized water to pH = 7, and dried in an oven at 85°C for 12 h. The as-prepared samples with KOH activation were denoted as WBPH 0.5 and WBPH 1, those with ZnCl_2 activation are denoted as WBHZ 0.5 and WBHZ 1 and those with H_3PO_4 activation were denoted as WBPA 0.5 and WBPA 1. For comparison, the magnetic biochar that was carbonized at 800°C without any activator was labeled as MWB.

2.3 Characterization of Magnetic Biochar/Ni Composites

N_2 adsorption/desorption isotherm was performed on a static volumetric adsorption analyzer (Micromeritics ASAP 2010, Shanghai, China) and calculated with the method of Brunauer-Emmett-Teller (BET). The microstructure and surface morphology of as-prepared sample was observed by scanning electron microscope (SEM, S4800, Hitachi, Japan) and transmission electron microscope (TEM, Joel-2100, JEOL, Japan). The element analyzer was used to determine the contents of organic elements (C, H, N, S and N) of as-prepared sample, and the content of metallic nickel was obtained by inductively coupled plasma emission spectrometer (ICP-OES; ICAP6000, Thermo Fisher Scientific, USA). The X-ray diffraction (XRD) patterns were recorded on an X-ray Diffractometer (Ultima IV, Rigaku Corporation, Japan) in the range of 2θ from 20 to 80°. The Raman spectra were recorded by Raman spectroscopy using a 532 nm excitation wavelength (InVia-Reflex, Renishaw, UK). At the same time, the surface functional groups of as-prepared sample were analyzed by Fourier transform infrared spectroscopy (FTIR, Nicoletteis 50, Thermo Fourier, USA). And the magnetic properties were studied using a vibrating Specimen magnetometer (VSM, 7407, Lakeshore, USA).

2.4 Batch Adsorption Experiments

0.1 g of magnetic biochar/Ni composites (MWB, WBPH 0.5, WBPH 1, WBHZ 0.5, WBHZ 1, WBPA 0.5 and WBPA 1) were added into 50 mL (2%, 4%, 8%, 16% and 20%) diesel solution for batch adsorption experiments, respectively, which was put into a water bath thermostatic oscillator and oscillate at 25°C for 3 h. And then under external magnetic field, the adsorbent was separated from the mixed solution at 5, 10, 20, 30, 60, 90, 120 and 180 min, respectively, and the adsorbed diesel by as-prepared sample was recovered and weighed. Moreover, the effects of diesel initial concentration and adsorbent dose on the adsorption capacities of diesel were also investigated.

To evaluate the stability of the prepared adsorbent, the repeat cycle experiments were also performed. The magnetic biochar/Ni composite with adsorbed diesel was added into ethanol for desorption. The as-prepared adsorbent was recovered by magnetic separation, and dried in an oven at 85°C for 12 h. The cycles of adsorption-magnetic separation-desorption were carried out for 5 times.

The adsorption efficiency of magnetic biochar/Ni composite to diesel was calculated according to Eq. (1):

$$q_t = \frac{W_t - W_0}{W_0} \quad (1)$$

where q_t (%) is the adsorption rate of diesel by adsorbent, w_t (g) is the weight of the adsorbent after adsorbing diesel, and w_0 (g) is the initial weight of the adsorbent.

2.5 Statistical Analysis

Statistical analysis was performed using Origin 8.5 (Origin Corp., USA); Jade 6.0 was used to process the XRD data.

3 Results and Discussion

3.1 Characterization of Magnetic Biochar/Ni Composites

3.1.1 Porous Structure

The N_2 adsorption-desorption isotherm was employed to determine pore characteristics of the as-prepared samples. As shown in Fig. 1, it can be seen that MWB, WBPA, WBHZ and WBPH conform to the IV isotherm model. After activation, N_2 adsorption capacities of magnetic biochar/Ni composites significantly enhance, and WBPA 0.5, WBHZ 0.5 and WBPH 0.5 possess higher N_2 adsorption capacities compared with WBPA 1, WBHZ 1 and WBPH 1. There are wide hysteresis loops between their adsorption and desorption branches ($P/P_0 > 0.4$), indicating the existence of mesoporous structure [37]. However, the hysteresis loop of WBN failed to close, which may be caused by an irreversible reaction during the adsorption-desorption process [38]. As shown in Table 1, the specific surface area and pore volume of magnetic biochar/Ni composites obviously increase after activation, among which, those of WBPH are maximum, followed by those of WBHZ and WBPA, indicating KOH is the optimum activator for the preparation of magnetic biochar/Ni composite. And the specific surface area and pore volume of WBPA 0.5, WBHZ 0.5 and WBPH 0.5 are higher than those of WBPA 1, WBHZ 1 and WBPH 1, and those of WBPH 0.5 are highest, up to 824.174 m^2/g and 0.445 cm^3/g , respectively. As the ratio of activator increases, the specific surface area and pore volume of magnetic biochar/Ni nanocomposite decrease, probably because more activator could consume more carbon of wakame, and further destroy pore structure of magnetic biochar/Ni composite.

Based on N_2 adsorption-desorption data, the non-local density functional theory (NLDFT) model is used to calculate pore size distribution (PSD) of as-prepared sample, it can be demonstrated that the PSD of magnetic biochar/Ni composites are in the range of 3.8-4 nm, belonging to mesoporous materials. It has been demonstrated that H_3PO_4 , $ZnCl_2$ and KOH as activators applied in the preparation of biochar, can be beneficial to the improvement of pore properties and the increase of oxygen functional groups [39], therefore in this study, the specific surface area and pore volume of magnetic biochar/Ni composites are remarkable improved, among which, KOH works best in the preparation of wakame biochar. After activation, magnetic biochar/Ni composites possess larger specific surface area and abundant functional groups, endowing them more active sites, which facilitates the binding and adsorption of diesel molecules [40]. Moreover, the well-developed porous structure is also conducive to the adsorption of organic molecules through the capillary effect of the pores. It can be concluded that the best ratio of wakame biochar to activator is 1:0.5, that is, WBPA 0.5, WBHZ 0.5 and WBPH 0.5 have relatively larger specific surface area, thus WBPA 0.5, WBHZ 0.5 and WBPH 0.5 were chosen as adsorbents in the following batch adsorption experiments.

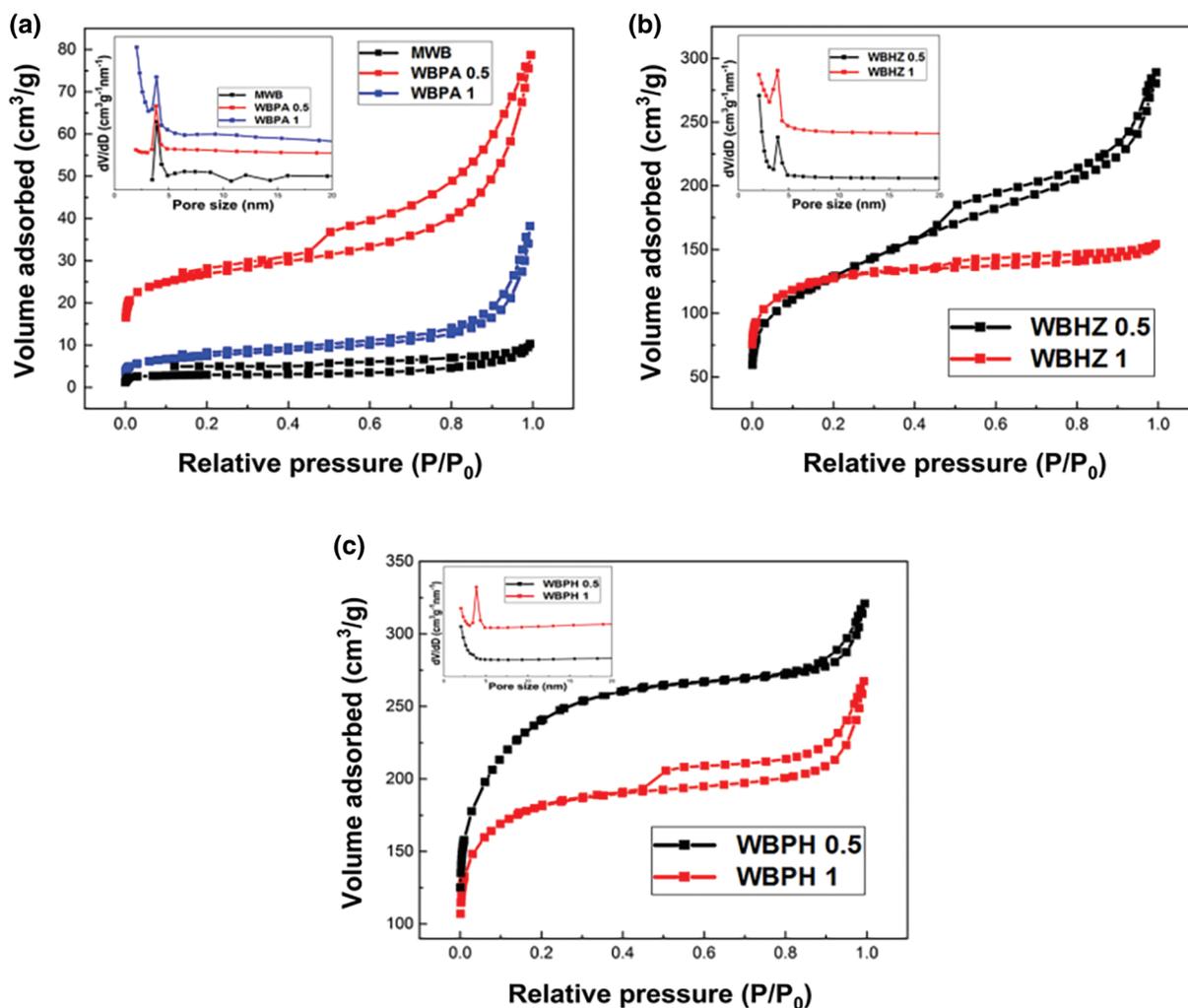


Figure 1: N₂ adsorption-desorption isotherm and pore size distribution of magnetic Wakame bio-carbon nanocomposite with different activators

Table 1: BET parameters of magnetic wakame biochar nanocomposites

Sample	S_{BET} (m ² /g)	V_{tot} (cm ³ /g)	Average pore diameter (nm)
MWB	9.151	0.011	4.787
WBPA 0.5	89.501	0.092	4.119
WBPA 1	25.726	0.033	4.238
WBHZ 0.5	455.626	0.373	2.141
WBHZ 1	422.897	0.226	2.275
WBPH 0.5	824.174	0.445	2.158
WBPH 1	601.501	0.346	2.302

3.1.2 Morphology and Structure Analysis: SEM and TEM

The morphology and microstructure of the magnetic biochar/Ni composites were analyzed by SEM (Fig. 2). It can be observed that MWB exhibits a relatively dense structure with a small number of holes and cavities. After activation, WBHZ 0.5 and WBPA 0.5 show irregular and fluffy structure with a large number of cavities, cracks and debris, while WBPH 0.5 presents a “honeycomb”-like regular pore structure, which can provide stronger adsorption driving force and more active adsorption sites for diesel adsorption. These carbohydrate polymers are pyrolyzed in the process, dehydration, dehydroxylation, condensation and polymerization form a dense block structure [41], which produces the Ostwald ripening effect, which is the growth of larger particles at the expense of smaller particles. The pores and cavities in the magnetic biochar/Ni composites act as the channels of the active sites, facilitate to bind more diesel molecules. In addition, during the high-temperature pyrolysis process, nickel ions are reduced to metallic nickel embedded in biochar, which have been observed in SEM images of the magnetic biochar/Ni composites, contributing to the separation and recovery of biochar.

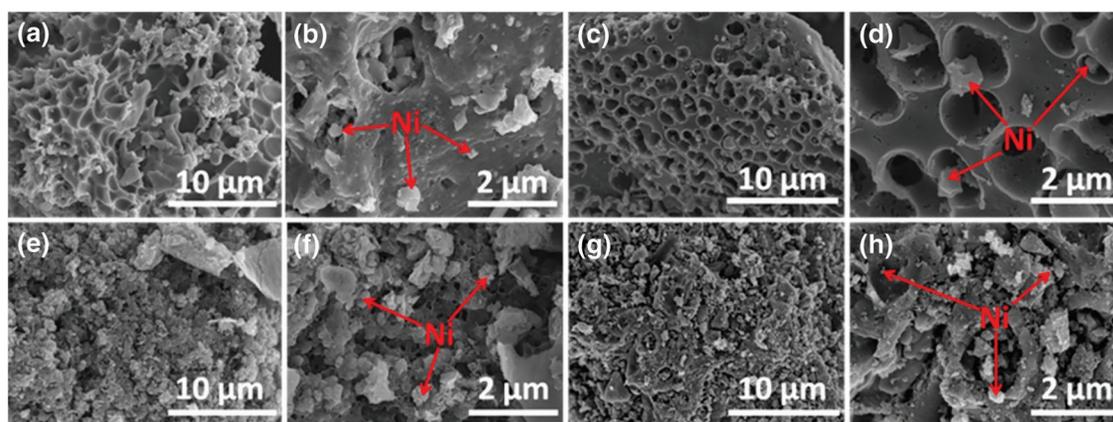


Figure 2: SEM image of magnetic Wakame bio-carbon nanocomposite. ((a), (b) are MWB; (c), (d) are WBPH 0.5; (e), (f) are WBHZ 0.5; (g), (h) is WBPA 0.5)

TEM was employed to further analyze the pore structure of the magnetic biochar/Ni composites, it can be seen from TEM images (Fig. 3) that the black dots in the picture may be reduced metal Ni particles, indicating the high uniformity and dispersibility of Ni particles on the magnetic wakame bio-carbon nanocomposite. The surface of the magnetic wakame bio-carbon nanocomposite material activated by the activation reagent has a layered structure, which is sponge-like and has irregular pores, indicating that there are a large number of uniform micropores. A large number of dense concave-convex pores indicate that the pores have been enriched after the activated magnetic biochar.

3.1.3 Analysis of Chemical Composition and Crystal Structure

According to the FTIR spectrum (Fig. 4a) of magnetic biochar/Ni composites, it can be observed that there is a slight change before and after activation of magnetic biochar/Ni composites. There is a broad band around 3400 cm^{-1} is the -OH stretching band of the alcohol or phenol group [42]. Due to the stretching vibration of the aliphatic -CH group, a characteristic band appears near 2910 cm^{-1} , due to the primary amine (NH) group Vibration, the characteristic band appears near 1586 cm^{-1} . In addition, the peaks appearing at $1400\text{--}1440\text{ cm}^{-1}$ can be attributed to the vibration of the -CH₂ and -CH₃ groups [43], while the C-O of alcohols, carboxylic acids and ethers the stretching vibration shows a broadband in the range of $1050\text{--}1210\text{ cm}^{-1}$, because during the pyrolysis process, different forms of oxygen in the macroalgae are converted into carbon-oxygen bonds in the form of bond chains. However, the out-of-

plane curvature of =C-H on the aromatic ring shows low-intensity vibration near 879 cm^{-1} , and the presence of a large number of organic active groups (such as -OH, -NH and -CH) help the adsorbent to dye dyes.

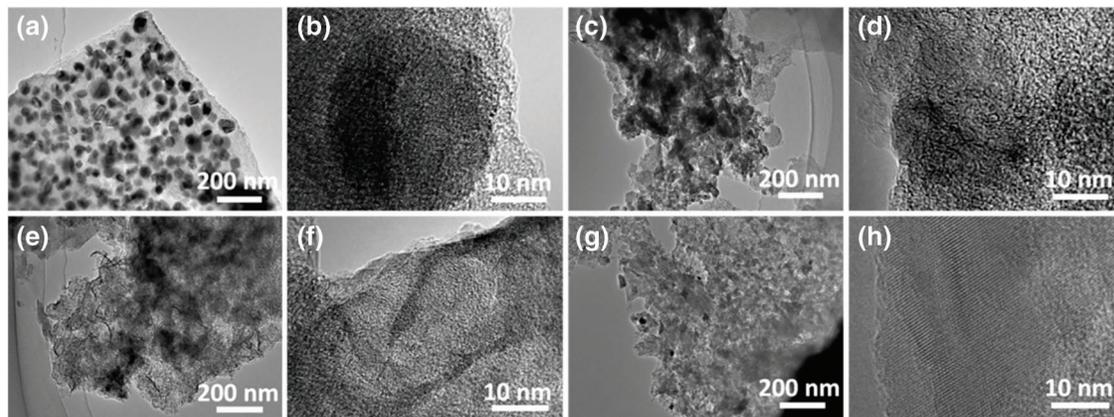


Figure 3: TEM image of magnetic wakame bio-carbon nanocomposite ((a), (b) are MWB; (c), (d) are WBPH 0.5; (e), (f) are WBHZ 0.5; (g), (h) is WBPA 0.5)

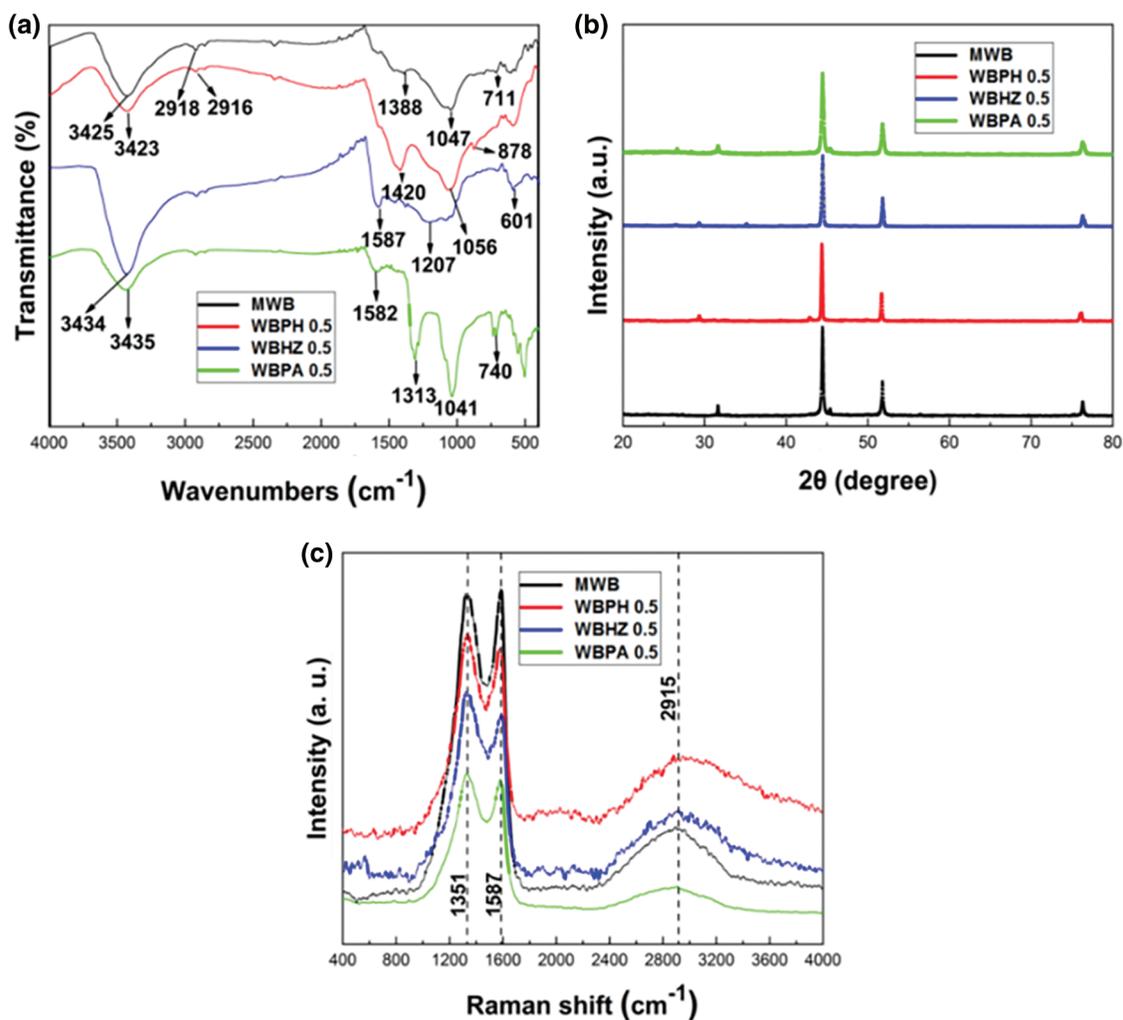


Figure 4: Chemical composition and crystal structure analysis diagram ((a) is FTIR, (b) is XRD, (c) is Raman spectrum)

The XRD pattern (Fig. 4b) of the magnetic biochar/Ni composites shows that the diffraction peak intensity of WBPA 0.5, WBHZ 0.5 and WBPH 0.5 is higher than that of MWB. This is because the activation reagent consumes part of the carbon element for pore formation. As a result, the metal Ni content increases, and the diffraction peaks are mainly concentrated between 40° and 80°. $2\theta = 44.480^\circ$, 51.830° and 76.350° diffraction peaks correspond to (1,1,1), (2,0,0), (2,2,0) element nickel [44], thus It proves that the metal Ni is successfully loaded onto the wakame magnetic biochar composite material. The existence of metal Ni makes it possible to conveniently recover the adsorbent material for recycling after the end of the adsorption experiment.

The Raman spectrum (Fig. 4c) of magnetic biochar/Ni composites have been obtained to investigate their graphitization state. There are three peaks located at 1351 cm^{-1} , 1587 cm^{-1} and 2915 cm^{-1} , corresponding to the D, G and 2D band, respectively. The D band corresponds to sp^3 hybridized carbon in disordered state, the G band is related to the vibration of sp^2 -hybridized carbon atoms in a graphitic layer [45], and the 2D band is attributed to the double resonant Raman scattering with two-phonon emissions [46]. The intensity ratio of the D and the G-band (I_D/I_G) is a measure of the disorder of as-prepared samples [47]. Compared to the I_D/I_G ratio of MWB (0.89), that of WBPA 0.5, WBHZ 0.5 and WBPH 0.5 are 1.05, 1.07 and 1.03, respectively, indicating that a large number of disordered carbons were contained in MWB, while WBPA 0.5, WBHZ 0.5 and WBPH 0.5 are relatively less, due to partial carbon being consumed during high temperature activation, which is consist with the results of elemental analysis.

3.1.4 Elemental Analysis and ICP Determination

Elemental analyzer and ICP-OES were employed to investigate the main components of the magnetic biochar/Ni composites, as illustrated in Table 2. It can be obviously seen that the carbon content of WBPH 0.5 (39.13%), WBHZ 0.5 (42.05%) and WBPA 0.5 (43.61%) are lower than that of MWB (51.98%), attributed to the consumption of some carbon elements during the activation process. As usual, the lower the O/C atomic ratio, the higher the hydrophobicity of biochar materials, and WBPA 0.5 has a lowest O/C ratio (0.151), indicating that it is more hydrophobic. The polar index (O+N)/C atomic ratio of WBPH 0.5, WBHZ 0.5 and WBPA 0.5 reflects the existence of polar groups in the magnetic wakame bio-carbon nanocomposite [48]. The H/C atomic ratio is usually used to estimate the aromaticity of biochar [49]. The H/C atomic ratios of WBPH 0.5, WBHZ 0.5 and WBPA 0.5 decreased by 0.334, 0.242 and 0.292, respectively, which indicates that the addition of activator increases the aromaticity of biochar. These features are conducive to the adsorption of diesel organic macromolecules.

Table 2: Elemental analysis of magnetic wakame biochar nanocomposites (mass, %)

Element	C	H	N	O	S	O/C	(O+N)/C	H/C	Ni
MWB	51.98	2.47	2.03	11.28	0.64	0.163	0.196	0.570	28.69
WBPH 0.5	39.13	0.77	1.58	13.37	0.14	0.256	0.291	0.236	29.57
WBHZ 0.5	42.05	1.15	2.81	9.98	1.26	0.178	0.235	0.328	33.70
WBPA 0.5	43.61	1.01	0.45	8.79	0.24	0.151	0.160	0.278	37.64

Besides, the nickel contents of as-prepared samples have been analyzed by ICP-OES, compared with the nickel content of MWB, those of the magnetic biochar/Ni composites increase remarkably, among which, that of WBPA 0.5 is maximum (37.64%). The loading of nickel could contribute to the separation and recovery of the magnetic biochar/Ni composites after adsorption.

3.2 Batch Adsorption Experiments

3.2.1 Effects of Different Adsorbents on Diesel Adsorption

The adsorption performances for diesel using seven different adsorbents (MWB, WBPA 0.5, WBPA 1, WBHZ 0.5, WBHZ 1, WBPH 0.5 and WBPH 1) have been investigated, as shown in Fig. 5. It can be observed that the adsorption capacities of the magnetic biochar/Ni composites rise sharply after activation, among which, those of WBPH are highest, followed by WBHZ and WBPA. As the ratio of activator increases, the adsorption capacities of diesel using the magnetic biochar/Ni composites decrease, which may be due to the collapse of the pore size caused by the excessive addition of activator in the process of high-temperature pore formation, resulting in a small specific surface area and reduced adsorption. And the adsorption capacity of diesel using WBPA 0.5, WBHZ 0.5 and WBPH 0.5 are 3.92, 7.75 and 9.75 g/g, respectively. At the initial stage of adsorption, the adsorption capacities of diesel using the magnetic biochar/Ni composites increase sharply, and the adsorption equilibrium is reached in about 20 min, because there is abundant porous structure, high specific surface area and various functional groups of the magnetic biochar/Ni composites at the beginning of adsorption reaction, rendering them plenty of active sites and adsorbing diesel molecules quickly, while as the reaction continues, more and more active sites are occupied, the adsorption capacity decreases until adsorption equilibrium.

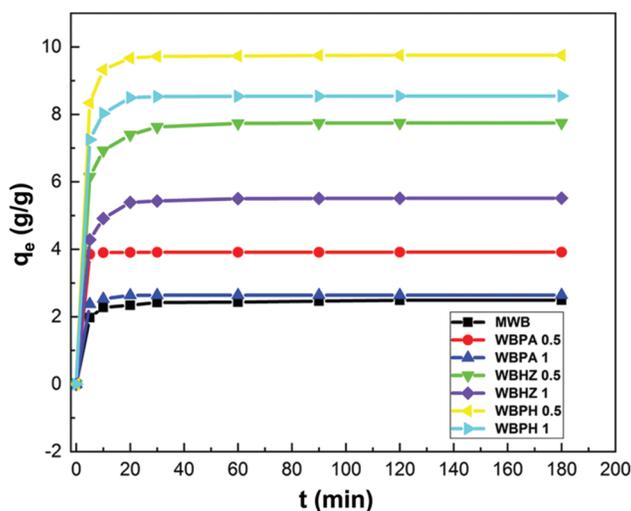


Figure 5: The adsorption performance of seven different adsorbents for diesel

3.2.2 Effects of Diesel Initial Concentrations on Diesel Adsorption

Fig. 6 shows that the adsorption capacities of diesel using WBPA 0.5, WBHZ 0.5 and WBPH 0.5 increase as the diesel initial concentration increases, among which, the adsorption capacity of diesel using WBPH 0.5 at 10 mL diesel concentration is highest, up to 13.476 g/g. Moreover, as the diesel initial concentration increases, the time to reach equilibrium of the diesel adsorption using the magnetic biochar/Ni composites is shorter, which can be attributed to more active sites exposed on their surface being available for the adsorption of diesel. And in the initial reaction period, the adsorption rate of diesel using the magnetic biochar/Ni composites are quite fast, and the adsorption system of diesel using WBPA 0.5 can quickly reach equilibrium, while those of WBHZ 0.5 and WBPH 0.5 take a relatively long time to reach equilibrium. As the adsorption processes, the adsorption rate of diesel using the magnetic biochar/Ni composites gradually decrease and flat out, attributable to vast active sites being occupied by diesel molecules, leading to competitive adsorption and lower the attractiveness to diesel molecules [50].

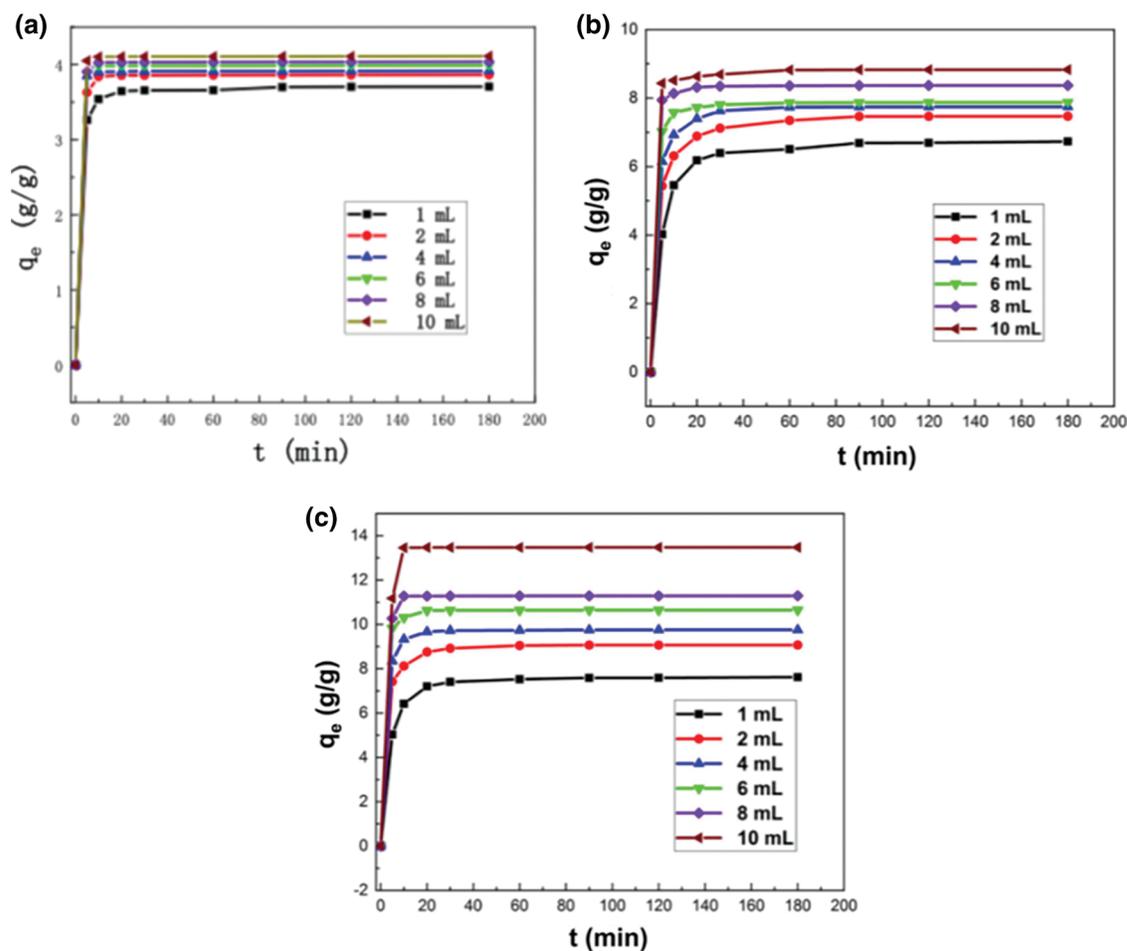


Figure 6: The adsorption performances of diesel using the magnetic biochar/Ni composites (a: WBPA 0.5, b: WBHZ 0.5, c: WBPH 0.5) at different diesel initial concentration (1, 2, 4, 6, 8 and 10 mL) in the range from 0 min to 180 min

3.3 Adsorption Isotherms and Kinetics Studies

3.3.1 Adsorption Isotherms Studies

The effects of adsorbent dosage on diesel adsorption using WBPH 0.5, WBPA 0.5 and WBHZ 0.5 have been analyzed, as shown in Fig. 7. It can be observed that the removal efficiency of diesel using the magnetic biochar/Ni composites remarkably rises and then levels off with the increase of adsorbent dosage in the range of 0.1–0.7 g, due to the availability of more active sites on their surface [51]. And the removal efficiency of diesel using WBHZ 0.5 is the highest, up to 100%, followed by WBPA 0.5 is 99.74%, and WBPH 0.5 is 46.55%. Therefore, considering the removal efficiency and practicability, the optimum adsorbent dosage is selected to be 0.6 g for diesel adsorption.

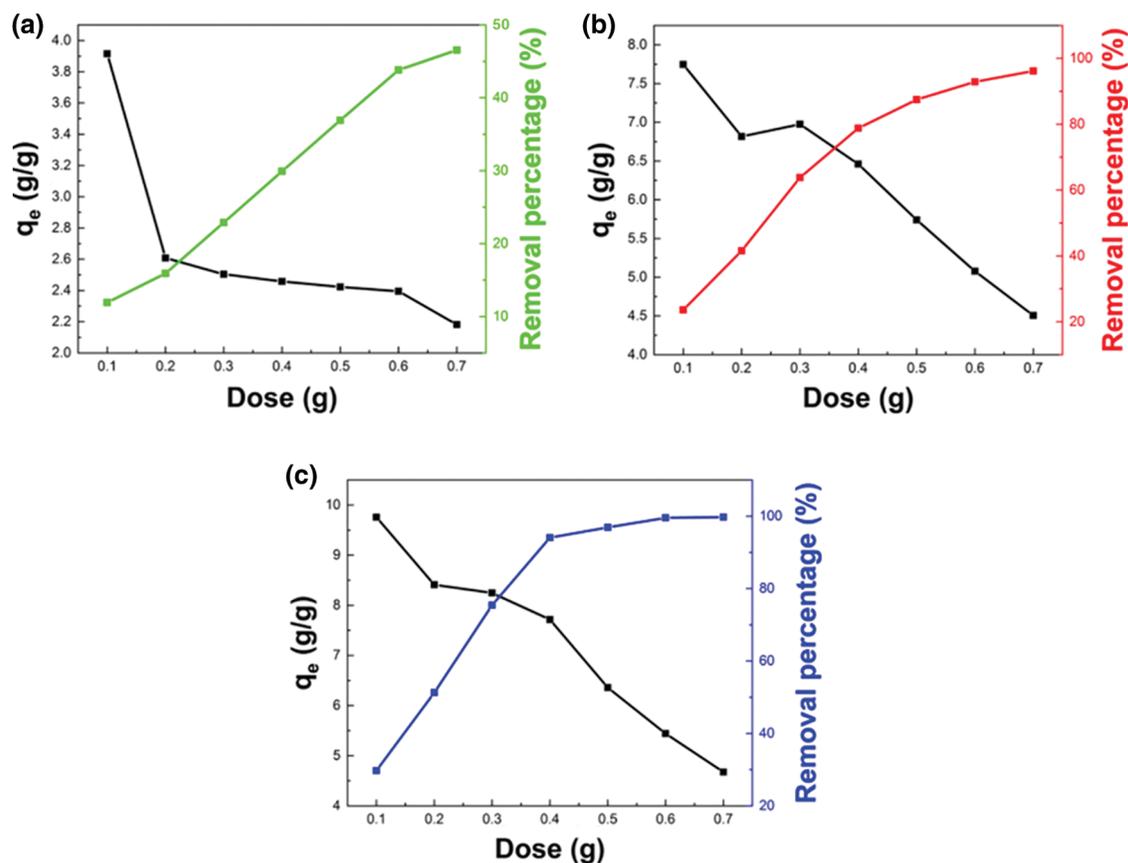


Figure 7: The effect of WBPH 0.5 (a), WBPA 0.5 (b) and WBHZ 0.5 (c) adsorbent dosage on diesel adsorption

3.3.2 Adsorption Kinetics Studies

In order to study adsorption equilibrium, adsorption isotherm model was chosen according to the properties and types of the system. The most commonly used models are Langmuir Eq. (2) and Freundlich Eq. (3).

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

$$q_e = K_F C_e^{1/n} \quad (3)$$

where C_e (g/L) represents concentration of diesel at equilibrium, q_e (g/g) and q_L (g/g) are adsorption capacity of diesel at equilibrium and saturation, respectively. K_L (L/mg) is the Langmuir adsorption equilibrium constant, K_F [(g/g) (L/g) $1/n$] is the Freundlich constant, and $1/n$ is the adsorption intensity factor or surface heterogeneity.

In order to study the diesel adsorption using the magnetic biochar/Ni composites, the traditional Langmuir and Freundlich adsorption isotherm models are employed to analyze the adsorption isotherms. Fig. 8 indicates the fitting of data with isotherm models, and adsorption parameters and regression data of the models are presented in Table 3. It can be demonstrated that Regression coefficient (R^2) of Langmuir model has higher value (0.999, 0.994 and 0.964) for the diesel adsorption using WBPA 0.5, WBHZ 0.5 and WBPH 0.5, indicating that Langmuir equation is more suitable for describing the diesel

adsorption using the magnetic biochar/Ni composites, and their adsorption processes are monolayer adsorption [52]. The calculated adsorption amount of diesel using WBPA 0.5, WBHZ 0.5 and WBPH 0.5 at equilibrium is 4.13, 8.79, and 13.05 g/g, respectively, which are in good combination with experimental data, i.e., the experimental value is 4.11, 8.83 and 13.47 g/g, respectively. Compared with the previous biochar removal of diesel fuel [53], the magnetic biochar/Ni composites have good adsorption capacity values for diesel.

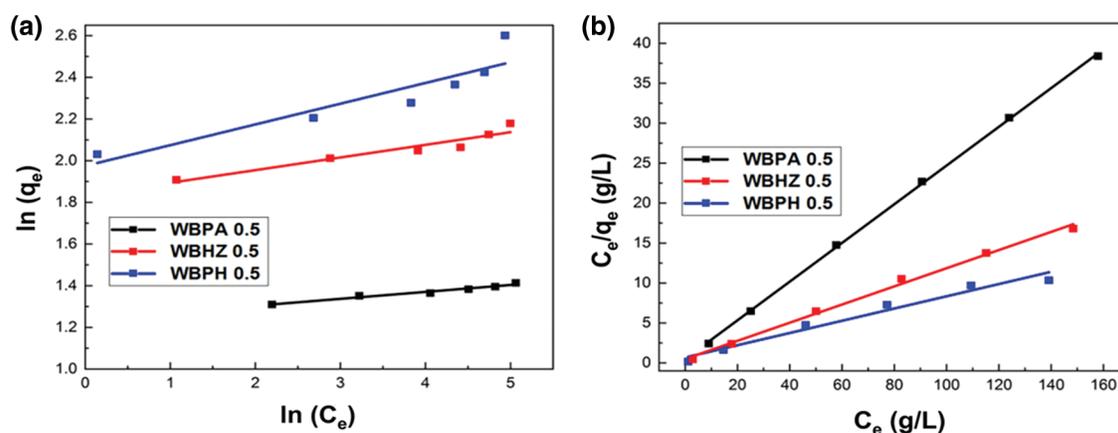


Figure 8: The Freundlich (a) and Langmuir (b) adsorption isotherm models

Table 3: Parameters of the adsorption isotherm model

Adsorbent	Freundlich			Langmuir		
	n	$K_F [(g/g)(L/g)^{1/n}]$	R^2	$q_L(g/g)$	$K_L(L/g)$	R^2
WBPA 0.5	30.05	3.45	0.965	4.13	0.481	0.999
WBHZ 0.5	16.47	6.25	0.892	8.79	0.231	0.994
WBPH 0.5	10.04	7.21	0.806	13.05	0.113	0.964

3.3.3 Adsorption Kinetics Studies

In order to further study the adsorption kinetics of the mixed system, the pseudo-first-order model Eq. (4), pseudo-second-order model Eq. (5) and the intraparticle diffusion model Eq. (6) are used for analysis and evaluation.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (4)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

$$q_t = k_{di} t^{1/2} + C_i \quad (6)$$

where q_e (g/g) and q_t (g/g) are the adsorption amount of diesel at equilibrium and at time t (min), respectively. k_1 (min^{-1}) and k_2 (g/g min) are the rate constant of the PFO and PSO, respectively. k_{di} ($\text{g/g}\cdot\text{min}^{1/2}$) is intraparticle diffusion model constant. C_i (g/g) is boundary layer thickness constant and t (min) is time.

Adsorption kinetic as a key factor determines the uptake rate of solute, representing the adsorption efficiency of adsorbent. Pseudo-first-order (PFO), Pseudo-second-order (PSO), and Weber-Morris

intraparticle diffusion model were applied for the kinetics model fitting of diesel adsorption data. Fig. 9 indicates the fitting of experimental data with the three kinetics models for diesel adsorption, and Table 4 provides the results of the PFO and PSO kinetics models fittings for diesel adsorption using the magnetic biochar/Ni composites. It can be demonstrated that the R^2 value in the PSO model of diesel adsorption using WBPA 0.5, WBHZ 0.5 and WBPH 0.5 is all 0.999, higher than that in the PFO model, indicating that the PSO model could better describe the adsorption of diesel using the magnetic biochar/Ni composites, being used to calculate the adsorption amounts of diesel at equilibrium is in good combination with experimental data. As is well known, the PSO equation model belongs to chemical adsorption, which means that chemical reaction is also involved in diesel adsorption process using the magnetic biochar/Ni composites [54].

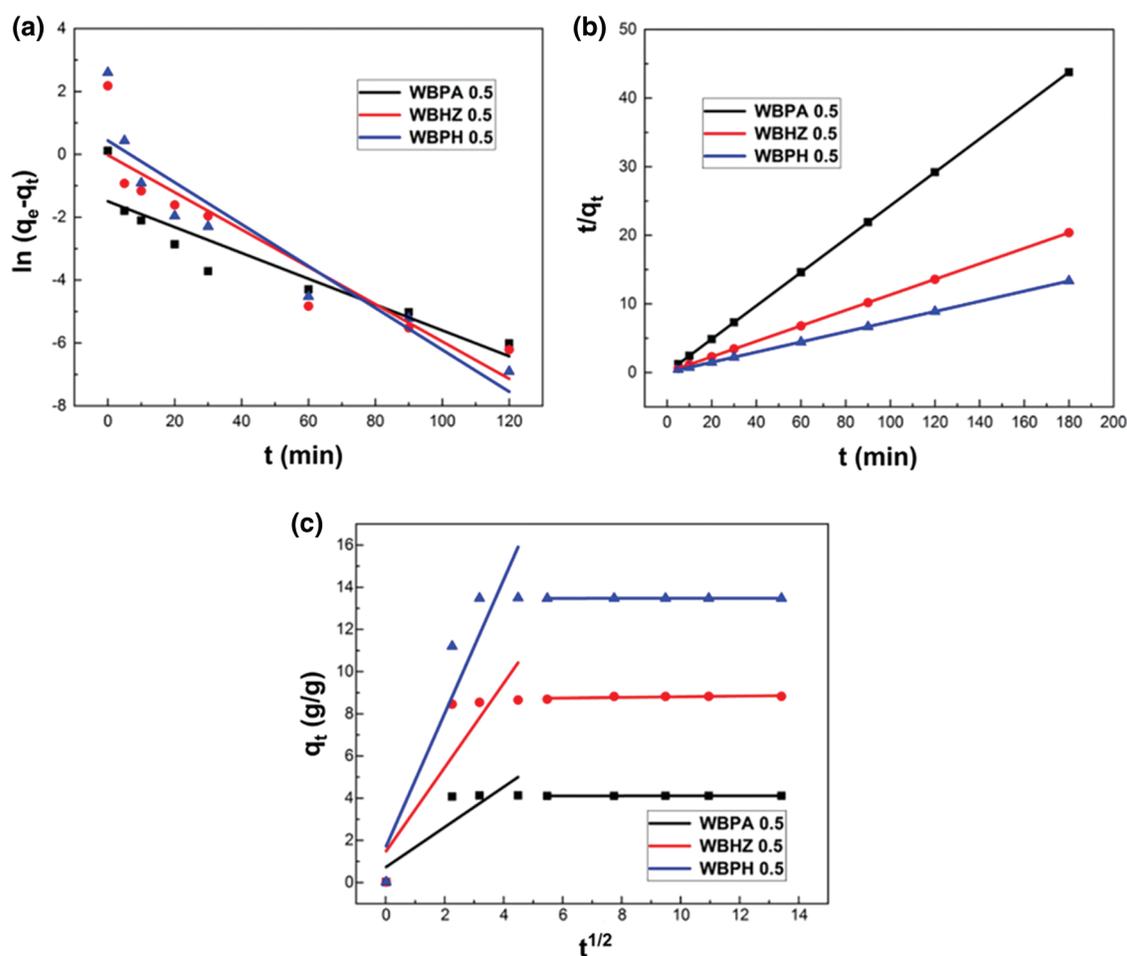


Figure 9: The Pseudo-first-order (a), Pseudo-second-order (b), and Weber-Morris intraparticle diffusion (c)

Table 4: The adsorption kinetic parameters of diesel using WBPA 0.5, WBHZ 0.5 and WBPH 0.5 in the PFO and PSO model

Adsorbent	$q_{e,exp}$ (g/g)	Pseudo-first order			Pseudo-second order		
		$q_{e,cal}$ (g/g)	k_1 (min^{-1})	R^2	$q_{e,cal}$ (g/g)	k_2 ($\text{g g}^{-1} \text{min}^{-1}$)	R^2
WBPA 0.5	4.11	0.22	0.041	0.817	4.11	4.172	0.999
WBHZ 0.5	8.83	0.98	0.059	0.829	8.85	0.114	0.999
WBPH 0.5	13.47	1.55	0.067	0.856	13.51	0.074	0.999

In order to analyze the control step of diesel adsorption process, the adsorption kinetics of the magnetic biochar/Ni composites for diesel are investigated by the Weber-Morris intraparticle diffusion model, as shown in Fig. 9c. The intraparticle diffusion parameters of diesel adsorption using WBPA 0.5, WBHZ 0.5 and WBPH 0.5 are shown in Table 5. It can be noted that the fitting of data using intraparticle diffusion model is linear but does not pass through the origin, so intraparticle diffusion is not a sole rate controlling adsorption process. Fig. 9c shows the intraparticle diffusion model has dual-linear characteristics between qt and $t^{1/2}$, indicating that the diesel adsorption using the magnetic biochar/Ni composites can be considered as a two-step process, among which, the first step rises sharply, being regarded as the outer-surface adsorption of the magnetic biochar/Ni composites, while the second step tends towards equilibrium, whose rate is limited by the intra-particle diffusion of particles. A larger slope can be observed from the first sharp section, indicating a higher removal rate of diesel oil, which can be attributed to the macroscopic structure of the magnetic wakame biochar composite material is closer to the microporous “honeycomb” structure than the macroporous “capillary” structure, and the “honeycomb” structure can provide stronger adsorption driving force and more active adsorption sites [55]. The slope of the second section is lower than that of the first section. This may be due to the slow diffusion of diesel molecules in the magnetic wakame bio-carbon nanocomposite material, resulting in a low removal rate, mainly due to the decrease of the micropore density gradient. The two-stage continuous mass transfer corresponds to the external to internal mass transfer and intra-particle diffusion in the pore and microporous structure of the magnetic wakame bio-carbon nanocomposite.

Table 5: Intraparticle diffusion model

Adsorbent	Intraparticle diffusion					
	k_{d1} (g/g min ^{1/2})	C_1 (g/g)	R_1^2	k_{d2} (g/g min ^{1/2})× 10 ⁻³	C_2 (g/g)	R_2^2
WBPA 0.5	0.953	0.714	0.755	0.781	4.101	0.951
WBHZ 0.5	1.997	1.465	0.768	0.714	8.652	0.943
WBPH 0.5	3.172	1.699	0.891	0.673	13.467	0.956

Therefore, in addition to the intra-particle diffusion resistance, the adsorption mechanism of the system is also affected. In addition, it was observed from the FTIR spectrum that the functional groups (such as -OH, -NH and -CH) in the magnetic wakame biochar composite material have the effect of promoting the binding of diesel molecules to the active sites on the surface of the material. BET shows that high specific surface area and rich pore structure help to improve mass transfer efficiency.

3.4 Magnetic Recovery Cycle Experiment

The magnetic wakame bio-carbon nanocomposite material can be separated from water under the action of an external magnetic field. The key to the sustainable application of this type of magnetic biochar is its reusability and good stability. The magnetic properties of WBPA 0.5, WBHZ 0.5 and WBPH 0.5 were measured using the VSM technique under a magnetic field between -20,000 Oe and 20,000 Oe, as shown in Fig. 10, the saturated magnetization (M_s) of the WBPA 0.5 reaches up to 102.47 emu g⁻¹, exhibiting good magnetic separation performance. After the five times recycling of adsorption and desorption, the adsorption capacity of WBPA 0.5, WBHZ 0.5 and WBPH 0.5 for diesel only decreased by 3.16%, 7.27% and 9.28%, respectively (Fig. 11), demonstrating their good cycle stability and reusability. Therefore, the magnetic wakame biochar composite material has great potential in actual industrial wastewater treatment.

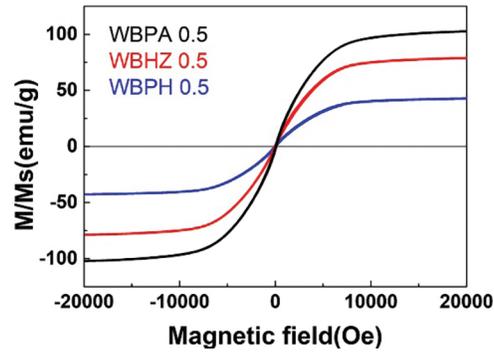


Figure 10: Magnetization curve of WBPA 0.5, WBHZ 0.5 and WBPH 0.5

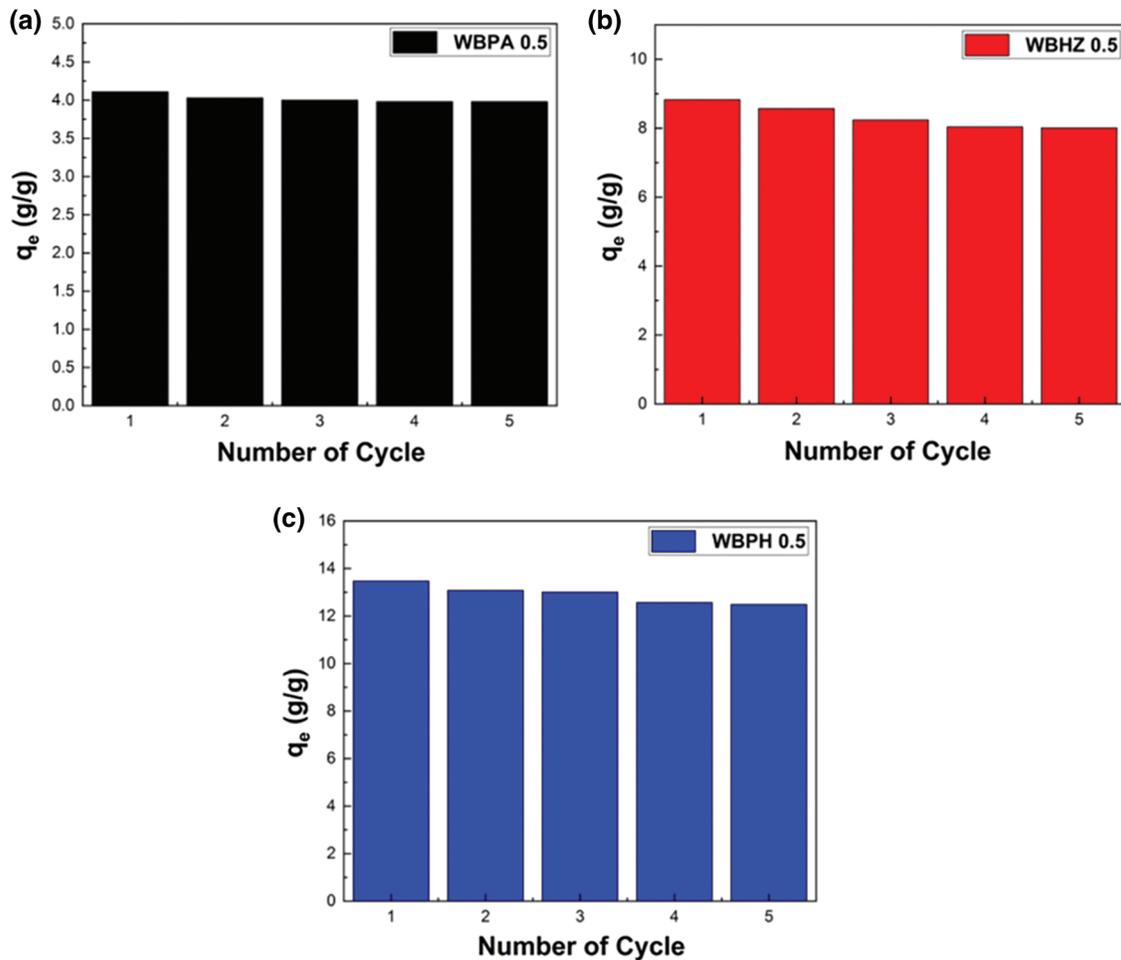


Figure 11: The reusability of magnetic wakame biochar composites

4 Conclusions

The magnetic wakame biochar/Ni composites were prepared with different activating reagents, which have larger specific surface area, abundant porous structure, and various reactive groups, endowing them with superior adsorption performance. The maximum adsorption capacities for diesel using WBPA 0.5,

WBHZ 0.5 and WBPB 0.5 are 4.11, 8.83, and 13.47 g/g, respectively. The adsorption process is more suitable for the Langmuir model and the Pseudo-second-order model. After five adsorption-desorption cycles, the biochar/Ni composites still have higher adsorption efficiency, exhibiting good stability and reusability. Therefore, the magnetic wakame biochar/Ni composites are expected to become potential adsorbents for the treatment of oily wastewater.

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