

Original Article

Nutrients Adsorption onto Biochar and Alum Sludge for Treating Stormwater

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ABSTRACT

In this study, *Eucalyptus wandoo* (EW) biochar and alum sludge and their mixture are used in batches to remove nutrients (ammonium-nitrogen (NH₃-N), nitrate-nitrogen (NO₃-N), nitrite-nitrogen (NO₂-N), and phosphate-phosphorus (PO₄-P)) from synthetic stormwater. First, batch tests were conducted using biochar and alum sludge separately with varying concentration (0.5–5 mg/L); dosage (2–10 g); pH (4–9); and contact time (0–24 h). The results revealed that the EW biochar alone could remove 100% of NO₂-N and NH₃-N while the alum sludge alone could remove 100% of PO₄-P. Next batch tests were carried out with the mixture of EW biochar and alum sludge of different proportions and the results revealed that the mixture of 8 g biochar and 2 g alum sludge gave the best combination for removing all nutrients (NH₃-N = 98.2%; NO₂-N = 99.4%; PO₄-P = 99.8%) except NO₃-N. The adsorption kinetics of mix-medium were studied for Intraparticle diffusion, liquid film diffusion and Lagergren pseudo first and second-order models. The nutrient adsorptions onto mix-medium show two-stage adsorption process following Intraparticle diffusion and liquid film diffusion. The results revealed that the pseudo-second order kinetic models fitted better with high R² (0.98–1.00) and small normalized standard deviation, Δq (0.00–0.62). The isotherm results revealed that the NH₃-N adsorption followed both Langmuir and Freundlich model while NO₂-N and PO₄-P adsorption followed Langmuir model better.

Keywords: adsorption, nutrients, biochar, alum sludge, stormwater

INTRODUCTION

Due to the expansion of urbanization, the volume of urban stormwater runoff has also been increased significantly [1–4]. This urban runoff consists of significant number of pollutants including nutrients, heavy metals, oil, grease and hydrocarbons. These chemicals may be released from vehicle emissions and fluid leaks from vehicles, domestic fertilizer, pesticides, refuse and pet faeces [1]. One of the major constituents found in urban stormwater runoff is nutrients (i.e., nitrogenous and phosphorous matter such as ammonium-nitrogen (NH₃-N), nitrate-nitrogen (NO₃-N), nitrite-nitrogen (NO₂-N), and phosphate-phosphorus (PO₄-P)). The presence of excessive nutrients in urban runoff may produce algal blooms (eutrophication) in receiving water bodies such as lakes, wetlands, streams, rivers or coastal waters. When the

algae starts to decompose, the bacteria grows and consumes dissolved oxygen (DO) from water and depletes the required DO which endangers the marine ecosystem [5]. It is therefore utmost important to remove excessive nutrients from stormwater for sustainable ecosystems.

The dissolved nutrients in water may be removed either by biological processes (e.g. nitrification or denitrification) or physical adsorption. Nutrients removal methods include reverse osmosis, electro dialysis, activated carbon adsorption, adsorption by green media and ion exchange with synthetic resins [6]. Among these methods, adsorption was found to be the most cost-effective and environment-friendly process because of its operational simplicity and economic viability [7]. Xuan *et al.* [8] and Kim *et al.* [9] used different types of low cost green sorption media such as tree bark, wood chips, wheat straw, tire crumbs, sawdust, alfalfa, mulch compost,

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paper (newspaper), cotton, and sulfur/limestone. Kim *et al.* [9] found 100% nitrate removal using Alfalfa and newspaper but only 60% with mulch compost. Recently, Harmayani and Anwar [1] used radiata pine sawdust to remove aqueous phase nitrogen species and found it very effective for $\text{NO}_3\text{-N}$ and $\text{NO}_2\text{-N}$ removal (100%). Other researchers have shown biochar to be a suitable medium for treating waste water [10–12]. Biochar is a charcoal-like material produced by heating biomass to high temperatures (300–1000°C) under low oxygen conditions (i.e., pyrolysis) [13]. Due to the microporous structure and cation exchange capacity (CEC) of biochar, it may be used as a good adsorbent for removing nitrogen species from water. Reddy *et al.* [11] used wood-derived biochar (pyrolysis at 520°C) to treat stormwater for removing total suspended solid (TSS), nutrients and heavy metals. However, the removal of phosphorous using biochar was found minimum (< 50%). Adhikari *et al.* [14] tested various adsorbent media such as red gum mulch, pine mulch, flyash, oyster shell, sawdust, clay, sand, zeolite, dolomite, alum and lime sludge for removing phosphorus from stormwater and found alum sludge the most effective adsorbent in removing phosphorus (99%). Nair and Ahammed [15] could remove 87% of phosphorus using alum sludge. Craig *et al.* [16] found 80% phosphorous removal enhancing the sand filter. Alum is used to remove natural organic matter from water and thus the alum sludge obtained from the treatment plant still has the capacity to remove phosphorus [14,17,18].

The current study used a new biochar derived from *Eucalyptus wandoo* (EW), alum sludge and a mixture of these adsorbents to remove nutrients from stormwater. The EW, commonly known as ‘white gum’, was formerly harvested as a commercial source of tannin in Western Australia and is used in both light and heavy construction [19]. The increasing use of EW in the construction industry has produced abundant amounts of wood waste such as wood chips, wood shavings and wood pellets. Again Australian water authorities have reportedly produced an alarming 150 to 43,500 tons of alum sludge per annum [20,21]. Victorian water industry, Australia assessed that a total cost of \$6.2 million per annum required to dispose alum sludge into landfills and sewers [20,21]. Therefore, the use of EW biochar and alum sludge would decrease the cost of disposing alum sludge and timber construction wastes, reduce the land pollution and help to protect water resources. Hence the biochar, alum sludge or their mixture may be used in stormwater management for a sustainable future. The objective of this research is to examine the adsorption characteristics of biochar, alum sludge and their mixture to remove nutrients from synthetic

stormwater. The quantification of adsorption capacity will help urban waterways managers to design and implement the stormwater treatment facilities in a cost-effective way.

MATERIALS AND METHODS

Adsorbent selection

The EW biochar, alum sludge and their mixture were selected as adsorbents for this study. The EW biochar was collected from Energy Farmers Australia Pty Ltd in Geraldton, Australia and the dewatered alum sludge were obtained from Neerabup ground water treatment plant, Perth, Australia. The EW biochar was produced from the waste wood of ‘*Eucalyptus wandoo*’ at a pyrolysis temperature of 400°C for approximately 10–15 minutes, although temperatures can vary through the kiln. The pyrolysis is a continuous process, processing up to 250 kg/h of feedstock, yielding 30% biochar by weight. The biochar production rate varies between 21.7–51.5% on a mass basis but the percentage yield has an inverse relationship with the pyrolysis temperature [22]. To remove fine particles, two-step sieve analyses were performed for biochar sample using dry and wet sieving methods [11] while only dry sieving was used for alum sludge due to the possibility of drain-out during wet sieving. The particle size of 2.36 mm were chosen for both adsorbents. The sieved adsorbents were washed with deionized water and the wash water (2 mL) was analyzed for any possible nutrient residues. After 6–7 washes, the nutrients were found negligible in washed water. The samples were oven dried and stored in an air-tight container at room temperature ($22 \pm 1^\circ\text{C}$).

Synthetic stormwater preparation

The synthetic stormwater containing nutrients were prepared using analytical grade chemicals purchased from Thermo Fisher Scientific, Sydney, Australia. The stock solutions of nutrients such as $\text{NH}_3\text{-N}$, $\text{NO}_3\text{-N}$, $\text{NO}_2\text{-N}$ and $\text{PO}_4\text{-P}$ were prepared using NH_4Cl , NaNO_3 , NaNO_2 and NaH_2PO_4 respectively. Deionized water was used to prepare all synthetic stormwater of nutrient concentrations (0.5–5 mg/L) based on the Australian Runoff Quality [2,23] and other similar studies [1,11,24]. The solutions pH were adjusted by dosing NaOH (0.1 M) or HCl (0.1 M) which were measured using a pH meter (HACH 40d with PHC 101 HAC electrode, HACH, Manchester, UK).

Characterization of adsorbents

Scanning electron microscopy (SEM) imaging and energy dispersive X-ray spectroscopy (EDS) of biochar and alum

sludge samples were conducted to characterize and observe the morphology and identify the surface elements. Sample preparation involved platinum coating (approximately 3 nm) using a Baltec MED 020 coater. The sample was observed through an ion beam scanning electron microscope (Zeiss Neon 40 EsB, Carl Zeiss, Oberkochen, Germany) at 15.0 kV and 11.0 mm working distance. An X-ray diffractometer (D8 Advance-Bruker aXS, Bruker, Billerica, USA) was used for powder X-ray diffraction (PXRD) patterns employing Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) at an accelerating voltage of 40 kV and current of 40 mA for 2θ ranging from 5 to 60°. A Micromeritics Tristar II3020 (Micromeritics, Norcross, USA) was employed to measure nitrogen adsorption-desorption isotherms to obtain the surface area, pore size and pore volume. Prior to nitrogen adsorption-desorption measurements, the samples were prepared at 180°C for 12 h under high vacuum.

Batch experiments

Batch adsorption experiments were conducted with EW biochar, alum sludge of 2.36 mm and their mixture with varying initial nutrient concentrations (0.5–5 mg/L), adsorbent dosages (2–10 g) and pH (4–8). Each adsorbent dosage was mixed with nutrient solution (0.5–5 mg/L; 100 mL) in a 250 mL Erlenmeyer flask. The pH values were kept constant at 6.5 (± 0.5) except the experiments with varying pH (4–8). Parafilm was used to cover the flasks to avoid any evaporation of the solution. The flasks were placed on a 16 flask capacity shaking platform (Innova 2100, New Brunswick Scientific, Midland, Canada) and shaken at 100 rpm at room temperature ($22 \pm 1^\circ\text{C}$). Two milliliters of solution was extracted using a syringe and filtered through a 0.45 μm syringe filter (GE Water and Process Technologies, Milwaukee, USA) at a predetermined time interval (5–60 min). The filtered water samples were analysed for nutrient species (NH $_3$ -N, NO $_3$ -N, NO $_2$ -N and PO $_4$ -P) using AQUAKEM 200 water analyser (Labmedics Analytical Solutions, Manchester, UK; nominal detection limit of 0.002 mg/L with a 1.5% measurement error at 95% confidence level) following the standard methods [25]. The data was recorded until the equilibrium concentrations C_e (mg/L) were reached. All experiments were carried out in duplicate/triplicate and the average values are reported. The variance between any replicate measurements was smaller than 1%. The amount of adsorption q_t ($\mu\text{g/g}$) was calculated using the nutrient concentration C_t (mg/L) measured at time t [1]:

$$q_t = \left(\frac{C_0 - C_t}{W} \right) \times V \quad (1)$$

where C_0 is the initial concentration (mg/L), W is the weight of biochar (g) and V is the volume of solution (L). The percentage removal was calculated by the ratio of difference between the initial concentration (C_0) and the concentration obtained at specific time (C_t):

$$\text{Removal (\%)} = \frac{C_0 - C_t}{C_0} \times 100 \quad (2)$$

RESULTS AND DISCUSSION

Surface characterization of adsorbents

SEM image and EDS of EW biochar and alum sludge are shown in **Fig. 1a–d**. The EDS of biochar shows that the main constituent of biochar is carbon (**Fig. 1b**). The biochar in this study was found acidic similar to the biochar used by Yao *et al.* [22] and Oh *et al.* [26]. The nitrogen adsorption-desorption isotherm in BET method shows type IV with strong hysteresis in adsorption-desorption branches indicating the mesoporous nature of biochar [27]. The surface area and pore diameter were also determined by N $_2$ adsorption-desorption isotherms for both medium. The surface area of alum sludge was found 148.55–179.13 m 2 /g by BET, Langmuir and single point method which was 7 times higher than the EW biochar. The pore diameter and micropore volume of alum sludge was found 8.66 nm and 0.3276 cm 3 /g by Barret-Joyner-Halenda (BJH) method which was 2 and 14 times higher than EW biochar. The surface area and pore volume of alum sludge confirmed that it may be a very good adsorbent. Alum sludge is produced as a by-product in groundwater treatment. One of the most common coagulant in groundwater treatment is Aluminium sulphate [14,18]. The SEM image of alum sludge in **Fig. 1c** showed heterogeneous structure and properties. This may be because of alum sludge is produced through a series of complex reactions including the dissipation of alum sulphate into Al $^{3+}$ and SO $_4^{2-}$ ions which produce various hydrolytic products such as [Al(H $_2$ O) $_5$ OH] $^{2+}$ [18,28]. These hydrolytic products endure complex adsorption and alteration of surface charge that creates colloids in the raw water and eventually forms the alum sludge [18,29,30]. This sludge is then dewatered and discarded as waste at disposal sites after flocculation, sedimentation and filtration in the water treatment process [14,18]. The EDS of alum sludge in **Fig.**

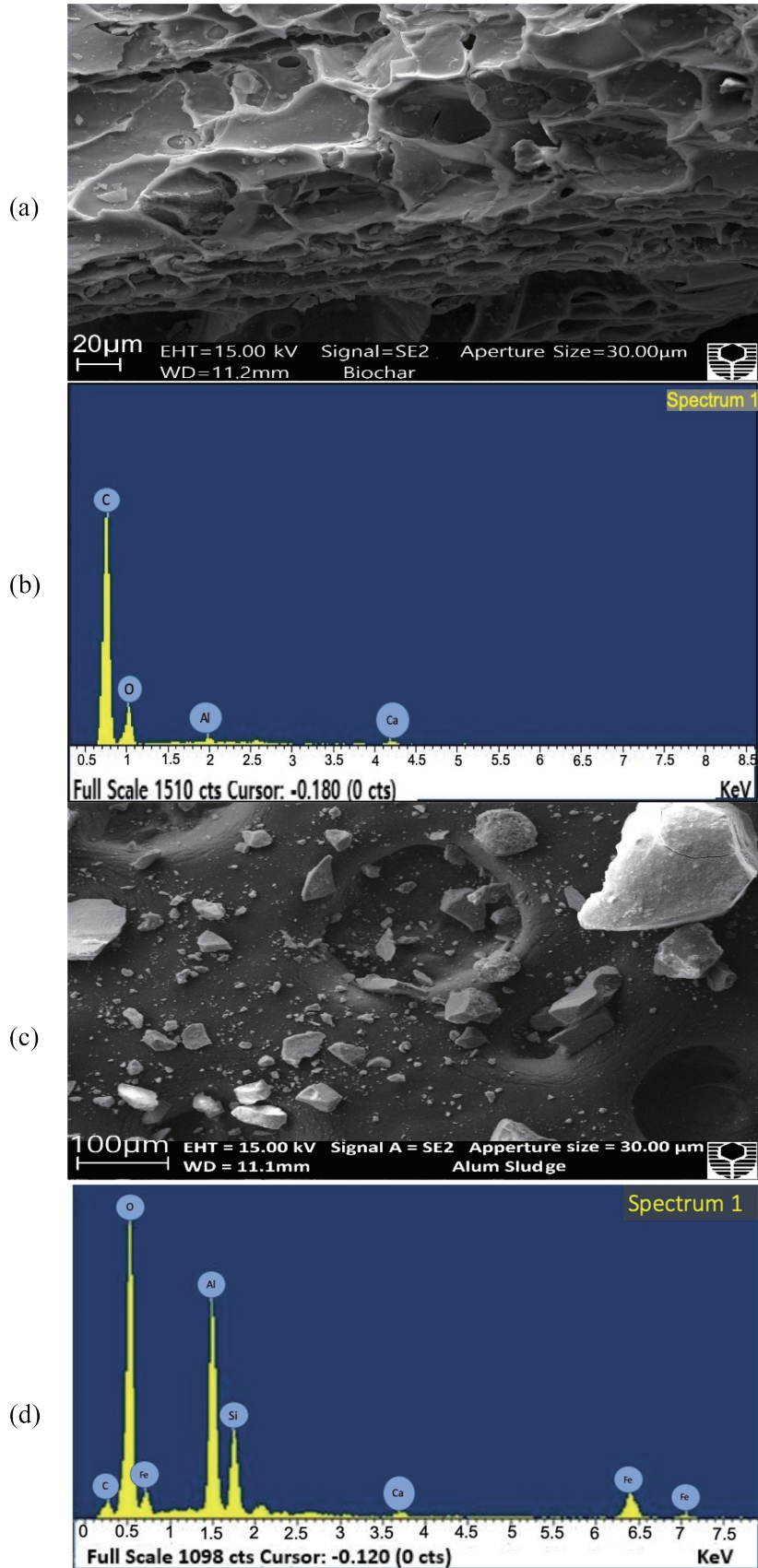


Fig. 1 Scanning electron microscopy (SEM) image and Energy dispersive spectroscopy (EDS) of EW biochar (a–b) and alum sludge (c–d).

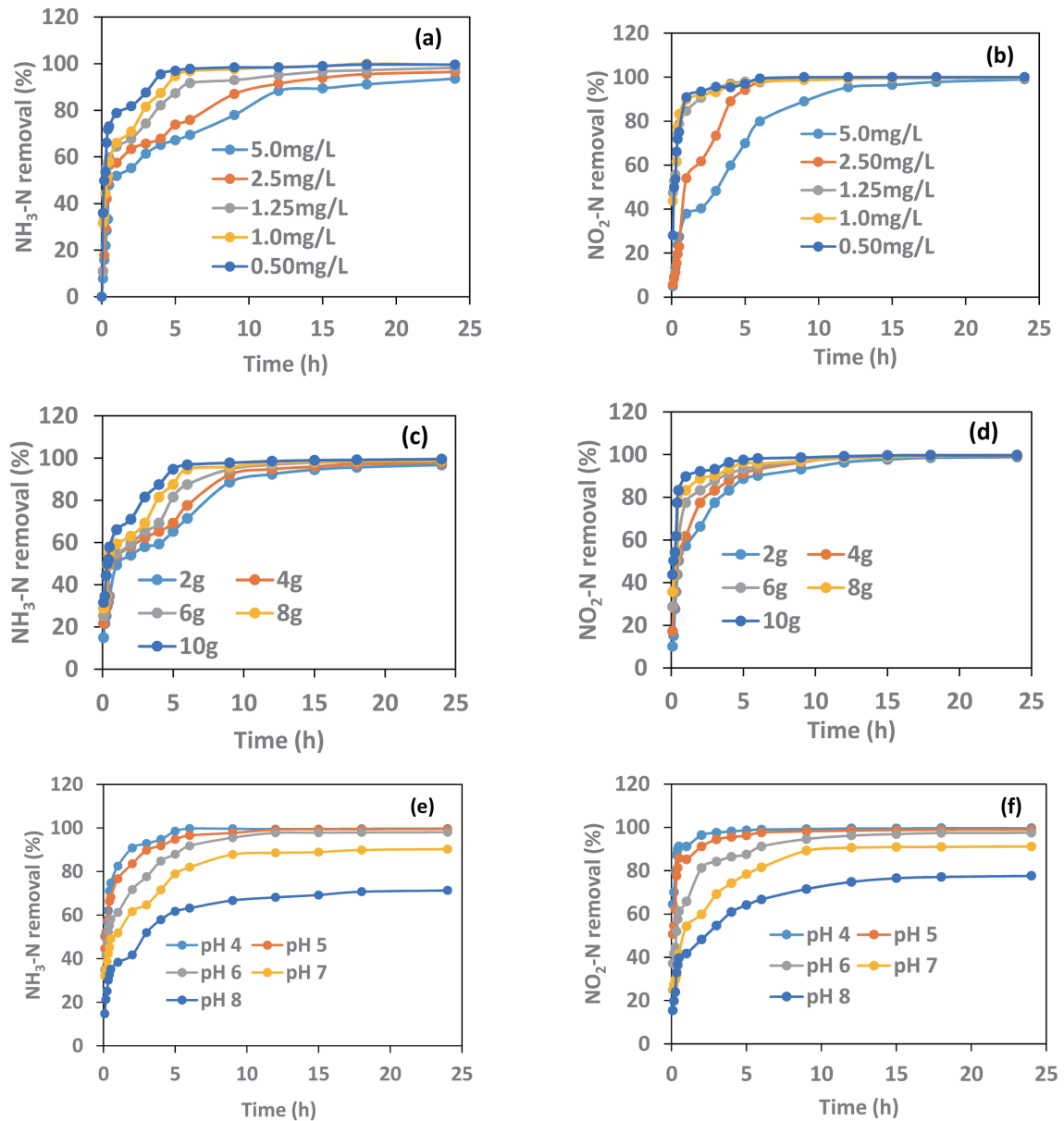


Fig. 2 The removal of $\text{NH}_3\text{-N}$ and $\text{NO}_2\text{-N}$ from stormwater using biochar with varying concentration (a-b), dosages (c-d) and pH (e-f).

1d confirmed the contents of oxygen (O), aluminium (Al), iron (Fe), silicon (Si), calcium (Ca), and carbon (C). Alum sludge is most effective to remove fluoride and phosphorus from aqueous solution via adsorption process because of the significant levels of existing aluminium [14,31,32]. The high removal of phosphorus is due to the presence of Al^{3+} forming ligand interactions on the solid surface of the alum sludge increase the adsorption process and chemical precipitation [18].

Nutrient removal using biochar

The effect of initial concentration

The percentage removal of nutrients in batch tests confirmed that the EW biochar is capable of removing $\text{NH}_3\text{-N}$ and $\text{NO}_2\text{-N}$ but not $\text{NO}_3\text{-N}$ or $\text{PO}_4\text{-P}$. That is why the adsorption results of $\text{NH}_3\text{-N}$ and $\text{NO}_2\text{-N}$ onto biochar are presented in this section. The effect of initial concentration (0.5–5 mg/L) on nutrient adsorption were checked in batches at constant pH (6.5 ± 0.5) and biochar dosage (10 g) and the results are shown in **Fig. 2a–b** for $\text{NH}_3\text{-N}$ and $\text{NO}_2\text{-N}$ removal. Faster removal was observed for both species at the beginning of

experiments. In first one hour of experiment with 0.5 mg/L concentration, 79% removal of $\text{NH}_3\text{-N}$ and 91% removal of $\text{NO}_2\text{-N}$ were observed. The removal percentage was eventually increased to 100% at its equilibrium concentration after 12 hrs. Harmayani and Anwar [1] showed 100% removal of $\text{NO}_2\text{-N}$ but 55% removal of $\text{NH}_3\text{-N}$ when raw sawdust of radiata pine was used as adsorbent. The increase of $\text{NH}_3\text{-N}$ removal in this study may be due to the difference in wood species, particle sizes and also the preparation process (i.e., pyrolysis process for biochar) of biochar which has mesoporous structure. However, the maximum removal of $\text{NO}_2\text{-N}$ was found 3–4 times faster than $\text{NH}_3\text{-N}$ at lower concentration (0.5–1.25 mg/L). Usually $\text{NH}_3\text{-N}$ may be removed by nitrification process but in this case, the batch experiment was too short to grow the nitrifying bacteria and thus there was no bacterial inoculation during the course of the experiment. In this study, the adsorption of $\text{NH}_3\text{-N}$ is probably due to the cation exchange of ionized ammonia from aqueous phase to the solid phase [11,33]. In a cation exchange mechanism, the ammonium ion species adsorbed onto the solid phase remain in free form and can readily be desorbed back into the aqueous phase if any change in concentration occurs in the aqueous phase (i.e. to retain the equilibrium between sorbed and aqueous $\text{NH}_3\text{-N}$). A certain amount of $\text{NH}_3\text{-N}$ is adsorbed onto biochar to saturate the empty sorption sites for a given concentration of $\text{NH}_3\text{-N}$. Hence, a portion of the sorbed $\text{NH}_3\text{-N}$ will desorb to regain the chemical equilibrium and the aqueous phase concentration will change. This may partly explain the apparent slower removal rate of $\text{NH}_3\text{-N}$ when compared with $\text{NO}_2\text{-N}$.

The removal rate with initial concentrations above 2.5 mg/L was lower for both contaminants. A one way analysis of variance (ANOVA) confirmed that there was significant difference ($p > 0.01$) of removal efficiency among different initial concentrations of $\text{NH}_3\text{-N}$ with respect to time but no significant variation ($p < 0.01$) was found for $\text{NO}_2\text{-N}$ at the 1% significant level. The maximum adsorption increased (5–50 $\mu\text{g/g}$) with increasing concentration (0.5–5 mg/L) because of higher availability of nitrogenous ions in the solution for both contaminants. Concentration provides an important driving force to overcome the mass transfer resistance of ions between aqueous and solid phase [1]. There is therefore a higher probability of collision between the ions and biochar surface due to the higher numbers of nitrogenous ions that are present at the higher concentrations. Similar results were attributed for ammonium sorption by poultry litter and wood biochar [34] and $\text{NH}_3\text{-N}$, $\text{NO}_2\text{-N}$ sorption by sawdust [1]. No significant difference ($p < 0.01$) was observed in ANOVA

analysis (1% significance level) for the adsorption of both contaminants for different initial concentrations.

The effect of adsorbent dosage

The effect of adsorbent dosages (2–10 g) was investigated under constant concentration (1 mg/L) and pH 6 and the results are shown in **Fig. 2c–d**. Increasing doses increased the surface area and adsorption sites and as a result, improved the removal process. The increasing rate of removal was faster for $\text{NO}_2\text{-N}$ adsorption than $\text{NH}_3\text{-N}$ for all dosages. The removal efficiency over 1 h increased from 57.2 to 89.7% and 49.4 to 66.2% for $\text{NO}_2\text{-N}$ and $\text{NH}_3\text{-N}$ adsorption respectively with an increase of biochar dosage from 2 to 10 g. These observations are consistent with those of Sun *et al.* [34] for methylene blue adsorption with biochars derived from Eucalyptus, palm bark and anaerobic digester residue. Babu and Gupta [35] also found similar results for adsorption of methylene blue for an increasing dosage of 2 to 8 g. ANOVA analysis (1% significance level) confirmed significant variation ($p > 0.01$) in removal efficiency but no significant difference ($p < 0.01$) for adsorption capacity for increasing dosage (2–10 g).

The effect of pH

The biochar used in this study was produced at 400°C pyrolysis temperature and the carbon content was 60–80%. The active carbon in biochar may show a decrease of pH and thus the initial biochar dosage may also have an influence on the experiments. But the effect of pH (4–8) was investigated here using a fixed biochar dosage (weight) of 2 g and the initial concentration of nutrients of 1 mg/L. Biochar contains surfaces that are charged, with the charge dependent on the pH of the solution [36] and thus the relative effect of ionic strength on adsorption onto these surfaces is also pH dependent. Therefore, it is important to observe the effects of solution pH on adsorption to understand its mechanism. The impact of pH on adsorption is dependent on biochar type and the contaminants of interest because it influences the adsorbent surface charge, as well as the level of ionization and speciation of the adsorbate [37]. Biochar carries surface functional groups, largely carboxylate ($-\text{COOH}$) and hydroxyl ($-\text{OH}$). The characteristics of these surface groups change as solution pH changes. Many of the functional groups on biochar (carboxylate and phenolate) may become protonated and positively charged at lower pH [34]. The effect of pH on $\text{NH}_3\text{-N}$ and $\text{NO}_2\text{-N}$ removal is shown in **Fig. 2e–f**. The results revealed that lower pH values (4–5) achieved a higher percentage of removal in comparison to

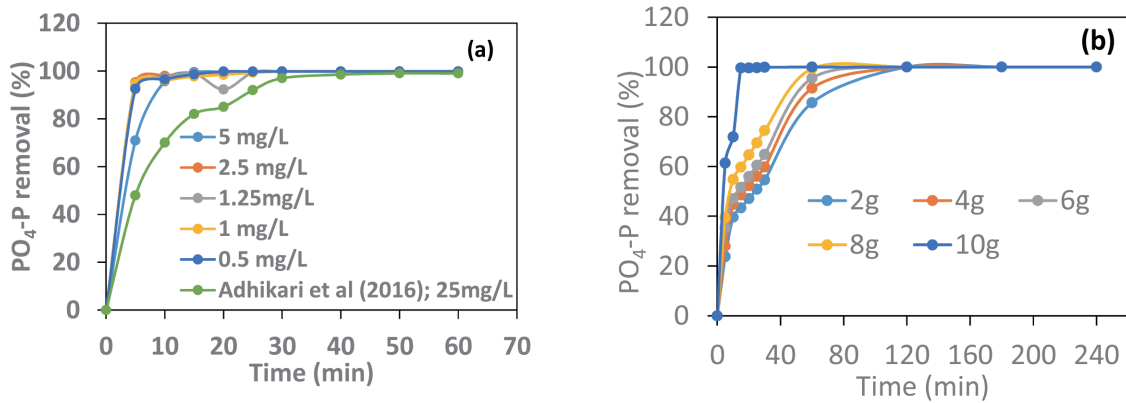


Fig. 3 Phosphorous removal using alum sludge: (a) Alum sludge of 10 g; Adhikari *et al.* [14] used 5 g of alum sludge (b) Phosphorous removal with dosage of alum sludge with initial concentration of 5 mg/L.

higher pH values (6–8) indicating the role of electrostatic repulsion between negatively charged adsorbent and anionic adsorbate at pH > 5. The decrease in removal with increasing pH may be also explained as the increase of OH⁻ competition for NO₂-N species for the adsorption sites of biochar and electrostatic repulsion on adsorption. Similar results were obtained by Oh *et al.* [26] using orange peel and water treatment sludge biochar and Dong *et al.* [38] using sugar beet tailing biochar for the adsorption of negatively charged fluoride and chromate ions respectively. The optimum pH for nitrogen removal was found to be 4–5 and 45–65% removal was found within 5 min with a drop of 23–30% at pH 8 for NH₃-N and NO₂-N respectively. ANOVA analysis (1% significance level) confirmed significant variation ($p > 0.01$) in adsorption between NH₃-N and NO₂-N but no significant difference ($p < 0.01$) was found for variation in pH 4–8.

Nutrient removal using alum sludge

The literatures show that alum sludge is capable of removing phosphorous from aqueous solution [14,15,17,18,32,39]. In this study the same alum sludge of Adhikari *et al.* [14] was chosen to check if it could remove nutrients from stormwater. The similar batch tests were carried out with varying concentration and dosage and the results are presented in **Fig. 3**. The results revealed that it could remove significant amount of phosphorous but very negligible amount of nitrogenous compounds (not shown). The effect of concentration are investigated with 10 g of alum sludge at pH 6 and the results are shown in **Fig. 3a** for phosphorous removal. The results revealed that phosphorous was removed almost 100% in first 10 minutes. The phosphorous removal also increases with dosage similar to biochar (**Fig. 3b**). Alum sludge is

abundantly produced in water treatment plant as a byproduct where aluminum salts are used as primary coagulant. It contains colloidal alum hydroxides which are mainly amorphous species. Because of the larger specific surface area and reactivity towards anion adsorption, alum sludge shows high adsorption capability to remove phosphorous from aqueous phase.

Nutrient removal using biochar and alum sludge mix

As EW biochar was found unable to remove PO₄-P but alum sludge could remove PO₄-P, next a mixture of biochar and alum sludge was taken for batch adsorption to remove nutrients (nitrogen and phosphorous) from water. Different proportions of biochar and alum sludge mix (by mass) was considered (biochar:alum sludge = 8 g:2 g; 6 g:4 g; 4 g:6 g and 2 g:8 g). The nutrient removal from each of these combinations revealed that the ration of biochar and alum sludge of 8 g:2 g provided the best combination and hence the results of this combination are presented in **Fig. 4**. Even it was only two grams of alum sludge but it could adsorb PO₄-P very quickly and reach equilibrium within a short time (within 10 mins) while NH₃-N and NO₂-N adsorption reached equilibrium in a bit longer period (6 h) which are similar to the results when the adsorbents were tested separately. The maximum percentage removal was found 98.2%, 99.4% and 99.8% for NH₃-N, NO₂-N and PO₄-P respectively at a lower concentration of 0.5 mg/L. However, the maximum percentage removal decreased by 20% and 10% for NH₃-N and NO₂-N respectively for increasing initial concentration from 1 mg/L to 5 mg/L but no removal drop was found for PO₄-P for all concentration. The removal of PO₄-P was much faster than nitrogen species (NO₂-N and NH₃-N) because the

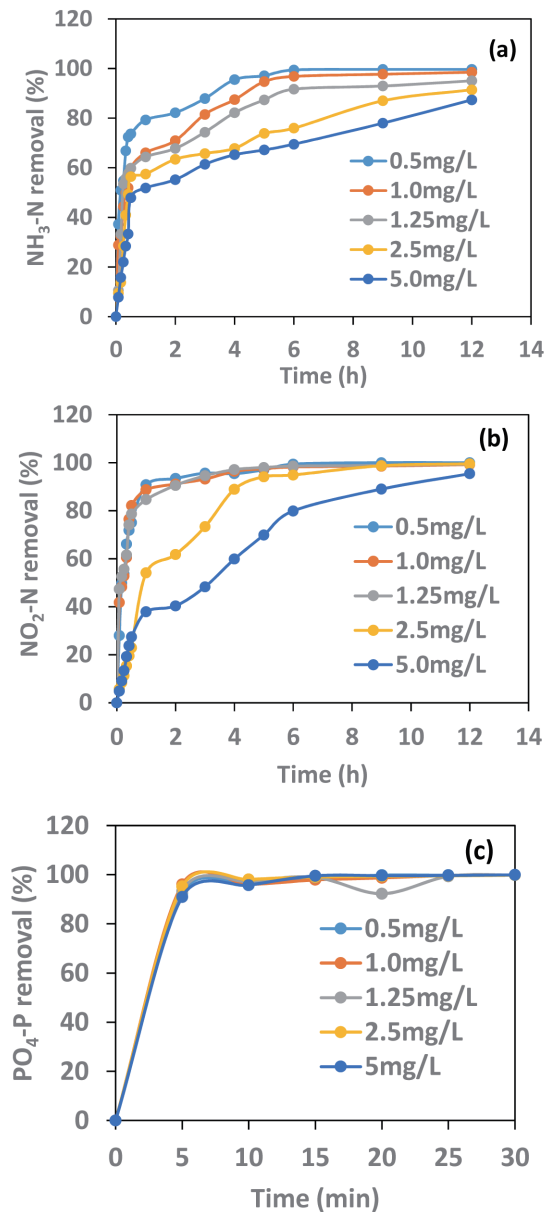


Fig. 4 The nutrient ($\text{NH}_3\text{-N}$, $\text{NO}_2\text{-N}$ and $\text{PO}_4\text{-P}$) removal from water using biochar and alum sludge mix [biochar : alum sludge = 8 g:2 g].

surface area, pore diameter and the micro pore volume of alum sludge was 7, 2 and 14 times higher respectively than that of EW biochar. Increasing the initial concentration from 2.5 to 5 mg/L increased the equilibrium time from 4 to 6 hours for both $\text{NO}_2\text{-N}$ and $\text{NH}_3\text{-N}$ respectively. The removal efficiency of $\text{NO}_2\text{-N}$ was similar to Harmayani and Anwar [1] but double for $\text{NH}_3\text{-N}$. They found the 100% and 55% removal efficiency for $\text{NO}_2\text{-N}$ and $\text{NH}_3\text{-N}$ respectively with raw sawdust adsorbent. The difference of removal efficiency may be due to different particle size and adsorbents. The dif-

ference of percentage removal was not significant ($p > 0.05$) for all nitrogen and phosphorous species for increasing the initial concentration from 2.5 mg/L to 5 mg/L.

Adsorption kinetics

In order to remove nutrients ($\text{NO}_2\text{-N}$, $\text{NO}_3\text{-N}$, $\text{NH}_3\text{-N}$ and $\text{PO}_4\text{-P}$) from aqueous phase, the batch experiments were conducted using EW biochar, alum sludge and their mixture. As discussed above, EW biochar was capable of adsorbing $\text{NO}_2\text{-N}$ and $\text{NH}_3\text{-N}$ respectively and alum sludge was capable of removing $\text{PO}_4\text{-P}$ only. It was assumed that their mixture will be also capable of removing these three nutrients ($\text{NO}_2\text{-N}$, $\text{NH}_3\text{-N}$ and $\text{PO}_4\text{-P}$) at the same time. This was tested using the mix medium of biochar (8 g) and alum sludge (2 g) and found it can remove all three nutrients ($\text{NO}_2\text{-N}$, $\text{NH}_3\text{-N}$ and $\text{PO}_4\text{-P}$) simultaneously with the same removal percentage. The equilibrium time for individual 8 g biochar (6 h) and 2g alum sludge (10 min) was exactly the same to their mix medium (Figs. 2–4). The adsorption kinetics were checked for single medium and their mixture respectively. The results revealed that the kinetics of $\text{NO}_2\text{-N}$ and $\text{NH}_3\text{-N}$ adsorption onto individual biochar and the kinetics of $\text{PO}_4\text{-P}$ adsorption onto separate alum sludge was found almost similar to the kinetics of mix-medium (< 5% variation for all parameters). As simultaneous removal of nitrogen and phosphorous is of interest for stormwater treatment, the detail kinetics of mix adsorbents (biochar : alum sludge = 8 g:2 g) are discussed in this section.

Intraparticle diffusion for mix medium

The adsorption kinetics was first studied using Intraparticle diffusion model which is used to describe the transport behavior of nutrient ions from aqueous phase to the solid-liquid interface [40]:

$$q_t = k_{di}t^{0.5} + Z_i \quad (3)$$

where k_{di} ($\text{mg/g h}^{0.5}$) is the intraparticle diffusion rate constant of stage i . The value of k_{di} can be determined from the linear plot of q_t and $t^{0.5}$. The Z_i is the intercept of stage i which is related to the boundary layer thickness. If this linear plot gives a straight line, the process is solely controlled by Intraparticle diffusion. The adsorption data collected at different time intervals of mix adsorbents are used to plot q_t versus $t^{0.5}$ and shown in Fig. 5. The results revealed that the plot of q_t versus $t^{0.5}$ clearly shows two-step adsorption for $\text{NH}_3\text{-N}$ and $\text{NO}_2\text{-N}$ for all concentrations while it shows the similar trend for $\text{PO}_4\text{-P}$ adsorption in higher concentration. The two-stage

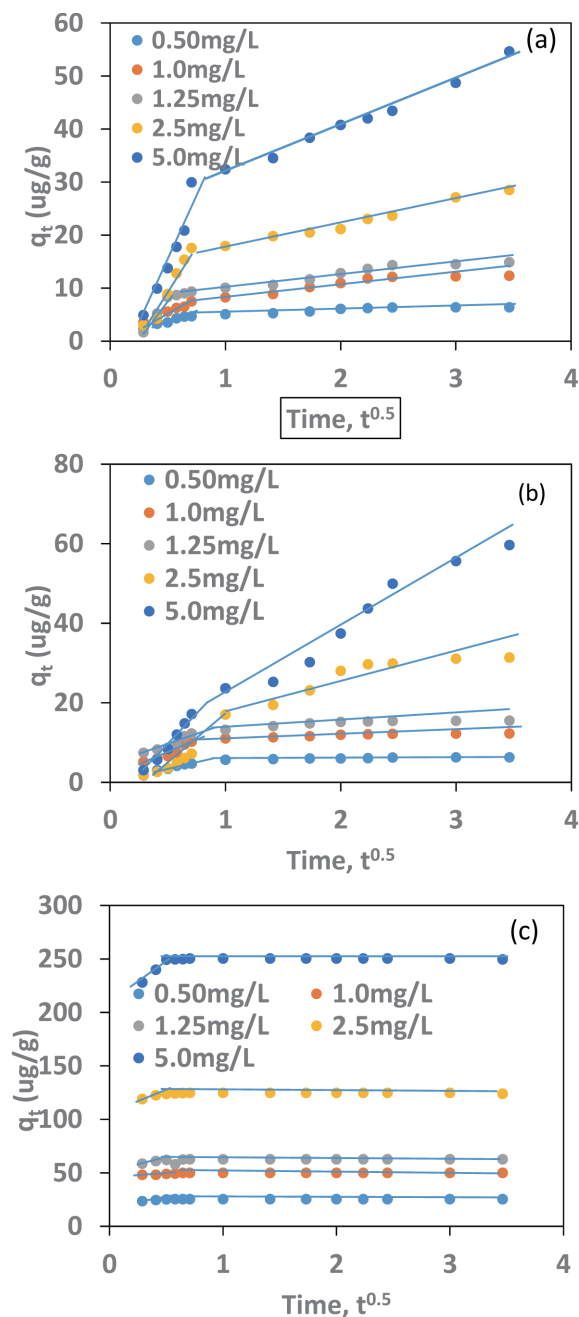


Fig. 5 The intraparticle diffusion plot for nutrient adsorption onto mix medium for (a) $\text{NH}_3\text{-N}$ adsorption, (b) $\text{NO}_2\text{-N}$ adsorption and (c) $\text{PO}_4\text{-P}$ adsorption.

adsorption parameters of Intraparticle diffusion are shown in **Table 1**. The first stage exhibits the surface adsorption onto the solid surface and the second stage describes the diffusion onto the adsorption site [1]. The most surface adsorption occurred in first 30 minutes of the contact time for all nitrogen species while it took lesser time for phosphorous adsorption. After this time, the diffusion becomes rate controlling and

the second stage of intraparticle diffusion starts. The stage one adsorption rate ($k_{d1} = 5.34\text{--}101.5 \mu\text{g/g h}^{0.5}$) shows much higher than the stage two adsorption rate constant ($k_{d2} = 0.21\text{--}17.59$) (**Table 1**). However, the results revealed that the higher initial concentration yields with larger diffusion rate. This may be because of the remaining higher concentration in liquid phase leads to a high diffusion rate because of larger driving force.

Liquid film diffusion for mix medium

The linear plots of q_t versus $t^{0.5}$ in **Fig. 5** for all nutrients do not pass through the origin but show two different intercepts (Z_1 and Z_2) for two-stage adsorption (**Table 1**). The higher concentration of nutrients shows higher intercepts which indicates it may not have only one adsorption mechanism [41]. In this situation, the mechanism may be explained by Boyd liquid film diffusion model [42]:

$$\ln(1-F) = -K_{fd}t \quad (4)$$

where F is the fraction of solute adsorbed at time t which may be calculated as the ratio of adsorption at time t (q_t) and at equilibrium (q_e), K_{fd} is the adsorption rate constant for liquid film diffusion (1/min). The linear plot of $-\ln(1-F)$ versus t (graph not shown) shows positive slope (K_{fd}) with R^2 (0.8–0.98) and a small intercept (–0.59–2.36). Small intercepts suggest the adsorption process occurs in a thin liquid film surrounding the adsorbent particles.

Lagergren kinetic model for mix medium

The solute adsorption performances may be described using Lagergren kinetic model such as Lagergren pseudo-first order and pseudo-second order kinetic models. These models can be expressed linearly as:

$$\text{Pseudo-first order model: } \ln(q_e - q_t) = \ln q_e - k_1 t \quad (5)$$

where k_1 is the rate constant of first order adsorption (1/h) which is calculated from the linear plot of $\ln(q_e - q_t)$ versus t .

$$\text{Pseudo-second order kinetic model: } \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (6)$$

where k_2 (g/mg h) is the rate constant of second-order adsorption which is calculated from the linear plot of t/q_t and t . The validity of these kinetic models are checked using normalized standard deviation Δq (%):

Table 1 Intraparticle diffusion and liquid film diffusion model parameters for nutrient adsorption onto mix medium (biochar:alum sludge = 8 g:2 g).

Nutrient	Intraparticle diffusion						Liquid film diffusion			
	C_0 (mg/L)	Z_1	k_{d1} ($\mu\text{g/g h}^{0.5}$)	R^2	Z_2	k_{d2} ($\mu\text{g/g h}^{0.5}$)	R^2	K_{fd} (1/min)	Intercept	R^2
NH ₃ -N	0.5	0.78	5.77	0.97	4.65	0.58	0.80	0.012	0.63	0.95
	1.0	0.65	9.44	0.96	6.97	1.79	0.83	0.0086	0.45	0.97
	1.25	-2.47	18.29	0.87	8.13	2.16	0.89	0.006	0.58	0.94
	2.5	-9.30	37.64	0.96	13.03	4.45	0.98	0.004	0.44	0.90
	5.0	-12.43	54.89	0.94	22.61	8.89	0.98	0.0036	0.39	0.91
NO ₂ -N	0.5	0.744	5.34	0.92	5.59	0.21	0.86	0.011	0.89	0.89
	1.0	2.54	9.21	0.88	10.86	0.466	0.78	0.008	1.1	0.91
	1.25	4.73	9.17	0.89	13.76	0.57	0.70	0.009	1.0	0.96
	2.5	-6.45	21.41	0.91	14.82	5.44	0.74	0.007	0.12	0.98
	5.0	-5.98	30.67	0.98	2.13	17.59	0.96	0.004	0.07	0.97
PO ₄ -P	0.5	21.45	7.38	0.99	25.4	0	-	0.32	1.49	0.97
	1.0	46.62	4.27	0.68	49.12	0.86	0.36	0.49	-0.59	0.86
	1.25	53.90	16.78	0.98	55.98	7.45	0.35	0.120	2.36	0.91
	2.5	112.61	23.01	0.96	123.73	1.12	0.53	0.181	1.66	0.99
	5.0	198.59	101.53	0.99	249.96	0.21	0.3	0.170	1.82	0.80

$$\Delta q(\%) = 100 \sqrt{\frac{\sum [(q_e(\text{exp}) - q_e(\text{cal})) / q_e(\text{exp})]^2}{N - 1}} \quad (7)$$

where N is the number of data points, $q_e(\text{exp})$ and $q_e(\text{cal})$ (mg/g) are the experimental and calculated adsorption capacity respectively.

These kinetic models were fitted with experimental data and the model parameters are shown in **Table 2**. The results revealed that the pseudo-second order kinetic models fitted much better with $R^2 = 0.98$ – 1.00 and a very small normalized standard deviation ($\Delta q = 0.00$ – 0.62) than the first order model. The pseudo first order kinetic model is based on the assumption of physical adsorption and the solute uptake rate with time is directly proportional to the ratio of the solute concentration and the amount of solid [43]. But the pseudo second order kinetic model relies on the assumption that the rate-limiting step may be chemical sorption or chemisorption comprising valence forces through sharing or exchange of electrons between sorbate and sorbent [44]. This indicates the nitrogen and phosphorous ions adsorbed onto the biochar and alum sludge mostly associated with chemical reactions. The adsorption of NH₃-N, NO₂-N and PO₄-P for pseudo second order kinetic model increased from 6.37–60.71 $\mu\text{g/g}$, 6.4–59.62 $\mu\text{g/g}$ and 25.4–249.85 $\mu\text{g/g}$ respectively as the concentrations of these compounds increased from 0.5 mg/L

to 5 mg/L. When comparing with previous studies, the adsorption of phosphate onto red mud samples treated with HCl, dewatered alum sludge and lime sludge were 0.58 mg/g, 55 mg/g and 44.5 mg/g [14,45]. Similarly, the adsorption capacity of NH₃-N and NO₂-N onto raw sawdust was found 2.59–17.57 $\mu\text{g/g}$ and 5–49.53 $\mu\text{g/g}$ respectively [1]. The difference is probably because of the differences in original materials, particle size, and the preparation conditions of biochar in the present study. However, the adsorption of biochar and alum sludge mixture used in this study were better than those raw sawdust prepared from radiata pine in Harmayani and Anwar [1].

Adsorption isotherm of mix adsorbent

Langmuir and Freundlich isotherm

The adsorption isotherm is studied to investigate the relationship between the adsorbed amounts with that of the solute remains in the bulk liquid phase using Langmuir and Freundlich isotherm. The Langmuir isotherm is applied when the adsorbed solute is assumed to have a monolayer coverage at a dynamic equilibrium between solid and liquid phase. The Langmuir isotherm describes the chemisorption by forming the ionic or covalent bond between solid and liquid phase [35]. The Langmuir isotherm is expressed as [46]:

Table 2 Kinetic parameters of Lagergren pseudo-first order and pseudo-second order models for mix adsorbent (biochar:alum sludge = 8 g:2 g).

Nutrient	C_0 (mg/L)	q_e, exp ($\mu\text{g/g}$)	Pseudo-first order				Pseudo-second order			
			q_e, cal ($\mu\text{g/g}$)	K_1 (1/h)	R^2	Δq (%)	q_e, cal ($\mu\text{g/g}$)	K_2 (g/mg h)	R^2	Δq (%)
NH ₃ -N	0.5	6.37	2.918	0.570	0.94	3.67	6.50	0.65	0.99	0.01
	1.0	12.30	7.885	0.524	0.97	1.61	12.72	0.18	0.99	0.01
	1.25	14.85	8.248	0.382	0.95	2.47	15.22	0.14	0.99	0.01
	2.5	28.57	18.174	0.263	0.90	1.66	28.90	0.05	0.98	0.00
	5.0	60.71	42.098	0.159	0.93	1.17	54.65	0.02	0.98	0.12
NO ₂ -N	0.5	6.4	2.561	0.647	0.89	4.50	6.50	0.85	0.99	0.00
	1.0	12.4	4.096	0.526	0.91	5.61	12.72	0.47	0.99	0.01
	1.25	15.52	5.430	0.574	0.94	5.28	15.62	0.38	0.99	0.00
	2.5	31.10	31.128	0.534	0.99	0.00	38.06	0.13	0.99	0.62
	5.0	59.62	55.147	0.274	0.97	0.07	66.25	0.01	0.96	0.15
PO ₄ -P	0.5	25.40	4.8	10.92	0.99	8.22	25.38	22.17	1.00	0.00
	1.0	49.90	8.02	10.21	0.80	8.80	50.00	8.00	1.00	0.00
	1.25	62.25	5.92	7.31	0.92	10.23	62.50	6.40	1.00	0.00
	2.5	124.75	10.66	8.91	0.98	10.45	125.00	6.40	1.00	0.00
	5.0	249.85	47.66	11.60	0.86	8.19	250.00	1.77	1.00	0.00

Table 3 Langmuir and Freundlich isotherm constants.

Species	Langmuir			Freundlich		
	q_m ($\mu\text{g/g}$)	K_L	R^2	n	K_F	R^2
NH ₃ -N	75	0.64	0.99	1.29	28.73	0.98
NO ₂ -N	34	4.23	0.96	1.24	65.04	0.70
PO ₄ -P	83	1.51	0.94	1.14	108.4	0.92

$$\frac{1}{q_e} = \frac{1}{q_m K_L} \left(\frac{1}{C_e} \right) + \frac{1}{q_m} \quad (8)$$

where q_e (mg/g) is the equilibrium adsorption, q_m (mg/g) is the maximum capacity of adsorbent for the adsorbate, K_L is the Langmuir constant (dimensionless) which can be obtained from the plot of $1/q_e$ versus $1/C_e$ and C_e (mg/L) is the concentration of the compound of interest (adsorbate) in solution at equilibrium. Another dimensionless parameter, the adsorption intensity (R_L) is used to indicate the type of adsorption process [47]:

$$R_L = \frac{1}{1 + K_L C_0} \quad (9)$$

$R_L = 0$ indicates irreversible adsorption, $0 < R_L < 1$ indicates favourable adsorption, $R_L = 1$ indicates linear adsorption and $R_L > 1$ indicates unfavourable adsorption.

The other isotherm model known as Freundlich isotherm assumes a heterogeneous surface adsorption and expressed as [46,48]:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (10)$$

where the constants K_F (mg/g) and n are the adsorption capacity and adsorption intensity respectively. These constants are obtained from a plot of $\log q_e$ versus $\log C_e$. The Freundlich isotherm is widely used for heterogeneous materials. The slope of the line of best fit is indicative of the heterogeneity of the adsorbent material, i.e. the smaller the slope of the greater the heterogeneity. The $1/n$ value indicates whether the adsorption process involved cooperative adsorption and/or chemisorption [46].

The adsorption equilibrium data were fitted with both Langmuir and Freundlich models and the isotherm parameters are shown in **Table 3**. The NH₃-N adsorption fitted

well with both Langmuir and Freundlich isotherm model ($R^2 = 0.98\text{--}0.99$) while $\text{NO}_2\text{-N}$ and $\text{PO}_4\text{-P}$ followed Langmuir model ($R^2 = 0.94\text{--}0.96$) better. The best fit for Langmuir model ($R^2 = 0.99$) for $\text{NH}_3\text{-N}$ adsorption suggests that the process was predominantly monolayer adsorption, which comprises both chemical and physical mechanisms. Similar results were indicated in previous literatures such as methylene blue adsorption onto biochar prepared from eucalyptus, palm bark, anaerobic digestion residue [34] and also onto activated carbon prepared from hazelnut husks [49]. Phosphorous and nitrogenous species adsorption by alum sludge and radiata pine sawdust were also showed similar trends [1,14]. The Langmuir constant (K_L) is related to the adsorption energy and was found in the range 0.64–4.23. The maximum Langmuir adsorption capacity (q_m) for nitrogen and phosphorous species were between 34–75 $\mu\text{g/g}$ and 83 $\mu\text{g/g}$ respectively. The separation factor (R_L) was less than one for all nutrients indicate the nutrients adsorption onto mix-medium was favorable (Fig. 6). The Freundlich constant (K_F) in equation (10) indicates the approximate adsorption capacity. The maximum value of K_F was found for $\text{PO}_4\text{-P}$ adsorption which also supports the findings of maximum Langmuir adsorption capacity (q_m). The factor $1/n$ indicates the strength of adsorption in the adsorption process ($1/n = 1$ indicates that adsorption partitioning are independent of concentration, $1/n < 1$ indicates normal adsorption and $1/n > 1$ indicates cooperative adsorption) [50]. The n values found above one for all parameters indicate it has favorable adsorption process.

Overall the results found in this study indicate that EW biochar and alum sludge mix can be used as an effective adsorbent to remove nitrogen and phosphorous from aqueous phase. This novel mix-medium is basically waste products and can be reused for water treatment reducing the waste load in landfill. The use of these waste materials in stormwater treatment (such as in catch basin insert, rain garden, swales and/or bioretention systems) will significantly reduce the cost of solid waste management and also improve the stormwater quality in receiving water.

CONCLUSIONS

The removal of nutrients from stormwater was investigated using adsorption method. The adsorption capability of EW biochar, alum sludge and their mixture was tested in batches. The EW biochar was found good adsorbent to remove $\text{NH}_3\text{-N}$ and $\text{NO}_2\text{-N}$ up to 100% but not effective for $\text{NO}_3\text{-N}$ or $\text{PO}_4\text{-P}$ removal. The separate experiments with

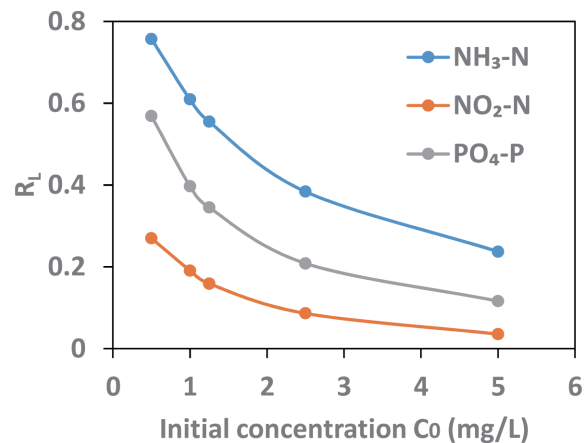


Fig. 6 Variation of adsorption intensity (R_L) with initial concentration.

alum sludge show very effective for removing $\text{PO}_4\text{-P}$ (100%) within a short period of time but found not effective to remove nitrogen from water. Based on this, a mix medium of biochar and alum sludge of different ratio was tested and found an optimum ratio of 8 g biochar and 2 g alum sludge removing both nitrogen and phosphorous effectively. This mix medium of adsorbent (8 g biochar and 2 g alum sludge) could remove $\text{NH}_3\text{-N}$, $\text{NO}_2\text{-N}$ and $\text{PO}_4\text{-P}$ maximum up to 98.2%, 99.4% and 99.8% respectively at a lower concentration of 0.5 mg/L. The adsorption kinetics shows two-step adsorption onto mix medium following Intraparticle diffusion and Liquid film diffusion. Pseudo-second order kinetic model was found better describing the adsorption process for all nutrients. But $\text{NH}_3\text{-N}$ adsorption followed both Langmuir and Freundlich isotherm while $\text{NO}_2\text{-N}$ and $\text{PO}_4\text{-P}$ adsorption followed Langmuir isotherm better. The EW trees are abundant in Australia commonly used in construction industry but leaving huge amount of wood waste. This wood waste can be reused for green energy in pyrolysis that leaves biochar. The water treatment plants are again producing significant amount of alum sludge that needs to be disposed in landfill. In order to reduce the waste in landfill, a mix medium of these waste materials (biochar and alum sludge) can be reused as green media for removing nutrients from stormwater and/or wastewater.

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