CHARACTERIZATION AND KINETICS STUDY OF ACTIVATED COCONUT SHELLS, COW BONES AND ZEOLITE BASED ADSORBENT FOR POME TREATMENT

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DEDICATION

This project is dedicated to Almighty Allah, the maker of all things and to my family especially my parents Mr. and Mrs. Adeleke who have being the pillar of my life from cradle.
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ABSTRACT

Palm oil mill effluent (POME) is a high strength agro-allied wastewater containing both organic pollutants and heavy metals. The discharge of POME into the environment without adequate treatment contributes to diseases affecting humans and aquatic lives. However, there is the necessity to reduce the pollutants to a very low level of discharge to reduce the impact of the toxic effect of the pollutants on the environment and the aquatic population. The conventional approach for the treatment of POME is expensive compared to the method of adsorption. The method of adsorption has shown to be cost and time effective for research. Thus, the objective of this study was to prepare composite adsorbent from activated coconut shell carbon (ACSC), activated cow bone powder (ACBP) and zeolite for the treatment of POME using the optimum particle size obtained in a batch adsorption study. The characterization of the ACSC, ACBP and zeolite was obtained using pendant drop contact angle experiment. The result illustrated that the contact angles of the ACSC, ACBP and zeolite respectively were 105.20°, 95.70° and 25.20°. The result of the contact angles showed that activated coconut shell carbon and activated cow bone powder were hydrophobic materials while the zeolite was hydrophilic. The investigation of the chemical composition of the materials using energy dispersive x-ray (EDX) indicated that the major elements of both ACSC and ACBP were predominantly C, Ca²⁺ and O and Si for zeolite and C, Si, O, Na, Mg, Ca and P as the major elements on the surface of the composite while the XRF showed that the composite contained CaO and SiO₂ as the major compounds. The point of zero charge (pHₚzc) of 5.28 achieved showed that the composite contained acidic surface which influenced cationic exchange in the supernatant and the surface of the composite. The CEC after adsorption was observed as 0.8918±0.0669 meq/g. The optimal batch adsorption of COD and NH₃-N was obtained at under fixed condition of pH 7, 105 minutes contact time at 150 rpm shaking speed and 150 μm particle size for ACSC,
ACBP and zeolite. The prepared composite adsorbent contained functional groups of CH, C=C, C-O-C, OH using the Fourier transform irradiation (FT-IR) analysis. The optimal operation parameters of the adsorption process for the reduction of COD and NH$_3$-N using the central composite design (RSM) was recorded at pH 10, 50 rpm of shaking speed for 2 h and by using 3 mm of composite particle size and 125 gL$^{-1}$ of the adsorbent at initial concentration of POME of 1 ml per 500 ml volumetric flask. The results revealed that the investigated factors evidently induced the reduction of the parameters. The experimental data of COD, NH$_3$-N, Cd, Fe and Pb from the batch study were fitted to the isotherm and kinetic models. The result of the isotherm study fitted best to the Langmuir equation model for COD, NH$_3$-N, Fe and Cd which indicated that the adsorption of the pollutants from the supernatant was favourable on a mono layer surface. The Freundlich isotherm fitted experimental data better than the Langmuir and the Temkin isotherm for Pb which showed that the adsorption process was effective on a heterogeneous surface. The investigation showed that the uptakes of COD, NH$_3$-N, Cd, Fe and Pb from the experimental data were fitted to the pseudo-second order kinetic model which implied that the process of adsorption was by chemisorption. Furthermore, the fixed bed packed composite adsorption was conducted and the experimental data were fitted to Thomas and Adams-Bohart model. The model parameters were obtained from the breakthrough curves, the effective adsorption of COD was obtained at lower flow rate influent concentration. Desorption of the spent adsorbent was suitably conducted using 0.5M NaOH and breakthrough was obtained at longer retention time. It can be concluded that a mesoporous and granular composite adsorbent was effective for the treatment of both organic and heavy metal pollutants. It was observed that both batch isotherm and kinetic study can be effectively applied for the treatment of POME using the composite adsorbent, although the effectiveness of the batch adsorption study showed to be more suitable than the fixed bed continuous column for the removal of pollutants of POME. However, due to the potential of the composite adsorbent for the treatment of POME, the treatment efficiency of the adsorbent has shown that the composite have the potential to be used for the treatment of pollutants of high strength wastewater.
Efluen kilang minyak kelapa sawit (POME) adalah air sisa agro-pertanian yang mengandungi bahan pencemar organik dan logam berat. Pelepasan POME ke dalam persekitaran tanpa rawatan yang mencukupi menyumbang kepada penyakit yang memberi kesan kepada manusia dan kehidupan akuatik. Walau bagaimanapun, terdapat keperluan untuk mengurangkan pencemaran kepada tahap pelepasan yang sangat rendah untuk meminimumkan kesan pencemar toksik terhadap alam sekitar dan populasi akuatik. Pendekatan konvensional untuk rawatan POME adalah mahal berbanding kaedah penjerapan. Kaedah penjerapan telah menunjukkan kos dan masa yang berkesan untuk penyelidikan. Oleh itu, objektif kajian ini adalah untuk menyediakan penjerap komposit daripada karbon teraktif tempurung kelapa (ACSC), serbuk tulang lembu teraktif (ACBP) dan zeolit untuk rawatan POME menggunakan saiz partikel optimum yang diperolehi dalam ujikaji penjerapan kelompok. Pencirian ACSC, ACBP dan zeolit diperoleh dengan menggunakan ujikaji sudut sentuhan titis loket. Hasil keputusan menggambarkan bahawa sudut sentuhan titis loket ACSC, ACBP dan zeolit masing-masing adalah 105.20°, 95.70° dan 25.20°. Hasil daripada sudut sentuhan menunjukkan bahawa karbon teraktif tempurung kelapa dan serbuk tulang lembu teraktif adalah daripada bahan hidrofobik manakala zeolit adalah daripada bahan hidrofilik. Penyiasatan komposisi bahan kimia yang menggunakan sinaran-x penyebaran tenaga (EDX) menunjukkan bahawa unsur-unsur utama ACSC dan ACBP adalah C, Ca\(^{2+}\), dan O sebagai unsur utama pada permukaan komposit manakala XRF menunjukkan bahawa unsur-unsur utama pada permukaan komposit mengandungi CaO dan SiO\(_2\) sebagai sebatian utama. Titik caj sifar (pH\(_{pzc}\)) adalah 5.28 telah dicapai menunjukkan bahawa komposit mengandungi permukaan berasid yang mempengaruhi pertukaran kationik dalam supernatan dan permukaan komposit. CEC selepas penjerapan diperhatikan sebagai 0.8918 ± 0.0669 meq/g. Penjerapan kelompok optimum COD dan NH\(_3\)-N didapati dalam keadaan tetap iaitu pH 7, 105 minit masa sentuhan pada kelajuan goncangan 150 rpm dan saiz partikel 150μm untuk ACSC, ACBP dan zeolit. Penjerap komposit yang disediakan
mengandungi kumpulan berfungsi CH, C=C, C-O-C, OH menggunakan analisis radiasi transformasi Fourier (FT-IR). Parameter optimum operasi bekerja bagi proses penjerapan untuk penurunan COD dan NH\textsubscript{3}-N menggunakan reka bentuk komposit pusat (RSM) direkodkan pada pH 10, kelajuan goncangan 50 rpm selama 2 jam dan menggunakan 3 mm saiz partikel komposit dan 125 gL\textsuperscript{-1} dari penjerap pada kepekatan awal POME 1 ml terhadap 500 ml kelalang volumetrik. Hasil keputusan didapati bahawa faktor-faktor yang dikaji secara jelasnya mendorong terhadap penurunan parameter. Data eksperimen COD, NH\textsubscript{3}-N, Cd, Fe dan Pb dari ujikaji kelompok dipadankan dengan model isoterma dan kinetik. Hasil kajian padanan isoterma terbaik adalah model persamaan Langmuir untuk COD, NH\textsubscript{3}-N, Fe dan Cd yang menunjukkan bahawa penjerapan bahan pencemar dari supernatant adalah digemari pada permukaan lapisan tunggal. Data eksperiman daripada isoterma Freundlich yang dipadankan adalah lebih baik daripada isoterma Langmuir dan Temkin untuk Pb yang menunjukkan bahawa proses penjerapan berkesan pada permukaan yang heterogen. Penyiasatan didapati menunjukkan bahawa pengambilan COD, NH\textsubscript{3}-N, Cd, Fe dan Pb daripada data eksperimen telah dipadankan dengan model kinetik pseudo-tertib kedua yang menunjukkan bahawa proses penjerapan adalah secara penjerapan kimia. Seterusnya, penjerapan komposit lapisan tetap yang telah dijalankan dan data eksperimen berikut telah dipadankan dengan model Thomas dan Adams-Bohart. Parameter model telah diperolehi daripada lengkung bulus, penjerapan COD yang berkesan ditunjukkan melalui kadar aliran yang lebih rendah. Penjerapan semula penjerap telah dilakukan dengan menggunakan 0.5M NaOH dan bulus didapati pada masa tahanan yang lebih lama. Secara kesimpulannya didapati bahawa penjerap komposit mesoliang dan butiran adalah berkesan untuk merawat kedua-dua bahan pencemar organik dan logam berat. Telah diperhatikan bahawa kajian isoterma dan kinetik kedua-duanya secara berkesan boleh digunakan untuk rawatan POME dengan menggunakan penjerap komposit, walaupun keberkesanan ujikaji penjerapan kelompok menunjukkan ianya lebih sesuai daripada turus penjerapan lapisan tetap untuk penyingkirkan bahan pencemar POME. Walau bagaimanapun, disebabkan oleh potensi penjerap komposit untuk rawatan POME, kecekapan rawatan penjerap telah menunjukkan bahawa penjerap komposit mempunyai potensi untuk digunapakai dalam rawatan pencemaran air sisa berkekuatan tinggi.
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<td>Binding surface area</td>
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<td>B</td>
<td>Temkin constant</td>
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<tr>
<td>B</td>
<td>Blank</td>
</tr>
<tr>
<td>Ce</td>
<td>Final equilibrium concentration</td>
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<tr>
<td>CO</td>
<td>Initial concentration</td>
</tr>
<tr>
<td>CO</td>
<td>Cobalt</td>
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<td>Cv</td>
<td>Crystal violet</td>
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<td>Cu</td>
<td>Copper</td>
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<td>Cr</td>
<td>Chromium</td>
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<tr>
<td>Cd</td>
<td>Cadmium</td>
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<td>CT</td>
<td>Outlet concentration</td>
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<td>D</td>
<td>Dilution factor</td>
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<td>Fe</td>
<td>Iron</td>
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<td>H</td>
<td>Initial rate of adsorption</td>
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<td>K</td>
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<td>Kf</td>
<td>Adsorbent adsorbed per unit equilibrium</td>
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<tr>
<td>Ki</td>
<td>Intraparticle diffusion rate constant</td>
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<td>KL</td>
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<tr>
<td>M</td>
<td>Mass</td>
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<td>mg/L</td>
<td>Milligram per liter</td>
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<tr>
<td>Mn</td>
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<td>N</td>
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<td>Nickel</td>
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<td>Number of sites occupied</td>
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<tr>
<td>P</td>
<td>Pressure</td>
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<tr>
<td>P&lt;sub&gt;o&lt;/sub&gt;</td>
<td>Vapour pressure</td>
</tr>
<tr>
<td>Q</td>
<td>Flow rate</td>
</tr>
<tr>
<td>q&lt;sub&gt;e&lt;/sub&gt;</td>
<td>Quantity of the adsorbed per unit mass of adsorbent</td>
</tr>
<tr>
<td>q&lt;sub&gt;o&lt;/sub&gt;</td>
<td>Maximum solid phase concentration of the solute</td>
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<tr>
<td>q&lt;sub&gt;t&lt;/sub&gt;</td>
<td>Amount of the adsorbed per unit time</td>
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<td>R</td>
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<tr>
<td>R&lt;sub&gt;L&lt;/sub&gt;</td>
<td>Separation coefficient</td>
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<td>Sample</td>
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<tr>
<td>U</td>
<td>Speed of gas out</td>
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<tr>
<td>V</td>
<td>Volume of solution</td>
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<tr>
<td>V&lt;sub&gt;eff&lt;/sub&gt;</td>
<td>Volume of effluent</td>
</tr>
<tr>
<td>V&lt;sub&gt;ε&lt;/sub&gt;</td>
<td>Volume porosity</td>
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<td>X</td>
<td>Amount of adsorbent in the column</td>
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<td>W</td>
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<td>Column bed height</td>
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<td>Λ</td>
<td>Time required for breakthrough at 50%</td>
</tr>
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<td>&gt;</td>
<td>Greater than</td>
</tr>
<tr>
<td>&lt;</td>
<td>Less than</td>
</tr>
<tr>
<td>°</td>
<td>Degree</td>
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<td>Atomic analyst spectrometer</td>
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<td>AF</td>
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<tr>
<td>ACBP</td>
<td>Activated cow bone powder</td>
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<td>ACSC</td>
<td>Activated coconut shell carbon</td>
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<td>AF</td>
<td>Anaerobic filter</td>
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<td>ASB</td>
<td>Activated sludge biomass</td>
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<td>ASBR</td>
<td>Anaerobic sequencing batch reactor</td>
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<td>ATA</td>
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<tr>
<td>BDDT</td>
<td>Brunauer, Deming, Deming Teller</td>
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<td>BDOC</td>
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<td>BET</td>
<td>Brunauer Emmet and Teller</td>
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<td>BOD</td>
<td>Biochemical oxygen demand</td>
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<td>BF</td>
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<td>CA</td>
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<td>CCD</td>
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<td>CPW</td>
<td>Crude petroleum wastes</td>
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<td>CR</td>
<td>Congo red</td>
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<td>CV</td>
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<td>DOE</td>
<td>Department of Environment</td>
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<td>DKR</td>
<td>Dubinin-Kagener Radushkevich</td>
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<td>EBCT</td>
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<td>EDX</td>
<td>Energy dispersive x-ray</td>
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<td>Empty fruit bunches</td>
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<td>EPA</td>
<td>Environmental protection agency</td>
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<td>FAS</td>
<td>Ferrous ammonium sulphate</td>
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<td>FO</td>
<td>Forward osmosis</td>
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<td>Fourier transform irradiation</td>
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<td>GAC</td>
<td>Granular activated carbon</td>
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<td>GCF</td>
<td>Global contamination factor</td>
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<td>HAP</td>
<td>Hydroxyapatite</td>
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<tr>
<td>ICF</td>
<td>Individual contamination factor</td>
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<td>ICP-MS</td>
<td>Inductively coupled plasma mass spectrometry</td>
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<td>INWQS</td>
<td>Interim water quality standard</td>
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<td>MAS</td>
<td>Membrane anaerobic system</td>
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<tr>
<td>MB</td>
<td>Methylene blue</td>
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<tr>
<td>MF</td>
<td>Micro filtration</td>
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<tr>
<td>MO</td>
<td>Methyl orange</td>
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<td>MSDS</td>
<td>Material safety and data sheet</td>
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<td>MTZ</td>
<td>Mass transfer zone</td>
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<td>NF</td>
<td>Nano filtration</td>
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<tr>
<td>OLR</td>
<td>Organic loading rate</td>
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<tr>
<td>OPC</td>
<td>Ordinary Portland cement</td>
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<tr>
<td>OPF</td>
<td>Oil palm fronds</td>
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<td>OPT</td>
<td>Oil palm trunk</td>
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<td>PAC</td>
<td>Powdered activated carbon</td>
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<td>Poly chlorinated biphenyls</td>
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<td>Palm oil mill effluent</td>
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<td>Palm oil mill sludge</td>
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<td>POFA</td>
<td>Palm oil fuel ash</td>
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<td>PPB</td>
<td>Part per million</td>
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<td>PSAC</td>
<td>Palm shell activated carbon</td>
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<td>PVA</td>
<td>Polyvinyl alcohol</td>
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<tr>
<td>RO</td>
<td>Reverse osmosis</td>
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<td>RSM</td>
<td>Response surface methodology</td>
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<td>SEM</td>
<td>Scanning electron microscopy</td>
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<tr>
<td>SS</td>
<td>Suspended solids</td>
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<tr>
<td>SWOT</td>
<td>Strength, opportunity, weakness and threat</td>
</tr>
<tr>
<td>TN</td>
<td>Total nitrogen</td>
</tr>
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<td>TOC</td>
<td>Total organic carbon</td>
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<td>Total solids</td>
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<td>Total suspended solids</td>
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<td>UASB</td>
<td>Up-flow anaerobic sludge blanket</td>
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<td>Up flow anaerobic sludge fixed film</td>
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<td>Ultra filtration</td>
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