LAPORAN PENELITIAN UNGGULAN PERGURUAN TINGGI

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Pengembangan biochar dari lumpur limbah cair kelapa sawit sebagai adsorben untuk pemurnian air

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LEMBAR IDENTITAS DAN PENGESAHAN
LAPORAN AKHIR PENELITIAN

1	Judul Penelitian	Pengembangan biochar dari lumpur limbah cair kelapa sawit sebagai adsorben untuk pemurnian air
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4	Lokasi Penelitian	Jakarta
5	Jangka Waktu Penelitian	6 (enam) Bulan
6	Biaya diperlukan	Rp. 44.000.000,-
7	Sumber Dana	Perguruan Tinggi

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RINGKASAN

Penelitian in bertujuan untuk mengembangkan dan mengoptimalkan penggunaan biochar yang dihasilkan dari lumpur limbah cair kelapa sawit sebagai adsorben yang efektif dalam proses pemurnian air. Limbah cair kelapa sawit mengadung kontaminan yang mencemari sumber air, dan penggunaan biochar sebagai adsorben dapat mengurangi kandungan kontaminan dan meningkatkan kualitas air limbah. Dalam penelitian ini, karaktersitik lumpur limbah cair kelapa sawit akan dipelajari dan dianalisis untuk mengetahui potensi pengembangan biochar dari limbah tersebut. Percobaan dilakukan dengan produksi biochar melalui proses pirolisis lumpur limbah cair kelapa sawit, dan mengkarakterisasi sifat-sifat fisik dan kimia dari biochar yang dihasilkan. Selanjutnya dilakukan serangkaian uji adsorpsi menggunakan biochar sebagai adsorben untuk menghilangkan kontaminan dari air limbah dengan engaruh parameter seperti waktu kontak, konsentrasi kontaminan, dan jumlah adsorben terhadap efisiensi adsoprsi

Hasil dari penelitian ini akan memberikan wawasan tentang kemampuan adsorpsi biochar dan pegaruh parameter operasional dalam pemurnian air limbah. Selain itu, evaluasi analisis ekonomi dan keberlanjutan dari peggunaan biochar dalam pemurnian air dilakukan untuk mengevaluasi potensi biaya dan manfaat, serta dampak lingkungan dari penggunaan biochar sebagai adsorben. Hal ini akan memberikan panduan praktis untuk penerapan teknologi ini dalam skala industri, dan diharapkan dapat digunakan sebagai dasar unutk pengembangan metode pemurnian air yang lebih efisien, berkelanjutan, dan berbiaya rendah. Penelitian ini memiliki implikasi yang signifikan dalam bidang pengelolaan limbah cair industri dan pemurnian air. Dengan menggunakan limbah cair sebagai bahan baku untuk produksi biochar dan mengoptimalkan penggunaanya sebagai adsorben, kami berharap dapat mengurangi dampak negatif dan memperbaiki kualitas air limbah yang dibuang ke lingkungan.

BAB 1. PENDAHULUAN

Dalam era industri modern, produksi limbah cair industri telah menjadi salah satu tantangan lingkungan terbesar yang kita hadapi. Limbah cair industri mengandung berbagai zat berbahaya dan polutan yang dapat mencemari sumber air dan ekosistem. Salah satu industri yang memproduksi limbah cair dengan konsentrasi polutan yang sangat tinggi adalah industri kelapa sawit. Limbah cair kelapa sawit dihasilkan selama proses ekstraksi minyak kelapa sawit dari tandan buah segar dan mengandung limbah organik, asam lemak bebas, bahan pengolahan minyak sawit, dan zat-zat lain yang mempengaruhi kualitas air dan kehidupan di sekitarnya. Dalam beberapa dekade terakhir, peningkatan kesadaran akan dampak negatif limbah cair kelapa sawit terhadap lingkungan telah mendorong upaya untuk mengelola dan mengolahnya dengan lebih efektif. Di tengah tantangan ini, juga terdapat peluang untuk mengubah limbah cair menjadi sumber daya bernilai. Salah satu pendekatan yang menjanjikan adalah penggunaan limbah cair kelapa sawit untuk produksi biochar.

Biochar, yang secara umum didefinisikan sebagai karbon terestrial yang stabil dan memiliki sifat biofisikokimia yang khas, adalah produk yang dihasilkan dari proses pirolisis pada suhu tinggi dari biomassa atau bahan organik lainnya (1). Namun, selama beberapa tahun terakhir, penelitian dan eksperimen telah menunjukan bahwa limbah cair industri dapat digunakan sebagai bahan baku untuk produksi biochar yang berkualitas. Limbah cair kelapa sawit mengandung berbagai bahan organik yang dapat menjadi sumber karbon untuk pembuatan biochar. Dalam proses pirolisis, lumpur limbah cair diberikan perlakuan termal di bawah kondisi tanpa okisgen, yang menghasilkan biochar dan gas samping (2). Biochar yang dihasilkan dari lumpur limbah cair kelapa sawit diharapkan memiliki sifat porositas yang tinggi, stabilitas terhadap dekomposisi, dan kemampuan menahan air dan nutrisi.

Pemanfaatan lumpur limbah cair kelapa sawit untuk produksi biochar memiliki beberapa manfaat yang signifikan. Pertama, ini membantu dalam pengolahan limbah cair kelapa sawit yang sulit dan mengurangi dampak negatifnya

pada lingkungan. Dengan mengubah limbah cair menjadi biochar, industri kelapa sawit dapat mengurangi risiko pencemaran air dan tanah serta membantu dalam upaya perlindungan lingkungan. Selain itu, penggunaan biochar dari lumpur limbah cair kelapa sawit sebagai adosrben dalam pemurnian air dapat membantu dalam pengelolaan air bersih dan limbah cair secara berkelanjutan. Dengan mengubah limbah cari menjadi biochar, dampak negatif pada lingkungan dan sumber daya air dapat dikurangi.

Penggunaan biochar sebagai adsroben dalam pemurnian air dapat mengurangi risiko pencemaran air dan meningkatkan kualitas air. Kemampuan adsorpsi biochar terhadap kontaminan dapat membantu menghilangkan zat-zat berbahaya dan mencemari air limbah, menjadikannya lebih aman untuk digunakan atau dibuang ke lingkungan. Proses pembuatan biochar dari lumpur limbah cair hasil rumah tangga *(municipal wastewater sludge*) sebagai bahan adsorben untuk proses pemurnian air telah dilaporkan di dalam beberapa publikasi melalui pirolisis dan terbukti dapat meningkatkan kemampuan adsorpsi biochar terhadap kontaminan terentu melalui modifikasi biochar dengan bahan tambahan atau melalui pengolahan lanjutan (3, 4). Namun, informasi mengenai biochar dari lumpur limbah cair kelapa sawit belum didiskusikan dan tidak banyak publikasi mengenai pembuatan biochar dari lumpur limbah cair kelapa sawit. Dalam penelitian ini, kami akan menjelajahi lebih dalam tentang potensi pengembangan biochar dari limbah cair kelapa sawit sebagai adsorben dalam proses pemurnian air. Kami akan melihat potensi penggunaan biochar untuk mengurangi kontaminan dalam air limbah, manfaatnya dalam pengelolaan limbah cair industri, dan upaya penelitian terkini dalam mengoptimalkan adsoprsi biochar. Hasil dari penelitian ini dapat digunakan sebagai informasi dalam pembuatan biochar dari limbah cair kelapa sawit, sehingga dapat menurunkan volume pembuangan limbah cair ke lingkungan sebagai tindakan pencegahan pencemaran lingkungan serta pengembangan *green technology* untuk meningkatkan kualitas pengolahan air bersih dan limbah cair.

BAB 2. TINJAUAN PUSTAKA

Semakin meningkatnya industrialisasi, industri kelapa sawit semakin menjamur di wilayah Indonesia yang dapat berdampak terhadap meningkatnya kerusakan lingkungan dari limbah cair yang dihasilkan oleh industri kelapa sawit. Limbah cair yang dihasilkan dari proses produksi kelapa sawit bersifat *high-strength harmful wastewater* karena mengandung *chemical oxygen demand* (COD) dan *biological oxygen demand* (BOD), padatan (*total solids*), minyak, logam berat, dan lignin yang sangat tinggi (5). Sekitar 50% limbah cair kelapa sawit terporduksi dari proses produksi kelapa sawit dengan kadar padatan sebesar 4–6% (6). Lumpur yang terbentuk dari proses sedimentasi pada kolam penampungan pengolahan limbah cair kelapa sawit hanya dikeringkan sebelum dibuang tanpa ada pengolahan lebih lanjut. Lumpur limbah cair kelapa sawit yang masih mengandung kandungan polutan berbahaya dapat merusak lingkungan badan air, seperti sungai, danau, bahkan air tanah, sehingga pengolahan lumpur yang efektif diperlukan untuk mengurangi dampak berbahaya akibat pembuangan lumpur limbah cair kelapa sawit.

Proses *dewatering sludge* dari limbah cair sangat populer karena dapat menurunkan kadar air yang mengandung bahan polutan (7). Air yang terpisah dari lumpur kering dapat diolah dengan pengolahan air konvensional, seperti koagulasi dan klorinasi. Lumur kering yang dihasilkan dapat diolah sebagai pupuk, bahan konstruksi, dan biochar. Studi mengenai pembuatan biochar dari lumpur limbah cair semakin populer dan memiliki manfaat yang signifikan pada kegiatan pengolahan air bersih dan limbah cair. Biochar memiliki *surface functional groups*, luas permukaan area spesifik yang besar, dan tinggi porositas, sehingga biochar sangat baik digunakan sebagai adosrben, katalis, atau *soil amendments* (8). Biochar dari lumpur memiliki efektivitas penghilangan kontaminan yang bergantung kepada luas permukaan area spesifik, kondisi operasi pembuatan biochar, dan aktifasi. Pembuatan biochar dari lumpur limbah cair kelapa sawit dapat dilakukan dengan metode pirolisis. Metode pirolisis sangat menguntungkan karena lumpur kering yang digunakan untuk

pembuatan biochar mengandung 50–70% bahan organik, dan proses pirolisis dapat menurunkan kadar emisi karbon melalui proses imobilisasi di biochar (1). Mengingat lumpur limbah cair kelapa sawit mengandung bahan organik yang cukup tinggi, pirolisis mampu membantu menurunkan bahan organik berbahaya sekaligus mengurangi volume lumpur yang dihasilkan industri. Pengembangan biochar dari lumpur limbah cair kelapa sawit sebagai adsorben pada pemurnian air merupakan potensi yang sangat baik untuk keberlanjutan pengolahan dan pengelolaan sumber daya air dan limbah cair sebagai hasil sebuah tujuan dari penggunaan kembali limbah (*waste recycling*).

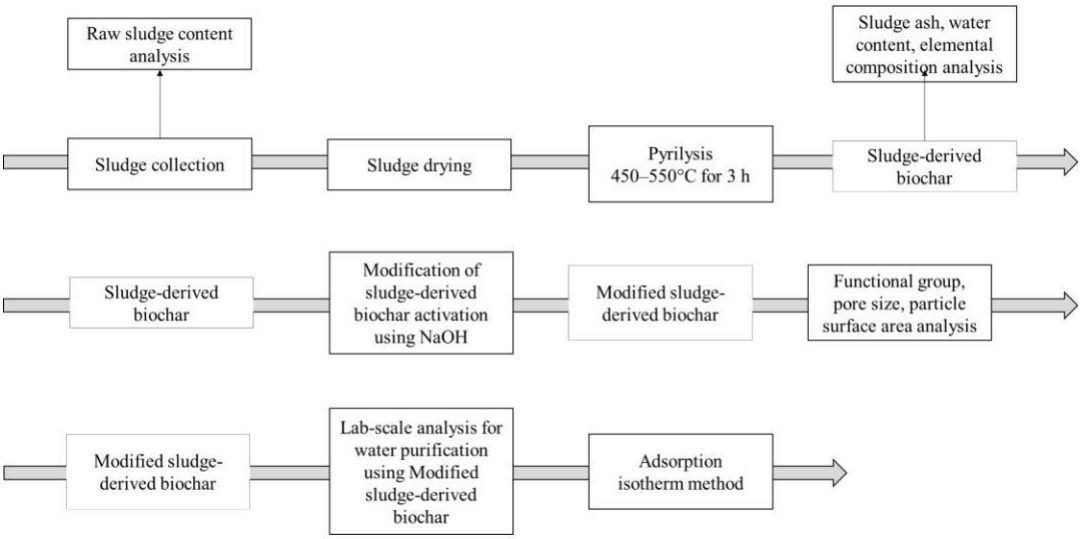
Biochar memiliki kemampuan adsorpsi yang tinggi dan dapat menghilangkan kontaminan di air, seperti pewarna, logam berat, phenol, bahan organik dan inorganik seperti bahan *pharmaceuticals* dan antiobiotik (9). Proses modifikasi/aktifasi biochar dapat meningkatkan kemampuan adsorpsi dengan menambahkan bahan aditif seperti karbon dioksida (CO_2), uap, oxidan, asam, basa, dan nutrien seperti nitrogen dan fosfor. Penggunaan oxidan seperti radial hidroksil dan atom oksigen dapat meningkatkan kapasitas adsorpsi biochar dalam mengurangi kontaminan organik (10). Namun, energi yang dibutuhkan dalam pembentukan spesies oxidan sangat besar dan residual oxidan yang menempel pada permukaan biochar dapat terlepas dan larut di dalam air karena tarikan elektron oleh ion OH di air sehingga meninggalkan kontaminan tambahan setelah proses pemurnian. Aktifasi biochar dengan CO_2 lebih ramah lingkungan dan rendah biaya energi. CO_2 dapat meningkatkan *mesopore* dan *micropores* pada permukaan biochar, sehingga kapasitas adsorpsi dan kapasitas pertukaran ion pun meningkat (4). Namun, studi oleh Singh et al. (4) menjelaskan bahwa penggunaan CO_2 dapat menunrunkan *functional groups* dan luas permukaan area spesifik pada biochar, apabila proses pirolisis mencapai 800°C, sehingga harus ada pengontrolan suhu pada tangki pirolisis.

Aktifasi menggunakan bahan alkali seperti NaOH dapat meningkatkan luas permukaan area spesifik dan meningkatkan *functional groups* pada biochar melalui proses pirolisis yang membutuhkan suhu 400–600°C sehingga meningkatakn

kapasitas adsorpsi bahan organik dan juga logam berat (9). Hu et al. (9) Menjelaskan bahwa penggunan NaOH meningkatkan luas permukaan area spesifik sebesar 10 kali lipat (81.4 m^2/g menjadi 907.9 m^2/g) dibandingkan CO_2 yang hanya sebesar 5 kali lipat (18.5 mg^2/g menjadi 109.0 m^2/g). Dengan meningkatnya luas permuakan area spesifik, kapasitas adsorpsi biochar juga akan meningakat. Proses aktifasi alkali juga tidak mengurangi *functional groups* pada biochar, sehingga dapat menghilangkan kontaminan organik, inorgnaik, dan logam berat. Walaupun masing-masing proses aktifasi memikili kekurangan dalam pengembangan biochar, studi intensif terhadap pemilihan aktifasi tersebut diperlukan untuk meningkatkan kapasitas adsorpsi dari proses aktifasi yang dipilih.

Pengembangan biochar dari lumpur limbah cair kelapa sawit masih kurang perhatian untuk didisuksikan sebagai teknologi ramah lingkungan dalam mengurangi volume lumpur yang dihasilkan. Penelitian mengenai limbah cair kelapa sawit cenderung terfokus kepada produksi biogas yang masih menyisakan lumpur dalam volume yang cukup banyak. Dalam pengembangan biochar, proses aktifasi menjadi faktor penting untuk meningkatkan efektifitas penggunaan dan aplikasinya. Evaluasi dampak proses aktifasi biochar dari lumpur limbah kelapa sawit menggunakan NaOH juga masih belum didiskusikan secara sistematis. Penelitian ini mendemonstrasikan potensi penggunaan lumpur limbah cair kelapa sawit dalam pengembangan biochar sebagai adsorben dan akan membahas secara komprehensif metode aktifasi biochar menggunakan NaOH untuk meningkatkan kapasitas adsorpsi biochar dalam menurunkan kadar kontaminan di air dan limbah cair. NaOH dipilih karena tidak terpengaruh oleh suhu pirolisi, dapat meningaktan luas permukaan area spesifik, dan efektif dalam menghilangkan logam berat dibandingakn dengan metode oksidasi dan CO_2. Penelitian ini diharapkan dapat memberikan informasi mengenai pengembangan biochar dari limbah cair sebagai upaya pengolahan dan pengelolaan limbah cair industri, khususnya indsutri kelapa sawit sebagai bentuk tujuan dari siklus ekonomi ramah lingkungan yang berkelanjutan.

BAB 3. METODE PENELITIAN



Gambar 1. *Flowchart* kegiatan penelitian melalui metode yang dipilih untuk pengembangan biochar dari lumpur limbah cair kelapa sawit dan aplikasinya untuk permurnian air melalui proses adsorpsi.

Secara singkat **Gambar 1** menjelaksan bahwa lumpur diambil dari tangki equalisasi instalasi pengolahan air limbah (IPAL) di PT. Incasi Raya, Padang, Sumatera Barat dan disimpan dalam 1 L tangki polypropylen yang sudah dibersihkan sebelumnya. Lumpur yang diambil kemudian dibawa ke laboatoirum dan dianalisa untuk mengetahui karakteristik awal sebelum proses pengeringan, seperti pH, COD, BOD, TS dan kadar organik dengan menggunakan metode APHA. Setelah itu, proses pengeringan dilakukan untuk mengurangi kadar air pada lumpur hingga mencapai 5% dengan menggunakan *drying oven* pada suhu 105°C hingga mencapai berat residu yang konstan. Setelah proses pengeringan, padatan yang tersisa dari lumpur dianalisa kadar air, kadar material organik, luas permukaan area spesifik, densitas pori, distribusi partikel dan komposisi elemen seperti Al, Si, Fe, P, K.

Padatan kering yang diperoleh akan dibakar dengan proses *pyrolysis-vacuum-carboniztion* yang dilakukan pada rentang temperature 450–550°C selama 3 jam di dalam tangki pirolisis. Setelah proses pirolisis, biochar yang dihasilkan dianalisa untuk kadar material organik, luas permukaan area spesifik, densitas pori, distribusi partikel, dan komposisi elemen. Biochar hasil pirolisis diaktifasi menggunakan larutan NaOH dengan perbandingan 2:1 dan diaduk selama 4 jam. Setelah itu dikeringkan pada suhu 105 selama 12 jam. Detail mengenai aktifasi biochar menggunakan larutan NaOH dapat dilihat pada rujukan Liu et al. (11). Apabila, biochar telah memenuhi kategori sebagai adsorben komersial, pengujian untuk pemurnian air bersih dan air limbah dapat dilakukan dengan menargetkan kontaminan spesisik yang dapat dihilangkan atau dikurangi kadarnya dengan moteode isotherm.

Kegiatan penelitian yang dilakukan dideskripsikan pada tugas dari masing-masing ketua dan anggota yang tersedia pada **Tabel 1**.

Tabel 1. Tugas dan tanggung jawab oleh ketua dan anggota penelitian pada masing-masing kegiatan penelitian.

No.	**Kegiatan**	**Penanggung jawab**
1	Pengambilan sampel, analisa sampel	Ketua, Anggota 2 dan 3
2	Penulisan laporan	Ketua, Anggota 1
3	Kegiatan penelitian meliputi pengeringan lumpur dan proses pirolisis	Ketua, Anggota 2 dan 3
4	Kegiatan penelitian meliputi aktifasi biochar	Ketua, Anggota 1, 2, dan 3
5	Penulisan laporan	Ketua, Anggota 1
6	Kegiatan penelitain meliputi uji biochar untuk pemurnian air	Ketua, Anggota 1, 2, dan 3
7	Penulisan laporan akhir, dan aritkel ilmiah untuk dipublikasikan	Ketua, Anggota 1, 2, dan 3

BAB 4. BIAYA DAN JADWAL

PENELITIAN 4.1 Anggara Biaya Penelitian

Tabel 2. Justifiasi anggaran rinci yang mengacu pada kegiatan penelitian yang akan dilakukan.

No.	Kegiatan	Biaya yang diusulkan (Rp.)	Keterangan
1	Gaji atau upah honorarium ketua dan anggota (Maks 30%)	3,000,000	Masing-masing mendapatkan upah sebesar 25%.
3	Bahan habis pakai dan peralatan penunjang (Maks 40-50%)	4,000,000	Biaya pembelian bahan dan biaya analisa hasil penelitian
4	Perjalanan (Maks 15%)	1,500,000	Akomodasi perjalanan, seperti transportasi dan konsumsi
5	Lain-lainnya (Maks 15%)	1,500,000	Biaya tak terduga dalam akomodasi perjalanan

4.2 Jadwal Kegiatan Penelitain

Tabel 3. *Timeline* kegiatan penelitian yang telah dilakukan selama periode 4 bulan mulai dari tahapan pengerjaan penelitian hingga kegaitan penulisan laporan akhir dan proses publikasi artikel ilmiah.

No.	Kegiatan	Oktober (Minggu ke-)				November (Minggu ke-)				Desember (Minggu ke-)				Januari (Minggu ke-)			
		1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
1.	Pengambilan sampel																
2.	Analisa sampel (karakteristik awal *sludge*) dan penulisan laporan kerja																
3.	Pengeringan *sludge*																
4.	Proses *pyrolsis*																
5.	*Biochar activation* dan penulisan laporan kerja																
6.	Uji *biochar* untuk pemurnian air bersih																
7.	Penulisan laporan dan proses publikasi artikel																

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LAMPIRAN 1

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Publikasi di Jurnal Nasional dan Internasional

1. Indra Setiawan, Ahmad Bahrudin, Moh Mawan Arifin, **Wahju Inggar Fipiana**, Vivi Lusia, 2021. Analysis of preventive maintenance and breakdown maintenance on production achievement in the food seasoning industry. OPSI 14(2), 253–261. doi:10.31315/opsi.v14i2.5540
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Hak Cipta

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C. BIODATA ANGGOTA PENGUSUL 2 DAN 3

Kegiatan penelitian ini melibatkan dua mahasiswa dari jurusan Teknik Sipil, Universitas Borobudur.

Tabel 4. Nama anggota pengusul mahasiswa yang terlibat dalam pelaksanaan penelitian ini.

Nama	Institusi	Nomor mahasiswa	Tahun masuk/Semester
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LAMPIRAN II

Kerjasama kegiatan penelitian dengan mitra kerjasama, dalam hal ini Jurusan Teknik Kimia Universitas Bung Hatta, Padang, Sumatera Barat, dan PT. Incasi Raya, Padang, Sumatera Barat.

Tabel 5. Daftar mitra kerjasama dalam melakukan kegiatan penelitian ini

No.	Nama mitra	Lokasi	Kegiatan kerjasama
1	Universitas Bung Hatta	Padang, Sumatera Barat	- Pengambilan sampel - Analisa sampel - Evaluasi hasil penelitian - Penulisan laporan dan publikasi ilmiah
2	PT. Incasi Raya	Padang, Sumatera Barat	- Pengambilan sample - Evaluasi hasil penelitian
3.	Pt. Kohken Watertech Indonesia	Bekasi, Jawa Barat	- Analisa samples - Evaluasi hasil penelitian

LAMPIRAN III

PUBLIKASI ARTIKEL ILMIAH

Luaran hasil penelitian berupa artikel ilmiah akan dipublikasikan di:

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Adsorption of Nitrate Nitrogen by Palm Oil Wastewater Sludge-Modified Activated Carbon

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***Abstract*—This work investigated the use of palm oil wastewater sludge (POWS) as an adsorbent for the adsorption of nitrate nitrogen (NO_3^--N) in water. The modified sludge-based adsorbent, hereinafter referred to as palm oil wastewater sludge-activated carbon (POWS-AC) was produced from a chemical activation process using sodium hydroxide (NaOH) and pyrolysis process at the temperature of 500°C. The produced POWS-AC had a specific surface area of 247.5 m^2/g and be used to remove NO_3^--N from aqueous solution. A batch mode adsorption process was conducted under different initial NO_3^--N concentrations (30, 50, and 100 mg/L), different POWS-AC dosages (0.1, 0.2, 0.5, and 1 g/L), and different pH solutions with the range of 4–13 for 24 hours adsorption time. The results showed that POWS-AC removed NO_3^--N 27 – 77% when the dosage of POWS-AC increased from 0.1 to 1 g/L in a low initial NO_3^--N concentration solution after 4 hours adsorption time with a pH of 7. Furthermore, the adsorption performances were well-fitted with a pseudo-second-order kinetic model and Langmuir isotherm model, showing that the primary mechanism of NO_3^--N adsorption was electrostatic chemosorption. This work suggested the potential use of POWS-AC in removing NO_3^--N from an aqueous solution.**

***Keywords*—activated carbon, adsorption, nitrate nitrogen, palm oil mill wastewater sludge**

I. INTRODUCTION

The rapid increase in urbanization leads to massive growth in agricultural activities utilizing fertilizer. Nutrients contained in fertilizer, such as nitrate/nitrite, phosphate, and potassium can lead to soil and water pollution when an excessive amount is used. In Indonesia, the standard for nitrate is 10 mg/L for drinking and clean water purposes [1], but the concentration of nitrate exceeds more than 10 mg/L in some rivers, lakes, and well water [2,3]. The high concentration of nitrate transferred from soil to groundwater and spread over lakes and seas can cause eutrophication. Nitrate can be harmful to human health and increase the risk of carcinogenicity in the human body. Nitrate in the form of nitrate nitrogen (NO_3^--N) in water is stable and has high solubility, resulting in low precipitation and adsorption rates of nitrate [4]. Several methods, such as ion exchange [5], electrochemical reduction [6], biological denitrification [7], and adsorption [4] have been used to eliminate NO_3^--N from water. The adsorption process is the most efficient method due to its low cost and ease of operation. Several studies have investigated the effectiveness of the adsorbent used for the adsorption process, considering the high adsorption capacity, ecological-friendly materials, good chemical stability, and easy reusability [8–10]. Preparing adsorbents from high-carbonaceous biomass has caught attention to minimize solid waste from various sectors (agricultural waste, industrial waste, water, and wastewater solid waste).

Numerous findings demonstrated the preparation of activated carbon (AC) made from coal, oil, wood, and biomass produced from industrial and agricultural activities [11–14]. Biomass-based materials for preparing the activated carbon as the adsorbent in the adsorption process have been explored to offer some potential ecological and environmental benefits. Shao et al. [15] modified bamboo as a renewable source for preparing activated carbon (Zr/CTAB/BAC) to remove nitrate and phosphate in wastewater. The investigation was done by giving the optimum preparation condition for adsorption at the temperature of 25 for 4 h adsorption, with the addition of Zr as the precursor. Nitrate and phosphate were removed by 34.1% to 93.7% and 59.3% to 99.4% with the addition of Zr/CTAB/BAC was 0.1–1.0 g. The study showed that the adsorption process was chemical adsorption and had a good effect on the removal of phosphate and nitrate in water. Biomass AC modified from orange peel/chitosan/iron removed nitrate 99,6% with the range of dose 0.05 – 0.15 g via the batch process. The adsorption capacity of the composite showed a good performance in the process of nitrate ion adsorption in the batch process [16]. The good performance of modified AC from various materials for nitrate adsorption has been regarded to be cost-affectivity, operation flexibility, and design simplicity. The removal of nitrate by adsorption is influenced by the contact between nitrate and adsorbent and the movement of nitrate from the solution to the surface of the adsorbent. Thus, it is challenging to improve the adsorbent from various materials for the adsorption of inorganic anions such as nitrate.

Biochar-based AC produced from various feedstock has been used for the adsorption process. Palm oil wastewater sludge (POWS) has potentially been used to create biochar for organic and inorganic remediation and adsorption of heavy metals and organic pollutants. POWS is highly nutritious and moist, with carbon and nitrogen content of around 37.5–38.5% and 2.7–4.7%, respectively, and a pH of around 8.0 [17,18]. The pyrolysis of POWS contained high carbon content, copiousness, and low cost, high removal capacity for heavy metals. Utilizing POWS from the palm oil industry as the modified AC for the adsorption process is challenging for sludge management and environmental protection. Amalina et al. [19] investigated the potential use of AC modified from POWS to remove total suspended solid and textile dye color with acid and base materials chemical activation. The results showed that chemical activation by KOH promoted better removal efficiency compared to H_3PO_4. Copper (Cu) and cadmium (Cd) were recorded at the

highest uptakes at 48.8 mg/g and 46.2 mg/g, respectively, using palm oil mill sludge biochar in the adsorption process [20]. The works verified the use of POWS played an important role in the removal of Cu and Cd. It has shown that POWS can be potentially used to remove pollutants, such as heavy metals, organic matter, and dyes from water and wastewater owing to the high carbon content that can be upgraded as modified adsorbent through pyrolysis and activation methods to develop the microstructure, functional group stabilization, large surface charge, and adsorption capacity.

However, limited findings on how POWS is utilized as an adsorbent to remove NO_3^--N from water. NO_3^--N contained a negative monovalent charge that results in low removal efficiency by traditional adsorption treatment. Considering the extensive scientific evidence on the utilization of POWS as AC (POWS-AC), this study aims to characterize the possible use of POWS-AC to remove nitrate from water by pyrolyzing POWS-AC at a fixed temperature of 500°C and activating POSW-AC by chemical activation using sodium hydroxide (NaOH). The readily used POWS-AC is comprehensively studied on the effect of different parameter conditions (POWS-AC dosage, initial NO_3^--N concentration, and pH of the solution) for adsorption treatment.

II. Literature Review

NO_3^--N is an important and valuable nutrient used in agriculture for plant growth. However, the excessive amount of NO_3^--N released from soil to water bodies, such as groundwater, lakes, well water, and ocean can be harmful to aquatic organisms. The concentration of NO_3^--N above 30 mg/L would increase spot disease in fish, eutrophication, and the risks of carcinogenicity exposure to humans [21–23]. Thus, the appropriate removal of NO_3^--N is required for ecological, health, and economic benefits. Investigations have been reported on the removal treatment for NO_3^--N to keep the standard NO_3^--N level below 10 mg/L for drinking and clean water purposes. However, NO_3^--N is found to have high solubility and stability in the water environment, resulting in low precipitation when conventional water treatment, such as coagulation-flocculation-sedimentation is used [4,24]. Advanced treatments have been proposed to increase the removal rate of NO_3^--N in water and wastewater, including advanced oxidation and reverse osmosis [25,26]. However, those treatments may cause several problems, such as the production of harmful byproducts and low treatment efficiency [25]. Adsorption has been widely used to remove contaminants in water and wastewater owing to its ease of operation, low cost, design simplicity, and high removal efficiency [8 –10]. Various adsorbents used in the adsorption process have been developed, including silica gels, zeolites, clay, and AC. AC adsorption is an excellent method because of the enormous surface area, high carbon content, and ease of preparation. AC adsorption has been developed and transformed into advanced magnetic nanocomposites that can be prepared from various materials, such as coal [11], biomass [12], wood [13], and sludge [27], to improve the sorption capacity of developed AC.

Conversion of sludge into adsorbent is challenging to deal with sludge issues. Numerous investigations have reported that sewage sludge from waste recycling processes [28], urban water treatment plants [29], and paper mill factories [30] could be converted into activated carbon through various activation methods. Palm oil industries treat their wastewater by conventional biological treatment, such as anaerobic digestion which generates large amounts of POWS. POWS may contain high nutrients originating from leaves, trunks, empty fruit branches, seed shells, and mesocarp fiber that could produce toxic substances such as ammonia and organic acids through composting [31,32]. The rich carbon content accounts for about 37.5% to 38.5 % found in POWS is favorable for preparing activated carbon [18]. POWS-AC was done by Amalina et al. [19] by comparing activating agent types to observe the mesopore characteristics of AC. The pyrolysis conditions, such as temperature and residence time have been investigated to observe the surface area of the AC from POWS [19]. The findings reported by Li et al. [30] that POWS-AC had a BET surface area of about 122 m^2/g to 186.4 m^2/g by controlling the pyrolysis temperature. POWS may contain lignin and other organic constituents derived from fiber materials [33]. The lignin content can be transformed into an aromatic hydrocarbon structure at high temperatures that is beneficial for activated carbon production. When the pyrolysis temperature exceeds 500°C, the carbon yield of POWS is high and is a favorable condition for the preparation of activated carbon from POWS [20]. However, some findings found that simple pyrolysis was not conducive to carbon formation due to the high ash content that can lead to the pores blocking [34,35]. Thus, the improvement of the produced AC quality after pyrolysis is required to promote better adsorption performance through activation and modification methods.

Activation and modification for AC preparation are necessary to improve the adsorption capacity of adsorbent. Sludge is soaked into an activation agent such as carbon dioxide (CO_2) and steam [36], oxidant [37], acid, or base [19]. The use of oxidants as activating agents such as hydroxyl radicals and oxygen can improve the adsorption capacity of AC for removing contaminants in water [37]. However, the required energy to form oxidant species is high and the residual oxidant attached to the surface of AC may be released to the solution due to electron attraction by OH^- in water, leaving the unwanted contaminants after adsorption. AC activation by CO_2 may improve mesopores and micropores on the surface of AC, thus increasing adsorption capacity [36]. However, a study by Sing et al [36] showed that CO_2 could decrease the functional groups and the specific surface area of AC if the pyrolysis temperature exceeds 800°C, thus controlling pyrolysis temperature is important when CO_2 is used as an activating agent. Chemical activation is widely used for AC preparation through heating and carbonation in an inert atmosphere. The chemical activator can expand the pores of AC through dehydrogenation and degradation, thus increasing the porosity [38]. The concentration of the activator, reaction temperature, and activation time influence the activation process. The most common chemical activators used are potassium hydroxide, zinc chloride, and phosphoric acids. NaOH has the ability to improve the specific surface area and functional groups of AC through 400-600°C pyrolysis temperature [39]. Hu et al. [39] demonstrated that NaOH was

more favorable to improving the specific surface area of AC ten times (81.4 m^2/g to 907.9 m^2/g) compared to CO_2 which was only 5 times improvement (18.5 mg^2/g to 109 m^2/g). Increasing the specific surface area, the adsorption capacity of AC increases, which is favorable for removing organic and inorganic contaminants, heavy metals, and nutrients.

Although limited studies of the use of POWS-AC in the adsorption process have been reported, extensive findings should be addressed to highlight the potential benefit of POWS-AC for water treatment as well as sludge management. In a study by Zaini et al. [40], POWS-AC was prepared to remove methylene blue by chemical activation and showed a similar removal rate with commercial activated carbon. POWS-AC had high mesoporous (average pore width 7.1 nm) which is suitable for removing methylene blue molecules (1.4 nm) from an aqueous solution. The adsorption behavior of cadmium (Cd) and copper (Cu) using POWS-AC showed a comparatively higher removal rate than commercial activated carbon [20]. The adsorption study showed the best adsorption performance of POWS-AC after pyrolyzing at 400°C for removing Cd and Cu. The contact time and shaking speed also enhanced the adsorption capacity of POWS-AC which had the highest uptakes of Cu and Cd at 48.8 mg/g and 46.2 mg/g, respectively. It is challenging to observe the potential use of POWS-AC to remove NO_3^--N from water since no publication has been reported on how the modified POWS-AC can remove NO_3^--N from aqueous solution. Accordingly, this work investigated the use of POWS-AC after the chemical activation process to remove NO_3^--N from water by observing the adsorption mechanism through adsorption kinetics and isotherms. This work gives directions for future sludge management and the adsorbent application from sludge-based adsorbent in order to improve water treatment sustainability.

III. Materials and Methods

A. Preparation of POWS-AC

POWS was collected from the second sedimentation tank of the palm oil wastewater treatment facility from a palm oil company in Padang, Indonesia. POWS was transferred to the laboratory and dried for 24 h at 105°C-oven to remove moisture content. The dried POWS was sieved through a 1 mm sieve. The granular POWS was soaked with a 2 M NaOH solution (m/v: 1:3) for 24 hours at room temperature. After the supernatant was removed, the sample was dried at 105°C until the weight was constant and sieved into a fine powder through a 0.1 mm sieve. After activation, POWS was pyrolyzed using a furnace at the fixed temperature of 500°C for 2 hours. After pyrolysis, POWS was rinsed 10 times with 50 mL Mili-Q water to remove residual NaOH and dried until reached constant weight. POWS after pyrolysis, hereinafter referred to as POWS-AC was stored in an airtight container before use for subsequent experiments. The characteristics of POWS-AC are shown in Table 1.

Table 1. Characteristics of POWS-AC

Parameters	Value
Pore volume (cm^3/g)	0.41
Specific surface area (m^2/g)	247.5
Average pore diameter (nm)	3.96

B. NO_3^--N Adsorption Performance

An adsorption study was conducted on the batch mode through agitation of the POWS-AC with 250 mL NO_3^--N solution in three different concentrations of 30, 50, and 100 mg/L contained in conical flasks. The effect of the adsorbent dosage was observed in different POWS-AC dosages of 0.1, 0.2, 0.5, and 1.0 g/L and the different pH of NO_3^--N solutions of 2, 4, 7, 10, and 13. The flasks were sealed and agitated using a magnetic stirrer at 120 rpm for 4, 8, 12, 16, 20, and 24 hours at room temperature. After shaking, the suspension was filtered through a 0.45 µm syringe membrane filter. The concentration of NO_3^--N was analyzed using APHA methods [41]. The experiments were done in duplication, the data indicated the average of two experimental results. The removal percentage (1) and adsorption capacity (2) of NO_3^--N were calculated.

$$R(\%) = \frac{C_0 - C_e}{C_0} x\ 100\% \quad (1)$$

$$q_e = \frac{(C_0 - C_e)}{m} x\ V \quad (2)$$

where R is the percentage of removal (%), C_0 is the initial concentration (mg/L), C_e is the equilibrium concentration for NO_3^--N (mg/L), V is the volume of solution (L), q_e is the adsorption capacity (mg/g), and m is the weight of POWS-AC (g).

C. Adsorption Kinetics and Isotherm

The adsorption kinetics study of NO_3^--N onto POWS-AC was evaluated by the pseudo-first-order kinetic and pseudo-second-order. The first-order model (3) studied the initial stage of the adsorption process, and the second-order (4) analyzed the entire adsorption process.

$$q_t = q_e(1 - e^{-k_1 t}) \quad (3)$$

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (4)$$

where q_t (mg/g) is the amount of NO_3^--N adsorbed at time t (h), k_1 (h^{-1}) is the rate constant of first-order adsorption, and k_2 (g/mg h) is the rate constant of second-order adsorption.

The adsorption isotherms describe the interaction between adsorbate and adsorbent and are crucial to determining the adsorption capacity of the adsorbent in order to optimize the use of the adsorbent. In this study, the adsorption process of POWS-AC on NO_3^--N was simulated using the Langmuir and (5) Freundlich (6) isotherm.

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \quad (5)$$

$$lnq_e = lnK_F + \frac{1}{n} lnC_e \quad (6)$$

where C_e (mg/L) is the equilibrium concentration, q_e (mg/g)

is the equilibrium adsorption capacity, q_m (mg/g) is the maximum adsorption capacity of the Langmuir model, and b, K_F and n are the isothermal model constants.

IV. Result and Discussion

A. Adsorption Capacity and Removal of NO_3^--N by POWS-AC

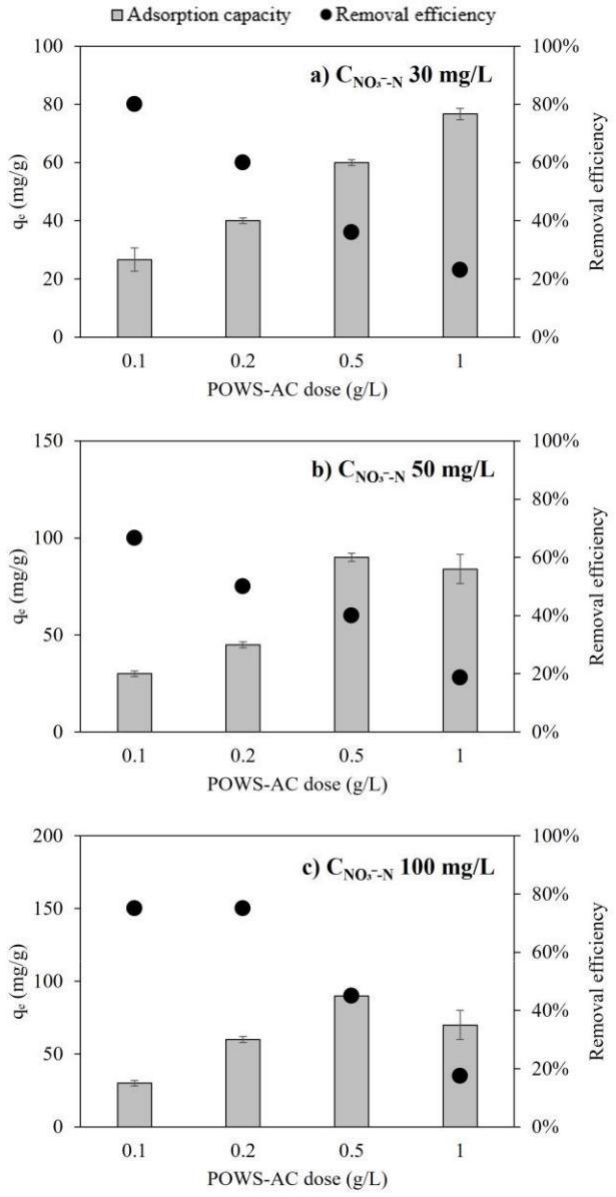

Fig. 1. Adsorption capacity of POWS on NO_3^--N and removal efficiency of NO_3^--N at different initial concentrations of NO_3^--N solution (C_{NO3^-N}: 30, 50, and 100 m/L) and different POWS-AC dose of 0.1, 0.2, 0.5, and 1 g/L after 4-hour adsorption process.

Fig. 1 shows the effect of the POWS-AC dose on the removal of NO_3^--N when the adsorption time was 4 h, the initial concentration of NO_3^--N was 30 mg/L, and the pH solution was 7. Removal of NO_3^--N increased from 27% to 77% when the POWS-AC dose increased from 0.1 to 1 g/L. The increase in the removal of NO_3^--N demonstrated that POWS-AC provided more adsorption sites when the POWS-AC dose increased [4]. The high initial concentration of NO_3^--N also showed the effect on the adsorption process by POWS-AC: the NO_3^--N decreased with the increasing initial concentration of the NO_3^--N at the same POWS-AC dosage.

The results demonstrated that initial concentrations of NO_3^--N at 100 mg/L resulted in a lower removal efficiency at 15–35% compared to those at 30 mg/L of NO_3^--N with the removal efficiency was 27–77% at the dosage of 0.1 to 1.0 g/L. The adsorption amount of NO_3^--N decreased from 150 mg/g to 35 mg/g with the increase in the POWS-AC dose due to the attraction of the adsorption site [4]. However, when the amount of POWS-AC increased from 0.5 to 1.0 g/L with the initial concentration of NO_3^--N were 50 and 100 mg/L, the removal efficiency decreased from 60 % to 56% and 45% to 35%, respectively. This suggested that the adsorption sites were loaded and covered by NO_3^--N so that the removal efficiency decreased as the adsorption capacity per unit weight of POWS-AC became higher compared to the initial concentration of NO_3^--N was 30 mg/L. The previous findings reported that the adsorbent dose affected the available adsorption sites, leading to either a decrease or an increase in the adsorbability of the adsorbent [4,42,43]. Therefore, subsequent experiments are performed to optimize adsorption parameters by using POWS-AC.

Adsorption time is an important parameter influencing the adsorption capacity. The amount of NO_3^--N adsorbed by POWS-AC and its removal with the increase in the adsorption time is shown in Fig. 2. The adsorption capacity of POWS-AC increased after the 24-hour adsorption process. When the POWS-AC dose was 0.2 and 0.5 g/L, the adsorption capacity remained the same after the 16- and 12-hour adsorption process, respectively. The concentration difference between the surface of the adsorbent and the nitrate in the solution was large, resulting in large mass transfer kinetics [44]. At the same time, the materials had many active sites, so the adsorption rate was fast for a 12-hour adsorption process. A POWS-AC dose of 1.0 g/L showed an increase in adsorption capacity until 20 hours and remained stable after 24 hours. The findings indicate that the difference in POWS-AC dose affected the adsorption process in the function of time. However, as the adsorption process continues, the effective adsorption sites gradually decrease, so the adsorption process also slows down, and the reaction tends to balance. The NO_3^--N may block the pore of POWS-AC, resulting in less or no available NO_3^--N adsorbed by POWS-AC. The increase in POWS-AC dose provided more active sites, thereby the adsorbability of POWS-AC could last for 20 hours. The adsorption capacity of POWS-AC was 225, 140, and 80 mg/g when the dose of POWS-AC was 0.2, 0.5, and 1.0 g/L, respectively, when the adsorption equilibrium was reached.

The effect of pH on the adsorption process was also observed and is shown in Fig. 3. The concentration of NO_3^--N reduced from 100 mg/L to 70 mg/L when the pH of the solution increased from 2 to 7, while pH above 7 decreased the adsorption capacity. This is probably due to the large amount of OH^- competed with NO_3^--N at a higher pH value for active sites on the POWS-AC surface. The higher pH value could also reflect the unfavorable electrostatic condition for anion adsorption that rendered greater electrostatic repulsion [45]. When the pH was 2 and 4, the amount of NO_3^--N adsorbed by POWS-AC was lower compared to pH 7. Lower pH would lead to the instability and

hydrolysis of adsorbent under acidic conditions, thereby indirectly reducing the adsorption performance.

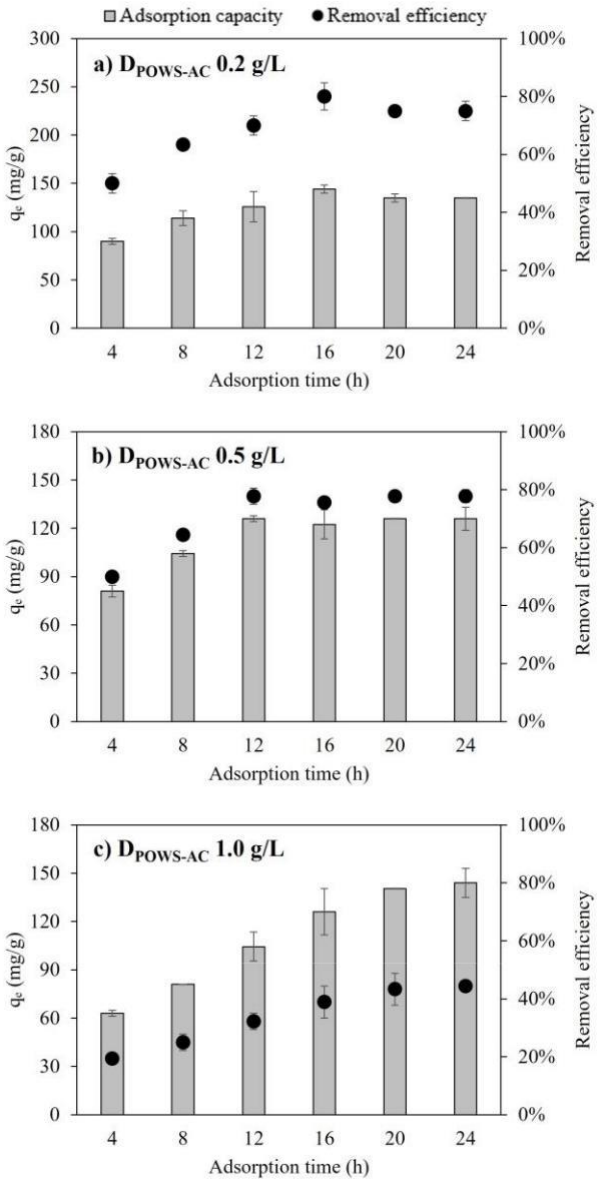

Fig. 2. Adsorption capacity of POWS on NO_3^--N and removal efficiency of NO_3^--N at initial concentrations of NO_3^--N solution (C_{NO3^-N}: 100 m/L) and different POWS-AC dose ($D_{POWS-AC}$: 0.2, 0.5, and 1 g/L) for 24 hours adsorption process.

B. Adsorption Kinetics and Isotherms

The adsorption kinetics of NO_3^--N on POWS-AC were studied with the difference in POWS-AC dosage when initial NO_3^--N solution concentration 0f 100 mg/L at pH 7 for 24 h adsorption process. Table 2 shows the kinetic parameters of pseudo-first-order and pseudo-second-order kinetic models. The first-order model and second-order model were used to match the kinetic data and the R^2 values of the second-order model were higher compared to the first-order model. With the increase in POWS-AC dose to 1.0 g/L, both models show a high R^2 value, indicating that the fitting results of the first and second-order models well matched the kinetic data assuming that chemical process predominated in the adsorption of NO_3^--N by POWS-AC at high dose [46]. The findings also demonstrated that the NO_3^--N adsorption by POWS-AC was influenced by the availability of active sites on the surface of POWS-AC.

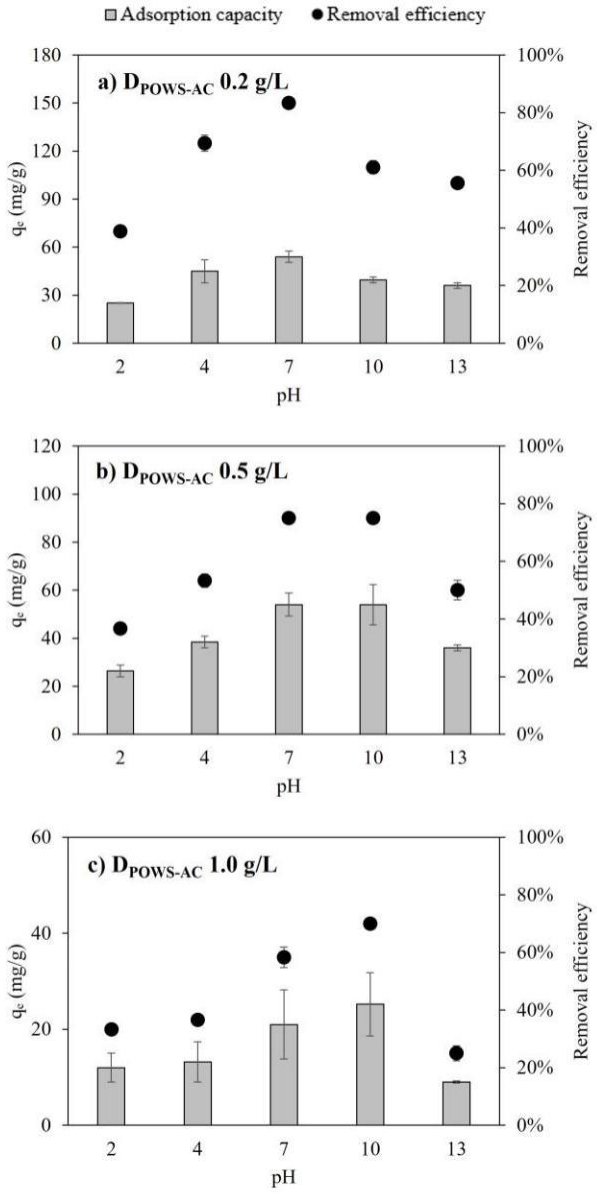

Fig. 3. Adsorption capacity of POWS on NO_3^--N and removal efficiency of NO_3^--N at initial concentrations of NO_3^--N solution (C_{NO3^-N}: 100 m/L), different POWS-AC dose ($D_{POWS-AC}$: 0.2, 0.5, and 1 g/L), and different pH solution 2, 4, 7, 10, and 13 after 4 hours adsorption process.

Table 2. Kinetic parameters for the removal of NO_3^--N by POWS-AC

Kinetic parameters		**POWS-AC dose (g/L)**		
		0.2	**0.5**	**1**
Pseudo-first-order	q_e (mg/g)	241.2	154.2	84.3
	k_1 (h^{-1})	0.048	0.076	0.174
	R^2	0.798	0.687	0.905
Pseudo-second-order	q_e (mg/g)	245.6	147.4	80.3
	k_1 (h^{-1})	0.075	0.158	0.147
	R^2	0.875	0.878	0.965

The adsorption isotherm was investigated to describe the interaction between NO_3^--N and POWS-AC and optimize the use of the adsorbent. The Langmuir and Freundlich models were used to normalize the NO_3^--N adsorption by POWS-AC from batch equilibrium with different doses and/or different initial concentrations. The equilibrium adsorption data were fitted to the Langmuir and Freundlich adsorption models. Both models show high R^2 values (>0.85) and could describe the adsorption behaviors on the surface. However, the Langmuir model shows a higher R^2 value and the adsorption

capacity of NO_3^--N compared to the Freundlich model, indicating the existence of heterogeneous adsorption sites. Therefore, POWS-AC is suitable for use as an adsorbent in the adsorption process for removing NO_3^--N from an aqueous solution.

Table 3. Langmuir and Freundlich parameters of POWS-AC adsorption experiments

Adsorption isotherms		**Initial NO_3^--N concentration (mg/L)**		
		30	**50**	**100**
Langmuir	q_m (mg/g)	36.2	60.1	104.3
	b (L/mg)	0.05	0.09	0.12
	R^2	0.947	0.961	0.984
Fruendlich	n	1.75	1.98	2.04
	K_F (mg/g) $(L/mg)^{1//n}$	2.47	2.17	2.14
	R^2	0.879	0.904	0.911

V. Conclusion

The adsorption process by POWS-AC demonstrated a good performance in removing the NO_3^--N from water. With the POWS-AC dosage range of 0.1–1 g/L, better removal of NO_3^--N was shown when the initial NO_3^--N concentration was 30 mg/L (27–77%). The maximum adsorption capacity of NO_3^--N was in the range of 36.2–104.3 mg/g when the initial NO_3^--N concentration was in the range of 30–100 mg/L according to the Langmuir isotherm model. Pseudo-first-order kinetic model and Langmuir isotherm model were the best modes to describe the adsorption process for NO_3^-N by POWS-AC. The adsorption capacity of POWS-AC for NO_3^--N decreased with the increase in POWS-AC dosage and the increase in pH from 2 to 7, indicating the adsorption process is chemically favorable. The study demonstrated that POWS-AC showed a favorable utilization for the NO_3^--N adsorption process from an aqueous solution by providing more evidence of the difference in adsorption parameters conditions. Future work shall be addressed to investigate more effects of the short adsorption time and high POWS-AC dosage as well as the use of POWS-AC in removing other pollutants, such as heavy metals.

Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

MYR conducted research, analyzed and validated data, wrote the original draft, reviewed and edited the original draft; WIF conducted the research, validated data, reviewed and edited the original draft; NLS conducted research, analyzed the data, wrote the original draft; RD validated data, reviewed original draft; all authors had approved the final version.

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