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Contrast effect of biochars and attapulgite clay on the adsorption and removal of cadmium ions from metal contaminated aqueous solution

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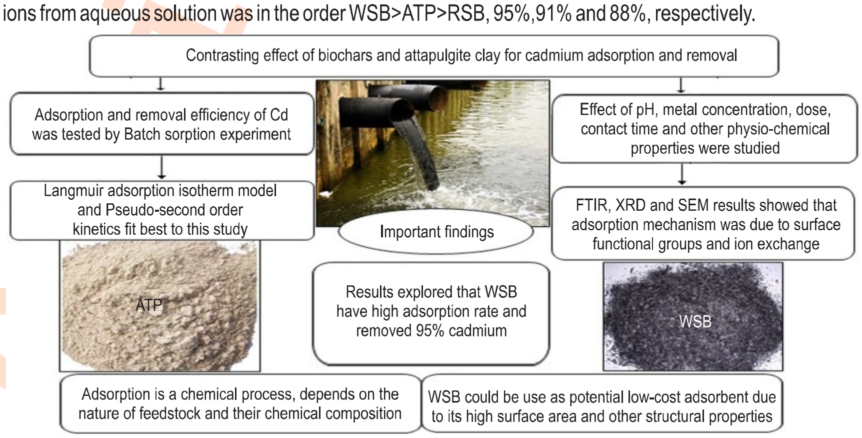
Abstract

Aim : To study the contrasting effect of adsorption and removal of cadmium ions using wheat straw biochar, rice straw biochar and attapulgite clay in contaminated aqueous solution.

Methodology : Batch sorption experiment was carried out to investigate the parameters influencing the adsorption capacity such as pH, initial cadmium concentration, adsorbent dose and contact time. The physical and chemical characteristics of biochars and clay were studied and adsorption mechanism was analyzed by scanning electron microscopy, infrared spectroscopy, Brunauer-Emmett-Teller and X-ray diffraction, which indicated high adsorption and removal of Cd^{+2}ions by wheat straw biochar was mainly due to the presence of surface carboxyl functional groups –OH, C-O, COOH that reacted Cd^{2+}ions.

Results : The adsorption effect of wheat straw biochar (WSB), rice straw biochar (RSB) and attapulgite (ATP) clay were compared. The results showed that adsorption isotherms were best fit to Langmui isotherm model. The adsorption kinetics study well matched with pseudo second order model and the maximum adsorption equilibrium of WSB, RSB and ATP reached to 100, 160, and 120 min, respectively. The results showed that adsorption rate was maximum at pH 6 with 0.1 g dose of adsorbent, 40 mg l^{-1} metal concentration, and contact time of 100 min at 30°C for WSB. The maximum percent removal of cadmium ions from aqueous solution was in the order WSB>ATP>RSB, 95%,91% and 88%, respectively.



Interpretation : The results explored that wheat straw biochar has high Cd^{2+}adsorption rate and removal efficiency in contaminated water than others. Hence, the results explored that WSB is a potential, low-cost adsorbent and can be used as cadmium decontaminant in polluted water with no secondary pollution.

Key words: Attapulgite, Adsorption isotherm, Biochar, Cadmium ions, Kinetics

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Introduction

Cadmium is considered as most toxic heavy metal which poses a negative effect on the environment and causes a hazardous threat to plants, human beings and animals due to easy accumulation and non-biodegradable activity (Anayurt *et al.,* 2009). Cd-contaminated food is the leading source of Cd entry in human body through food chain (Dai *et al.,* 2012). Cadmium content is increasing in the environment mainly due to mining operations, electroplating, plastics, batteries, petroleum refineries and fertilizers (Kadirvelu *et al.,* 2001). Human activities have contributed about 13,000 of total 30,000 tons of annual Cd^{+2} into the environment (Gallego *et al.,* 2012). Thus, removal of cadmium has become one of the main focus of research, using low-cost natural adsorbent for wastewater treatment (Ali, 2010). Some techniques have been exploited for wastewater treatment, such as chemical precipitation, ion exchange, filtration, and adsorption (Barakat, 2011). Among these methods, adsorption is emerging as an attractive method for removal of heavy metals due to its low-cost and environment friendly nature (Gupta *et al.,* 2009).

Recently, more attention has been made on the use of natural adsorbent as an alternative to replace the conventional adsorbent. Biochar, which results from thermal degradation of organic materials such as agricultural biomass, wood, crop straws, manure and other solid wastes materials (Laghari *et al.,* 2016) is a pyrogenic carbon-rich solid material with high porosity, large surface area, enriched surface functional groups and mineral components. All these physio-chemical properties renders it to be the best adsorbent to remove pollutants from aqueous solutions (Ahmed *et al.,* 2016). The properties of biochar depend on the nature of feedstock used and pyrolysis conditions (Nsamba *et al.,* 2015). Previous studies have suggested that biochar can be used as an effective material for sorption of heavy metals from wastewater (Zhang *et al.,* 2012; Regmi *et al.,* 2012), as well as an amendment for immobilization of heavy metals in contaminated soils (Mohan *et al.,* 2014). Thus, biochar application has been a core interest of many researchers to remove the pollutants from aqueous solution (Tan *et al.,* 2015). Biochar is effective in removal of competitive heavy metals from aqueous solutions, but a detailed analysis concerning the adsorption process have only focused on lead. There is still a lack of data concerning the sorption mechanism of cadmium ions separately (Inyang *et al.,* 2012).

Additionally, there is still a need for research work concerning the influence of pH, ions exchange, thermodynamics, contact time and sorption and desorption process. Many studies have distinguished an effective removal of cadmium ions using biochar produced from different agricultural wastes. High potential of rice straw, sugarcane bagasse, pinewood and rice husk to remove Pb and Cd^{+2} from aqueous solution in the range of 0.004–0.66 $mmolg^{-1}$ has been reported (Xu *et al.,* 2013). Recently, twenty-one different kinds of biochar adsorption capacity have been compared for heavy metals suggesting that biochar produced at low pyrolysis temperature (350°C) can ensure high removal efficiency than fast pyrolysis biochars (Wang and Liu, 2017). Attapulgite is a fine-grained natural clay available in many parts of the world. It is acrystalline magnesium silicate mineral with fibrous morphology. There is an upsurge interest in recent years to use clay to remove heavy metals from contaminated water, because it is non toxic, naturally available, has unique structural properties, high surface area and moderate cation exchange capacity (Wang *et al.,* 2017), which could be a best source for adsorption and immobilization of heavy metals from the solutions (Chen and Wang, 2009). Hence, ATP has become a promising adsorbent for removal of heavy metals from aqueous solutions (Wang and Wang, 2010).

In previous studies, different kinds of biochar have been studied for the removal or minimization of cadmium ions from aqueous solution by applying different techniques. Based on the physio-chemical properties of feedstock used for the production of biochar showed a different degree of metal sorption (Wang *et al.,* 2018). On the other hand, very few literatures are available on the utilization of attapulgite for decontamination of heavy metals from soil and water. Further studies are required to introduce new naturally available adsorbent for cadmium removal in metal contaminated water. Heavy metal contamination posed serious threat to agricultural soil and water for a long time in Baiyin city, Gansu, China. Attapulgite clay is a rich available resource in some parts of the Baiyin area that can be the best option to utilize for heavy metal immobilization locally. In this study, the contrast effect of wheat straw biochar (WSB), rice straw biochar (RSB) and attapulgite clay (ATP) were examined for the adsorption analysis of cadmium ions from aqueous solution. The batch sorption experiment was conducted to analyze the effect of adsorbent dose, initial metal concentration, pH, contact time and molecular study was examined by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and X-ray diffraction (XRD) and BET to understand the adsorption mechanism.

Materials and Methods

Characterization of biochars and attapulgite clay : The elemental analysis of WSB and RSB total carbon (C), total hydrogen (H) and nitrogen (N) contents were determined by Elemental Analyzer (Carlo-Erba NA-1500). Surface morphology of the samples were determined by X-ray photoelectron spectroscopy (XPS) using a Thermo Scientific (ESCALAB250 spectrophotometer, USA) and scanning electron microscopy (SEM) using JSM-7600F (JEOL Ltd., Japan). FTIR spectra was utilized to observe the surface functional groups on biochars and clay by Thermo Electron Nicolet-360, USA. X-ray diffraction (XRD) was used to observe the changes in mineral crystals of WSB, RSB and ATP using a computer controlled diffractometer (X'Pert PRO). Brunauer-Emmett-Teller (BET) was used for specific surface area analysis of WSB that was carried out in Lanzhou University by Tristar 3200, Micrometrics, USA. Ash content was measured heating the WSB and RSB in a muffle furnace at 800°C for 4 hr. The pH of biochar and clay was

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measured (1:10 w/v, biochar in distilled water) with a digital pH meter (PHS-3E, Shanghai INESACo., Ltd). The concentration of Cd^{+2} ions in aqueous solution was analyzed by atomic absorption spectrometer (AA-7000, Shimadzu).

Preparation of stock solution : A synthetic stock solution of Cadmium was prepared by adding 0.1 g cadmium nitrate (commercially purchased) in one litre distilled water. All the working solutions were processed by diluting the stock solution with distilled water to get the desired cadmium concentration from 20 to 100 mg l^{-1}. The stock solution was stored at room temperature 25±5°C. The initial pH of aqueous solution was set in the range of 3 to 8 and adjusted by adding NaOH and HNO_3. The amount of adsorbent dose was kept in the range of 0.05 to 2.5 g, respectively.

Batch sorption experiment : The batch sorption experiment was carried out with a different mass of adsorbent to determine the adsorption characteristics of WSB, RSB and ATP onto cadmium ion adsorption. The samples were air dried and sieved through 0.3 mm, 60 mesh. The solution was prepared by weighing accurately 0.1 g WSB, RSB and ATP in 150 ml, stock solution of Cd (NO_3). $4H_2O$ diluted to 20 to 100 mg l^{-1} and total volume of solution was 40 ml, the pH was kept at 6 and agitated at constant temperature shaker (THZ-82) for 4 hr at a constant speed of 180 rpm. After oscillation, the samples were centrifuged (TG-16G) for 5 to 10 min at 1000 rpm and filtered through a nylon filter (0.45 µm). Finally, the cadmium concentration in the filtrate was analyzed by atomic absorption spectrometer (AAS), according to manufacturer instructions. All these experiments were carried out in triplicate (n=3),under equally defined and optimized conditions at constant temperature of 25±5°C. The influence of pH on adsorption of cadmium ions onto WSB, RSB and ATP was investigated at initial pH ranging from 3 to 8 with 0.1 g adsorbent and 40 ml Cd solution. In these experiments, the important parameters influencing adsorption mechanism such as pH of the aqueous solution, initial cadmium concentration, adsorbent dose and contact time were studied. The removal efficiency and adsorption capacity of cadmium ions by adsorbents were calculated by the formula described by Bhatt *et al.* (2012).

Sorption isotherm: To estimate the adsorption capacity and intensity of cadmium ions onto biochar and clay surface, Langmuir and Freundlich isotherm models were used to fit the experimental data of sorption isotherms. Langmuir isotherm assumes that adsorption was observed at homogeneous surface containing a limited number of adsorption sites. Once a surface site absorb metal ions then no more sorption can take place at that specific site, which indicate that the surface reaches a maximum equilibrium capacity, while Freundlich model is a purely empirical isotherm which indicates heterogeneous adsorption with non-uniform distribution of energy level. The linear form of Langmuir isotherm model

$\left(\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m}\right)$ and Freundlich model ($lnq_e = \ln(k_F) + \frac{1}{n} lnC_e$)

was followed as described by Pathania *et al.* (2016).

Kinetic study: Adsorption kinetics was proposed to explain the adsorption mechanism. In batch sorption kinetics experiment, a known mass of wheat straw biochar, rice straw biochar and attapulgite clay, 0.1 g and 40 ml Cd^{+2} solution of the desired concentration (40 mg l^{-1}) at pH 6 were placed in conical flasks (150 ml), and kept under isothermal conditions in a constant temperature shaker at 140 rpm at 25°C. Triplicate samples were sequentially collected from the shaker after 0, 20, 40, 60, 80,100, 120, 140 and 160 min. The samples were filtered and the filtrate was analyzed by AAS. The maximum adsorption capacity of WSB, RSB and ATP was 100, 160 and 120 min, respectively. The adsorption capacity was determined by pseudo-first order and pseudo-second order model. The linear form of pseudo-first order ($Log(q_e-q_t)=Logq_e-K_1t/2.303$) and pseudo-second order model ($t/q_e=1/(k_2q_e^2)+(1/q_e)t$) was calculated as described by Wang *et al.* (2018).

Statistical analysis: Microsoft Excel 2007 was used for the data record and basic analysis, SPSS software was used for data documentation and statistical analysis of the data to find mean and variance. Origin software (8.6 version) was used for drawing figures of adsorption isotherm and kinetic study.

Results and Discussion

WSB and RSB was prepared via slow pyrolysis at 600°C and 450°C, according to manufacturer. The pH value of both biochar and attapulgite was determined by mixing biochar to deionized water in 1:10 ratio Sorption of cadmium ions onto the surface of adsorbents were examined by SEM as presented in Fig.1. The surface of WSB was uneven and showed regular pore structures along with micropore channels. The elemental composition of biochar greatly depends on the source material (Sun *et al.,* 2014). The SEM and XPS surface elemental analysis indicated different composition such as WSB was dominated by carbon (77.82 wt%) and contained moderate content of oxygen-containing groups (14.32 wt%), along with low amount of Si, Ca, Cl and K (Fig.1).

On the other hand, RSB have low carbon content (46.38%) with unclear surface pores. The O/C to H/C ratio of biochar depends on the pyrolysis process, mainly due to demethylation and decarboxylation (Ashworth *et al.,* 2014). High pyrolysis temperature (>500°C) can raise the alkaline properties of biochar and increase aromatic character of O/C and H/C ratios that help in exchange of cations (Novak *et al.,* 2013). Attapulgite has rod-like morphology, and ambiguous structures of length of 1µm to several µm stacked into bundles as reported by Wang *et al.* (2017). Attapulgite has a large surface area, the rough void surface of Attapulgite is due to the van der Waals forces, and formation of hydrogen bonds that leads to many bumps caused by aggregation (Wang *et al.,* 2018).

The FTIR spectra of WSB, RSB and ATP before and after cadmium sorption reveals in (Fig. 2) the changes in vibration frequency at (Ahmed *et al.,* 2016) 4 cm^{-1}. The characteristic bands at 3743-32000 corrospended cm^{-1} to O-H stretch, 2364, 1545 and

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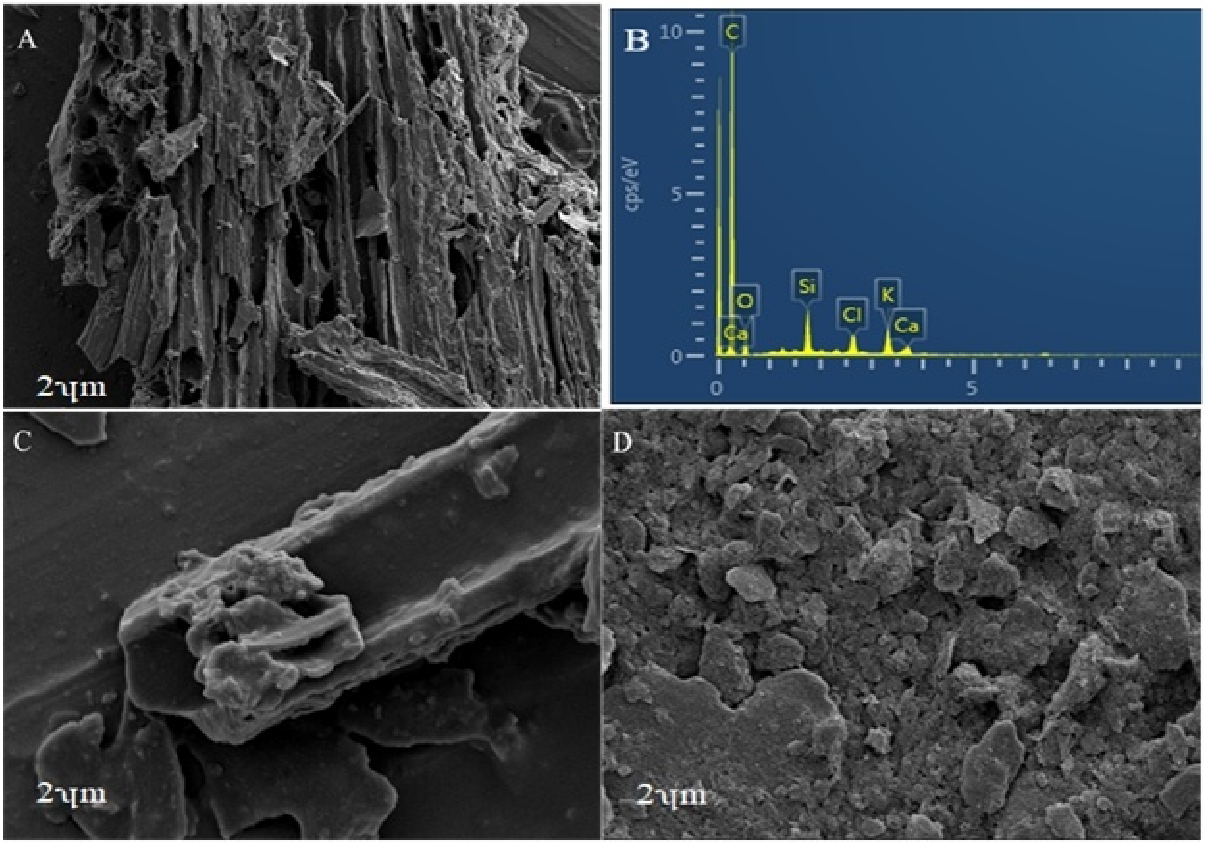

Fig. 1: Scanning electron micrographs after adsorption of cadmium ions onto; (A) Wheat straw biochar (WSB); (B) X-ray photoelectron spectroscopy (XPS) analysis of WSB; (C) Rice straw biochar (RSW) and (D) Attapulgite (ATP) clay.

1093 to -C=O, N-O or COOH and C-O of WSB, respectively, while peaks at 468 of RSB was due to O-Si-O stretch (Ding *et al.,* 2016). Attapulgite characteristic peaks showed a minor difference in structural changes whereas the frequency band at 1026 was possibly assigned to Si-O-Si stretching vibrations (Wang *et al.,* 2017). The peak alteration and drift from the original wavelength in the FTIR analysis reflected that cadmium ions was adsorbed onto the functional groups that changed the position of peaks after treatment with cadmium solution.

X-ray diffraction spectra of WSB, RSB and ATP are presented in Fig. 3. There were 4-6 sharp peaks in WSB and RSB, which showed peak differences after sorption process.The WSB and RSB before and after adsorbing cadmium showed characteristics peaks at $2\theta = 26^{\circ}$ which indicate that the attachment of cadmium or other cations onto biochar surface may change the entire configuration and showed some extra peaks. Larger distance was attributed due to the presence of hydroxyl–OH and carboxyl O=C-O or C-O functional groups as described (Lyu *et al.,* 2016). The intensity of WSB and ATP appeared at $2\,\theta = 50^{\circ}$ revealed that salt diffraction peaks could be the reason for ion exchange reaction between cadmium and other ions. Since there was no precipitation the ion exchange chemical reaction may be the main adsorption mechanism.

The effect of WSB, RSB and ATP on the adsorption capacity is shown in Fig. 4. The Langmuir and Freundlich model distinguish the adsorption effects and mechanism. (Pathania *et al.,* 2016). Langmuir model is mainly based on the assumption that maximum sorption corresponds to saturated monolayer of sorbent onto a specific homogenous surface containing specific number of adsorption sites (Yu *et al.,* 2016). The maximum adsorption was obtained by wheat straw biochar due to their distinctive physical properties and chemical composition. WSB has high carbon content and large surface and are more porous than RSB, due to different composition and pyrolysis conditions. High pyrolysis temperature can lead to high ash content in biochar, which can alter the chemical composition of biochar and influence the adsorption capacity (Ma *et al.,* 2016). WSB showed 25% ash content which corroborates with previous studies (Wang

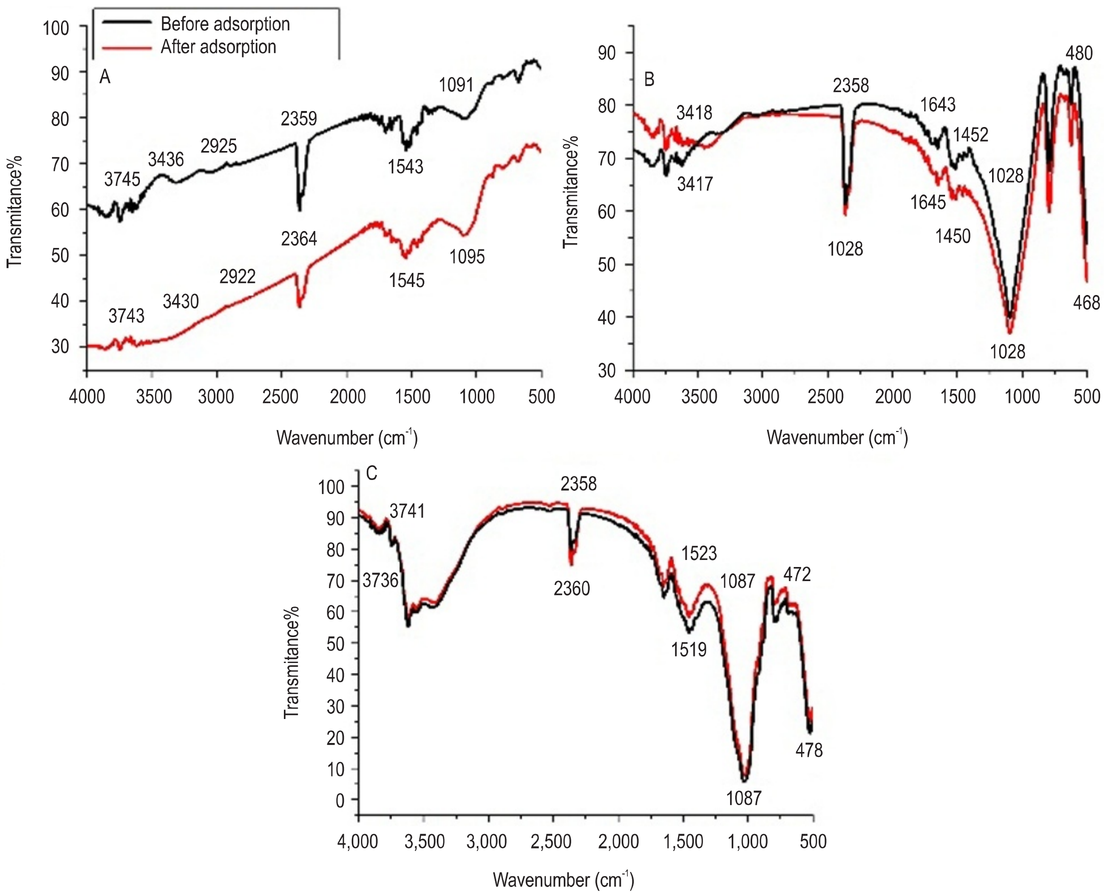

Fig. 2 : FTIR spectra before and after cadmium ion adsorption onto; (A) WSB), (B) RSB and (C) ATP.

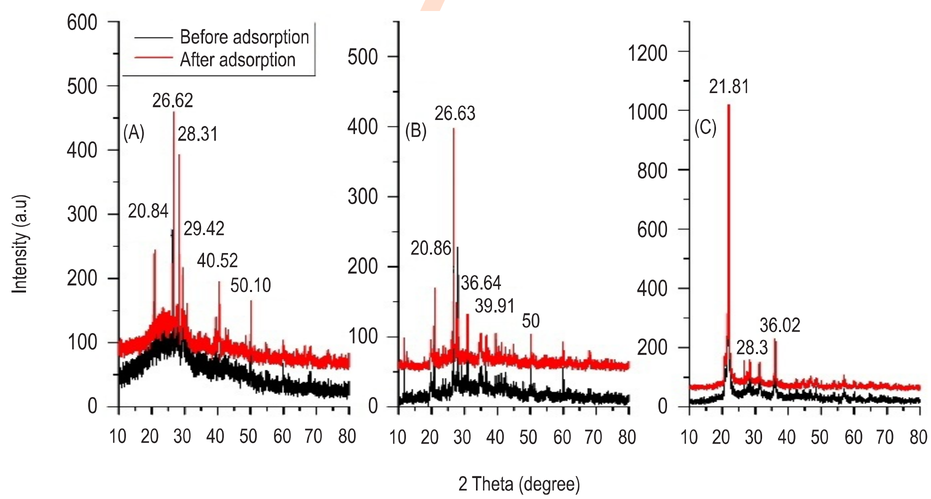

Fig. 3 : X-ray diffraction analysis and alteration in peaks after adsorption of cadmium by (A) WSB; (B) RSB and (C) ATP.

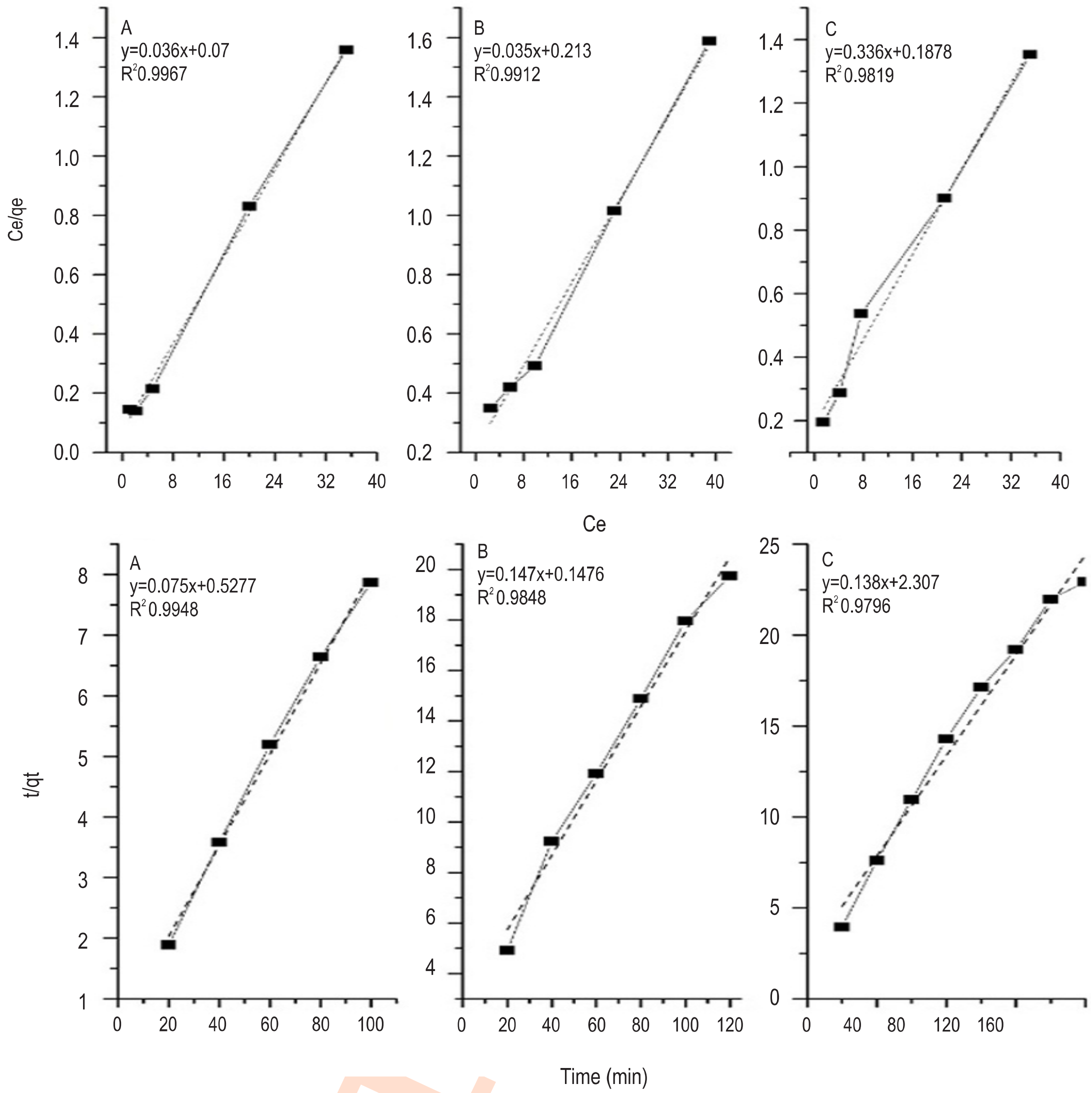

Fig. 4: Langmuir adsorption isotherm and pseudo-second order kinetics effect the adsorption capacity of cadmium ions onto (A) WSB; (B) ATP and (C) RSB in aqueous solution (C0: 40 mg l^{-1}; sample dose: 0.1 g, V: 40 ml; pH 6 at 25°C).

and Liu, 2017; Trakal *et al.,* 2014). Freundlich isotherm is satisfactory empirical and used for heterogeneous sorption energy system. The parameters of adsorption q_e, correlation coefficient (R^2), k_f and n values were analyzed from linear correlation equation ($\ln qe = \ln (K_F) + 1/n \ln C_e$), (Wang *et al.,* 2018), as shown in Table 1. However, evaluation of correlation coefficients (R^2), Langmuir isotherm model showed that R^2=0.9967, 0.9912, 0.9819 of WSB, ATP and RSB, was higher than Freundlich isotherm model (Fig. 4). The greater value of correlation coefficient assured that Langmuir isotherm fits well, explaining that the adsorption of cadmium ions can be considered as monolayer process as the surface consists of finite number of homogenous adsorption sites. The dimensionless separation factor (R_L) was found in the range of 0-1, which indicates favorable adsorption process. The details are mentioned in Table 1. The effect of contact time of cadmium adsorption onto the WSB, RSB and ATP is shown in Fig. 4.

The cadmium sorption characteristics of all sorbent were performed at the time interval of 20 to 240 min, which initially high removal efficiency within 20 min and then reached the equilibrium around 100 min to 160 min. The initial concentration of Cd^{+2} was

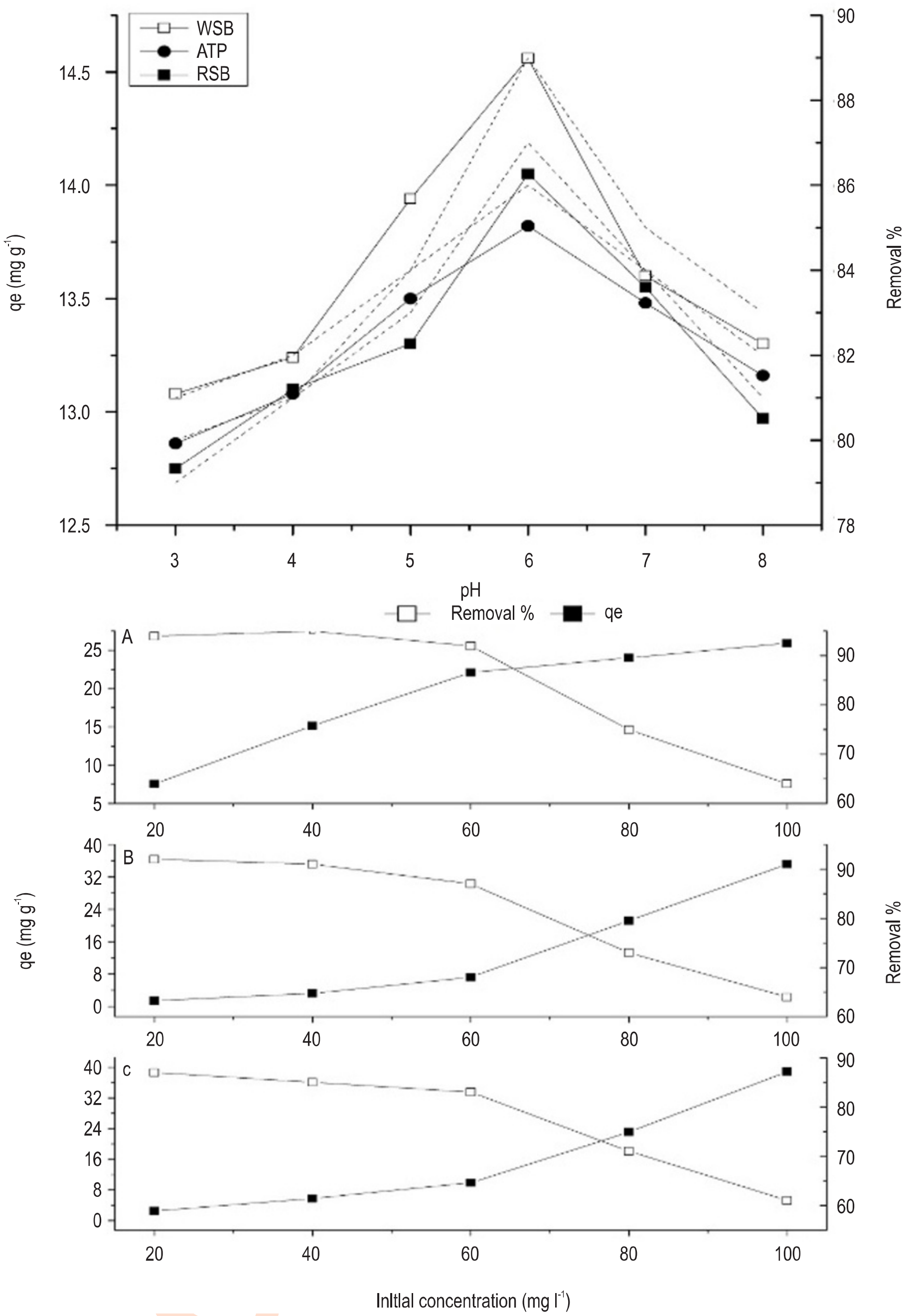

Fig. 5 : Batch sorption experiment parameters; pH and initial metal concentration effect on adsorption and removal of cadmium ions by (A) WSB; (B) ATP and (C) RSB.

40 mg l^{-1}. Initially, more surface adsorption sites were available and many functional groups were attached to cadmium ions. The adsorption sites were constantly occupied with time, which in turn slowed down the adsorption process. The pseudo-first order and pseudo-second order isotherm models were applied to interpret the adsorption kinetics. The maximum equilibrium adsorption capacity (q_e) and correlation coefficient (R^2) of WSB were 13.31 mg g^{-1} and 0.9948, respectively. ATP also showed high adsorption capacity and the sorption amount reached 6.65 mg g^{-1} in 120 min, which accounted for 96.75 % for its total removal. In pseudo-

Table 1 : Langmuir and Freundlich isotherm models parameters for cadmium ion adsorption onto Wheat straw biochar (WSB), Rice straw biochar (RSB) and Attapulgite (ATP) clay at pH6

	Langmuir isotherm				Freundlich isotherm		
Type of adsorbent	**qm (mg g^{-1})**	**KL (mg)**	**RL**	**R^2**	**Kf (mg g^{-1})**	**n**	**R^2**
WSB	27.21	0.49	0.05	0.9967	0.8384	3.30	0.6776
ATP	28.58	0.164	0.021	0.9912	0.5589	2.28	0.8329
RSB	29.76	0.17	0.021	0.9819	0.7424	2.78	0.8043

Table 2 : Kinetics parameters of pseudo-first order and pseudo-second ordermodels for cadmium ion adsorption onto Wheat straw biochar (WSB), Rice straw biochar (RSB) and Attapulgite (ATP) clay

Type of adsorbent	**Pseudo-first order model**			**Pseudo second order model**		
	qe (mg g^{-1})	**K1 (min^{-1})**	**R^2**	**qe (mg g^{-1})**	**K^2 (g mg^{-1} min^{-1})**	**R^2**
WSB	2.2924	0.8838	0.6088	13.3155	0.0106	0.9948
ATP	2.3665	0.7112	0.4787	6.6577	0.0090	0.9800
RSB	2.6989	0.001636	0.7108	4.5106	0.0166	0.9796

second order model, the time reaching the equilibrium and the adsorption capacity was in order: WSB>ATP>RSB. WSB was characterized with high surface area (4.58 m^2g^{-1}) with a pore volume of 0.007 cm^3g^{-1} which is similar to the previous findings of Sun *et al.* (2014) and Ma *et al.* (2016). The high surface area with micro-pores can be effective for the adsorption of Cd^{+2} ions by chemical interaction process including surface adsorption, precipitation and ion exchange (Ma *et al.,* 2016). Production conditions such as slow pyrolytic temperature (600 °C) of WSB can attribute high adsorption capacity due to high surface area (Sun *et al.,* 2014). The adsorption mechanism corresponded well with pseudo-second order model. The comparison of adsorption efficiency of cadmium ions using different adsorbent is shown in Table 2.

All the adsorbents having alkaline pH and the solution pH may regulate due to the surface charges and the degree of ionization of adsorbents. The pH was alkaline, WSB (9.54), RSB

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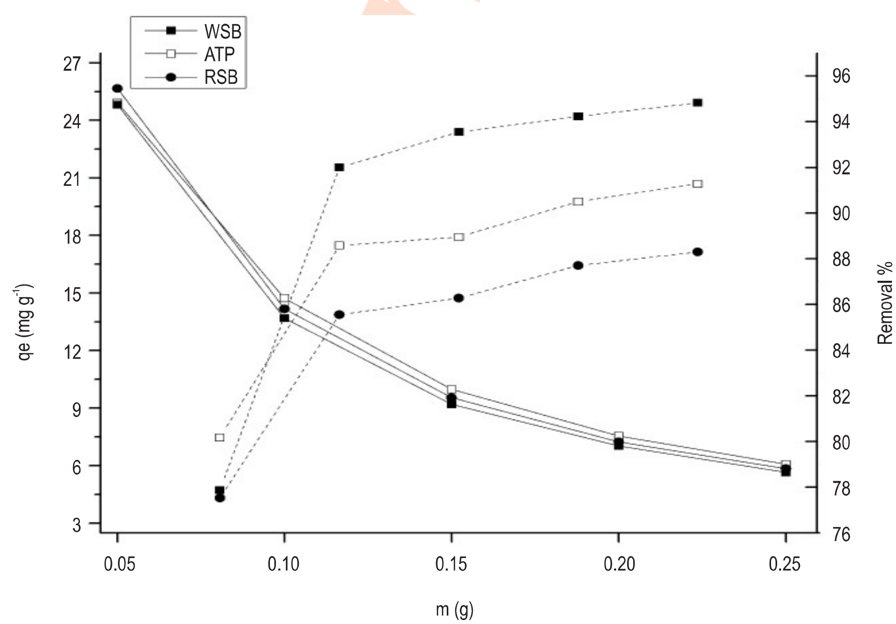

Fig. 6: Dose effect on adsorption and removal of cadmium using WSB, ATP and RSB in aqueous solution.

(9.12) and ATP (8.45). The effect of pH on Cd^{+2} adsorption was studied at pH 3.0 to 8.0, and the increase in the pH caused the increase in adsorption capacity of Cd^{+2} while maximum removal efficiency of three adsorbents was observed at pH 6. The adsorption capacity of WSB, ATP and RSB were highest (14.56 mg g^{-1} and 14.05 mg g^{-1} and 13.82 mg g^{-1}) at pH^{6}, (Fig. 5). The effect of pH on the adsorption process could initially increase the adsorption capacity to pH^{6} as protons compete with cadmium ions resulting in low adsorption capacity in strong acidic solution. When pH became more alkaline, the adsorption curves started declining.

Further, at high pH, heavy metals can be removed from the surface due to ion-exchange and electrostatic interaction by deprotonating the functional groups (Wang *et al.,* 2018). ATP clay has negative charge in solution. It is evident that competition starts between the cations and metal ions with negatively charged surface of ATP clay (Potgieter *et al.,* 2006). So it explains that electrostatic interactions precipitation, and chemical reaction are the main mechanism to interfere with Cd^{+2} adsorption (Park *et al.,* 2011). The effect of initial metal concentration (Co) of cadmium ions on the degree of its removal by WSB, RSB and ATP (in term of adsorption capacity and removal efficiency) was studied. The adsorption experiment was run at an initial concentration of 20, 40, 60, 80 and 100 mg l^{-1} at a constant adsorbent dose of 0.1 g at pH^{6} (Fig. 5). The adsorption capacity of all adsorbent significantly increased with the increase in C_o, because the increase in driving force of the concentration gradient at solid-liquid interface can increase the metal ions attachment onto the adsorbent (Komkiene and Baltrenaite, 2016). Thus, increase in cadmium ion concentration from 20-100 mg l^{-1} resulted in increased adsorption capacity, while removal efficiency rapidly decreased after 60 mg l^{-1}. The relationship between adsorbent dosage and Cd^{+2} adsorption capacity and removal efficiency is shown in Fig. 6. Addition of dose increased the percent removal of cadmium ions in the solution.

The WSB and ATP increased their removal efficiency from 78 to 95% and 80 to 93%, but the best adsorption dose was observed at 0.1g which was used for the rest batch experiment, because both adsorption capacity and removal efficiency meet at this concentration, and the maximum removal efficiency of WSB, ATP and RSB was found approximately 95%, 91% and 88% respectively. The adsorption capacity per unit increased with the increase of dosage, but the adsorption capacity per unit adsorbent decreased due to specific surface area of adsorbent increase with the increase of dosage. The adsorption rate of cadmium ions decreased with further addition of adsorbent dose. The possible reason is that during the reaction process, the high dose may lead to agglomeration phenomenon of WSB, which hinders the diffusion cadmium to the surface of adsorbent, resulting in decreased cadmium ion adsorption per unit mass (Ma *et al.,* 2016).

In this study, WSB, RSB and ATP were used for the removal of cadmium ions in contaminated aqueous solution by batch sorption experiment. The physico-chemical properties of biochar and clay were investigated, while the cadmium adsorption was detected through AAS. Both BCs and clay effectively removed cadmium ions from aqueous solution and their removal efficiency and adsorption capacity were studied. All the three adsorbent reached maximum removal efficiency at pH^{6}. The results indicated that WSB was more effective adsorbent for Cd^{+2} ion removal from aqueous solution. The adsorption isotherm data for all adsorbent was best fitted to the Langmuir model, and the maximum adsorption capacity was recorded at 40 mg l^{-1} Cd^{+2}. The results of adsorption kinetics showed that adsorption could be the best fit to pseudo-second order model. Hence, the results based on batch sorption experiment indicated that WSB is low-cost potential adsorbent for cadmium removal from aqueous solution. Furthermore, it is an environmental friendly approach to treat contaminated water without causing secondary pollution. The secondary use of these adsorbents can be determined in water and soil.

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