

CHITOSAN ADDITION EFFECT IN H₃PO₄ ACTIVATED PAPERMILL-SLUDGE WASTE CARBON-BASED COMPOSITES FOR CADMIUM (II) IONS REMOVAL

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ABSTRACT

The use of paper mill sludges as a precursor for activated carbon preparation is one of the few attractive alternatives for absorbing metal ion application due to the high carbon content of cellulose fibers. This study aims to prepare paper-mill sludges with waste-based activated carbon (PPAc) by using an H₃PO₄ activation agent and combine with chitosan to become a composite for the removal of cadmium (II). The activated carbon/chitosan composite (PPAcCh) structure was evaluated using FT-IR (Fourier Thermal-Infrared) and XRD (X-ray diffraction) while the morphology was determined by SEM-EDX (Scanning Electron Microscope and Energy Dispersive X-ray Spectroscopy). The Cd (II) ion removal was determined by Atomic Absorption Spectroscopy (AAS). The influence of various parameters, such as the effect of concentration of H₃PO₄, agitation speed, flow rate, pH, and chitosan initial concentration in Cd ion removal was investigated. The resultant PPAcCh composite potentially exhibits good performance at Cd(II) metal ion removal.

Keywords: Activated Carbon/Chitosan, Adsorbent, Cadmium, Composites, Paper Mill Sludges.

RASĀYAN J. Chem., Vol. 18, No.1, 2025

INTRODUCTION

The paper industry is a major agro-industrial commodity in Indonesia, with a production capacity of 10 million tons of pulp and 17 million tons of paper, requiring approximately 45 million cubic meters of raw materials¹. The industry produce quite large solid waste. The most significant contribution of solid waste is the sludge waste, which contain 90% solid phase and 10% water, and often causes problems in wastewater treatment units². The papermill sludge waste contains carbon derivative material such as lignocellulose (lignin, hemicellulose, and cellulose) and has potential to be processed into useful materials due to its versatile uses. Papermill sludge waste can be used for agriculture field³, construction materials⁴, and producing biofuels⁵. The papermill sludge waste also has potential as activated carbon precursor because of its high carbon derivative content which has advantage as sustainability, waste management, cost-effectiveness, and tunable properties. Activated carbon has widely used as an industrial-scale adsorbent especially for liquids and gases purification/separation, as well as catalysts and supports⁶.

On the other hands, activated carbon is a highly effective material for heavy metal removal⁷ due to its high surface area and functional group presence⁸. The material can effectively remove lead, mercury, cadmium, copper, and arsenic⁹. The specific effectiveness of each metals adsorption is based on (i) activated-carbon surface functional group and (ii) metal-ion charge and size¹⁰. Activated carbon for heavy metal removal has been used in various application such as drinking water treatment⁷, wastewater treatment and metal chelation medicine¹¹.

Cadmium (Cd) is non-biodegradable heavy metal, contained on certain products like batteries and paints. If the product is exposed to the environment by human negligence, Cd can enter the environment through rocks, soil, and water. Once Cd is in water, it can be absorbed by plants and drank up by animals¹². Cd contaminated drinking water can pose health threats in human organs such as kidney dysfunction,

hypertension, diarrhoea, abdominal pain, and bone disorders. Some common methods like coagulation, adsorption, electrochemistry, membrane, solvent extraction, ion exchange, and biosorption were used to remove heavy metals from water¹³. Afterwards, adsorption is more efficient, economical, and environmentally friendly for reducing contaminant¹⁴. Activated carbon based adsorbent is excellent material for Cd removal, however several challenges still need to be improved⁸. Incorporating biopolymer, synthetic polymer, and conducting may improve the performance of activated carbon based adsorbent. They offer enhanced selectivity, increased capacity, improved regeneration, and mechanical stability¹⁵.

Chitosan, Polydopamine, and Polyethylenimine are recent investigated polymer types for activated-carbon supporting materials in heavy metal removals and become promising approach in water treatment applications. Modified chitosan in pollutants adsorption application also has been widely reported. However, the investigating number of chitosan for activated-carbon supporting materials still needs to be increase. Chitosan, chitin derivative is the second most abundant natural polysaccharide after cellulose. Its chelating groups (amino groups) strongly adsorb anionic metals through electrostatic attraction¹⁶. Chitosan and activated carbon based composite have been developed using a range of carbon sources, such as commercially available activated carbon, coconut shell charcoal, renewable waste tea, seeds from the Sapotaceae family, *Typha latifolia* leaves, and olive stones. These composites are created using a surface modification method in which chitosan is utilized to modify the activated carbon's surface¹⁷. This paper investigates the research gap regarding the minimal exploration of glutaraldehyde cross-linked chitosan integrated with activated carbon obtained from paper mill sludge waste for the adsorption of Cd ions. This study aims to make a composite of glutaraldehyde cross-linked chitosan combined with activated carbon chemically activated with phosphoric acid derived from paper mill sludge waste, using the column adsorption method and determining the optimal conditions for the adsorption process, including pH, flowrate, and adsorbent dosage.

EXPERIMENTAL

Material and Methods

The paper mill sludge was obtained from PT. Toba Pulp Lestari at Desa Sosor Ladang, Pangombusan Porsea, Kecamatan Parmaksian, Kabupaten Toba Samosir, Sumatera Utara, Indonesia. The chitosan was extracted from lobster shrimp shell waste sourced from Percut Sei Tuan, Deliserdang, North Sumatra, Indonesia. During this study, the chemicals used were of analytical grade and purchased from Merck without any purification. A 1000 mg/l Cd(II) ion stock solution was obtained by dissolving a standard cadmium solution. Distilled water was added to the stock solution to prepare working solutions at the appropriate concentrations.

The analyses were conducted using Fourier Transform Infra-Red (FTIR) (Agilent 630 Cary Series), Shimadzu XRD 6000 X-Ray Diffraction (XRD), ContraAA 300 series Atomic Adsorption Spectrophotometry (AAS), Zeiss type EVO MA 10 Zss Scanning Electron Microscopy Electron Dispersive X-ray (SEM-EDX), and NOVA LX 4 Brand Quantachrome Gas Sorption Analyzer (GSA)

Activated Carbon from Papermill Sludge Waste (PPAc) Preparation

Activated carbon from paper mill sludge waste (PPAc) was produced through a heat treatment process. The cleaned and dried paper mill sludge waste (PP) was initially heated in an oven at 110°C for 24 hours. The heated PP was then ground into a fine powder using a grinding device and passed through a 200-micron sieve. The resulting powder underwent physical activation in a furnace at 600°C for 1 hour. Subsequently, the powder was mixed with phosphoric acid solutions at concentrations of 10%, 30%, and 50% by weight, stirred for 4–7 minutes at 85°C to allow the H₃PO₄ to penetrate the powder's interior. Finally, the activated carbon (PPAc) was neutralized with distilled water and dried in an oven at 105°C for 2 hours.

Chitosan/Activated Carbon Composites (PPAcCh) Preparation

The chitosan (Ch) solution was prepared by dissolving 2, 3, 4, 5, and 6 g chitosan powder into 100 mL of acetic acid (2%, v/v) at room temperature for 24 h. One gram of activated carbon was dispersed into each of 100 mL chitosan solution by stirring at 250 rpm and heated at 60°C for 4 h. Using a syringe, the resultant solution dropwise was added into 0.1 M of NaOH solution to make the beads and stirred until 4 hours in order for solidification. The beads then were neutralized using distilled water. The dried beads was

immersed in glutaraldehyde solution (5.5%, v/v) overnight to form activated carbon-based chitosan gels composite. The gels then were washed using distilled water, dried at 60°C in an oven for 24 h, and stored in a desiccator. The product was labeled based on chitosan composition (2%-6%) i.e. PPAcCh1 for chitosan 2%, PPAcCh2 for chitosan 3%, PPAcCh3 for chitosan 4%, PPAcCh4 for chitosan 5% and PPAcCh5 for chitosan 6% respectively.

Activated Carbon (PPAc) and Chitosan/Activated Carbon Composites (PPAcCh) Adsorption Capacity

The adsorption process was performed to evaluate the impact of key parameters, including flow rate, pH, and the initial concentration of Cd (II). In each experiment, 1 g of activated carbon was added to 50 mL of Cd(II) solution in an adsorption column flask. The mixture was stirred using a magnetic stirrer for 2 hours and then filtered through a column with flow rates of 3, 4, and 5 mL/min. In this study, the pH levels were adjusted between 5 and 7, and the initial Cd (II) concentrations were set at 10, 50, and 100 mg/L. The pH was adjusted to the desired level using 0.1 N HCl or 0.1 N NaOH solutions. After stirring, the solutions were filtered using Whatman No. 42 filter paper. The amount of Cd (II) ions adsorbed was determined by calculating the difference between the initial and final concentrations. The composite exhibiting the highest adsorption efficiency was selected for further analysis.

Biocomposites (1 g) with different compositions were loaded into a dry column, and 10 mL of MQ water was added. The mixture was homogenized at a pH of 6.0. A 50 ppm Cd²⁺ solution was then passed through the column at a flow rate of 4 mL/min. The effluent was collected, and the Cd (II) concentration remaining in the effluent was measured using AAS.

Cd(II) Metal Ion Removal using Chitosan/Activated Carbon Composite (PPAcCh)

Adsorption of cadmium (II) ions was prepared using column adsorption method. Adsorption of cadmium (II) ions was carried out in the same aqueous solution for 50 mg/l concentration of cadmium (II) ions. 1 g of PPAcCh were supplemented one at a time to column containing 100 ml of 50 mg/l of cadmium (II) solutions. Solids were allowed to settle down and were removed using syringe filtration. Resulting filtrate (25 ml of each sample) was diluted into 100 ml of distilled water (the pH = 2 was conditioned by using HNO₃). The metals ions filtrates then were analyzed using Atomic Absorption Spectrophotometer (AAS).

Characterization and Analysis

The functional groups present in activated carbon, chitosan, and the chitosan-based activated carbon adsorbent were analyzed using Fourier Transform Infrared Spectroscopy (Agilent Cary 630, USA). The mineral phases were identified using X-Ray Diffraction (Shimadzu 6000, Japan), while the surface morphology and elemental composition were examined with Scanning Electron Microscopy coupled with Energy Dispersive X-ray analysis (SEM-EDX, Zeiss MA10, Göttingen, Germany).

The BET surface area and pore size of the chitosan-based activated carbon were measured through N₂ adsorption using a surface analyzer (Quantachrome Novatouch LX4, USA). Before conducting gas adsorption measurements, the adsorbent was degassed under vacuum at 100°C for 24 hours. The N₂ adsorption isotherm was obtained at 77 K by plotting the adsorbed volume (cc/g) against relative pressure (P/P₀).

RESULTS AND DISCUSSION

Characteristics of Activated-Carbon/Chitosan Composite

The Structure

Functional groups of activated carbon-based chitosan composite structure was investigated using Fourier Transform Infrared Radiation (FTIR) and carried out at 700-4000 cm⁻¹ (Fig.-1). Fig.-1a showed the characteristics of chitosan i.e. 1021 cm⁻¹, 1423.8 cm⁻¹, 1640 cm⁻¹, 1640 cm⁻¹, and 3280 cm⁻¹ which indicates the presence of C-O, C-H, amine group (-NH₂), C-H aliphatic, and overlapping vibrations of -OH with -NH₂. The (-NH₂) overlapped peak of -OH is determined by a broader peak of -OH¹⁹. Fig.-1b showed the characteristics of active carbon i.e. 775 cm⁻¹, 1043 cm⁻¹, 1565 cm⁻¹, 2102 cm⁻¹, and 3205 cm⁻¹ which indicates the presence of alkanes C-H, C-O, aromatic C=C bonds, C-H, and -OH group²⁰. Furthermore, Fig.-1(c-g) showed the characteristic FTIR spectrum of activated carbon composite containing amine

functional group due to chitosan mobilization²¹. The composite shows a C=N band at 1635 cm^{-1} indicating glutaraldehyde had successfully crosslinked amine groups of chitosan to form a gel. The interaction that occurs between chitosan and chitosan/activated carbon is a physical interaction.

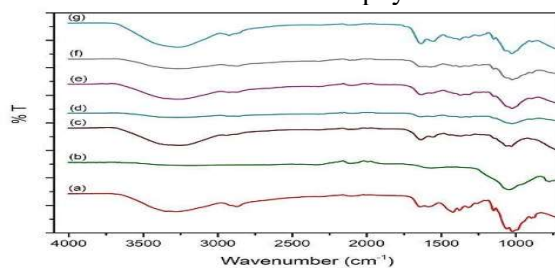


Fig.-1: FT-IR Spectrum of : (a) Chitosan (Ch), (b) Papermill-Sludges Activated Carbon (PPAc), (c) PPAcCh1, (d) PPAcCh2, (e) PPAcCh3, (f) PPAcCh4, and (g) PPAcCh5

Activated-carbon/chitosan composite structure also was determined by XRD diffractogram (Fig.-2). Fig.-2a showed broad peaks at $2\theta = 9.9^\circ$ and at $2\theta = 20.3^\circ$ indicating chitosan characteristics²². Fig.-2b showed broad peak around $2\theta = 20^\circ - 28^\circ$ with two sharp peaks at around $2\theta = 20^\circ - 23^\circ$ and at 26.6° , then a sharp peak around $2\theta = 40^\circ - 45^\circ$ indicating activated carbon contained graphitic carbon²³ and the sharp peaks indicating of a low crystallinity²⁴. Afterwards, Fig.-2(c-g) showed the activated carbon-chitosan composite diffractogram which has slightly similar to activated carbon without amine area of chitosan. The broad peaks at $2\theta = 9.9^\circ$ and at $2\theta = 20.3^\circ$ were decreased due to amine group of each chitosan monomer was crosslinked by glutaraldehyde²⁵. The height and level of the peaks were influenced by the activation process and the use of chemical activators, which caused a shift in the hexagonal plate from initially having a high level of regularity (crystalline) to becoming irregular (amorphous). The X-ray diffraction pattern showed a carbon (C) peak which has formed crystals in the graph, indicating that the activated carbon formed graphite and amorphous, composed of carbon atoms that are covalently bonded to form a hexagonal structure like flat plates stacked on the top of each other.

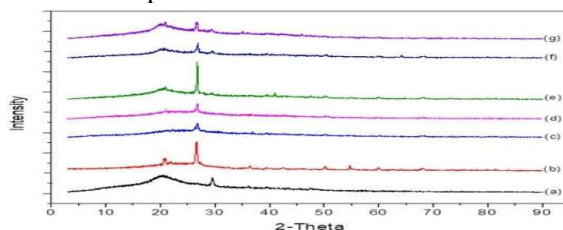


Fig.-2: The XRD Spectra of: (a) Chitosan (Ch), (b) Papermill-Sludges Activated Carbon (PPAc), (c) PPAcCh1, (d) PPAcCh2, (e) PPAcCh3, (f) PPAcCh4, and (g) PPAcCh5

The Morphology

Composite morphology was determined using Scanning Electron Microscopy (Fig.-3). Fig.-3a showed solid and smooth surface without porosity of chitosan, it had flat shape and regular structure²⁶ according to XRD analysis that the chitosan has a clear crystalline structure. Fig.-3b showed very irregular surface and pores with different sizes and shapes of activated carbon surface morphology²⁷. The irregular morphological forms were caused by the influence presence of tar and volatile compounds which were not completely decomposed²⁸ according to XRD analysis which showed that activated carbon of this research has amorphous phase. Afterwards, Fig.-3(c-g) showed a rigid surface of activated-carbon/chitosan composite. The composite is distributed homogeneously by the crosslinking of glutaraldehyde. The crosslinked reaction produced a denser and tighter structure so the structure can not be easily cracked and increased its mechanical properties²⁹. In other hands, Fig.-3e showed a non-uniform particle area due to polymer fibers presence, it had a rough surface and large size of pores.

Activated-Carbon/Chitosan Adsorption and Desorption Properties

The adsorption-desorption isotherm of activated carbon/chitosan composites was analyzed using the Brunauer–Emmett–Teller (BET) method to determine the pore radius, pore volume, and surface area of the material. The isotherms for the activated carbon/chitosan composites are presented in Fig.-4.

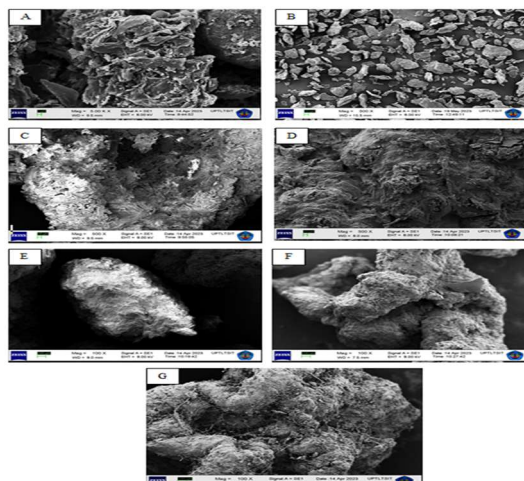


Fig.-3: The SEM Images of : (a) Chitosan (Ch), (b) Papermill-Sludges Activated Carbon (PPAc), (c) PPAcCh1, (d) PPAcCh2, (e) PPAcCh3, (f) PPAcCh4, and (g) PPAcCh5

As per IUPAC classifications, micropores have diameters below 2 nm, mesopores range between 2 nm and 50 nm, and macropores exceed 50 nm. The smallest pore size distribution of the activated carbon/chitosan composite appeared during the adsorption branch of the isotherm process, indicating the most likely pore size concentration at 3.25 nm (Fig.-3b). The BET analysis showed that the surface area and pore volume of activated carbon (PPAc) were 135.422 m²/g and 0.11 cm³/g, respectively. When chitosan was incorporated into the composite (PPAcCh), the BET surface area and pore volume significantly decreased to 2.55 m²/g and 0.006 cm³/g, respectively. These changes in surface area and pore volume suggest structural modifications in the composite as chitosan content increased, while activated carbon remained a controlling factor. The addition of chitosan led to a reduction in both the surface area and pore volume of the composite. A comparison of the properties based on chitosan mass is summarized in Table-1. Among the composites, PPAcCh5 exhibited the highest adsorption/desorption performance, while PPAcCh2 showed the lowest. The amount of chitosan immobilized within the composite materials significantly influenced adsorption and desorption capabilities. The isotherm analysis confirmed that the composite material is classified as mesoporous. Similar BET studies have reported that activated carbon derived from secondary sedimentation sludge demonstrated a surface area of 765.8 m²/g and an average pore diameter of 3.75 nm³⁰. Activated carbon from cosmetics-industry sequencing batch reactor (SBR) waste exhibited a surface area of 97 m²/g³¹, while activated carbon from sludge waste had an average granule size of 134.3 μm and a specific surface area of 1013.63 m²/g³².

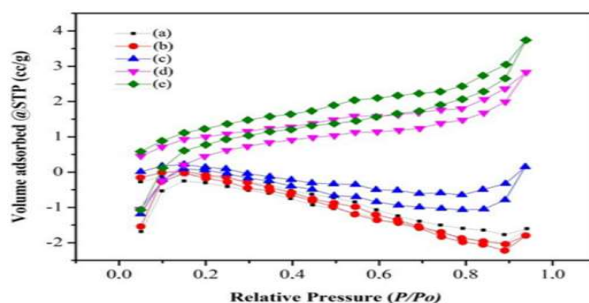


Fig.-4: The Adsorption-Desorption Isotherm of Activated-Carbon/Chitosan-Based Composite: (c) PPAcCh1, (d) PPAcCh2, (e) PPAcCh3, (f) PPAcCh4, and (g) PPAcCh5

Table-1: Active Carbon-Based-Chitosan Measurement Result

Materials	Measurement Results		
	Surface Area (m ² /g)	Pore (nm)	Pore Volume (cc/g)
PPAc	135.422	1.65609	0.112136

PPAcCh1	0.116019	13.4885	2.4906×10^{-3}
PPAcCh2	1.71588	3.24864	2.78714×10^{-3}
PPAcCh3	0.0967003	4.87042	0.235485×10^{-3}
PPAcCh4	1.72391	5.09124	4.38841×10^{-3}
PPAcCh5	2.55428	4.54009	5.79834×10^{-3}

PPAc (papermill-sludge waste-based activated carbon)

PPAcCh (PPAc activated carbon/chitosan based composite)

Adsorption Isotherm of Activated Carbon-Based Chitosan Adsorbent

Adsorption isotherm is the equilibrium relationship between the concentration of solutes (adsorbate) and the concentration of adsorbent particles at a certain temperature. The best adsorbent is the one that has adsorption capacity (Q) and adsorption effectiveness (EA) which is calculated by the equation below.

$$Q = \left(\frac{C_o - C_e}{M} \right) \times V \quad (1)$$

$$EA = \left(\frac{C_o - C_e}{C_o} \right) \times 100\% \quad (2)$$

The mechanism of papermill sludge waste activated carbon/chitosan based composite in Cd(II) metal ion adsorption was analyzed using langmuir (3) and Freundlich (4) adsorption isotherms equations³³.

$$\frac{C_e}{Q} = \frac{1}{Q_{max}} C_e + \frac{1}{Q_{max} \cdot K_L} \quad (3)$$

$$\text{Log } Q = \text{Log } K_F + \frac{1}{n} \text{Log } C_e \quad (4)$$

Where Qmax indicates the maximum adsorption capacity (mg/g), KL denotes Langmuir's constant (L/mg), KF denotes Freundlich's constant (L/mg)^{1/n}. The Qmax and KL values are obtained from the Ce/Q vs Ce plot and are linearly progressed so that a slope of 1/Qmax is obtained. The KF value is obtained from the Log Q vs Log Ce data plot and progressed linearly so that a slope of 1/n is obtained. The parameters and isotherms of Langmuir and Freundlich adsorption models from the results of flow rate variance and activated-carbon pH variations were written on Table-2.

Table-2: Parameter Model Isotherm Adsorption

Sample	Langmuir			Freundlich		
	Q _{max} (mg/g)	K _L (L/mg)	R ²	K _F	n	R ²
Flow Rate Variation	0.67957 mg/g	0.0503	1	788.31	0.5693	1
pH Variation	1.4206 mg/g	0.1122	0.9727	27.302	1.3085	0.9757

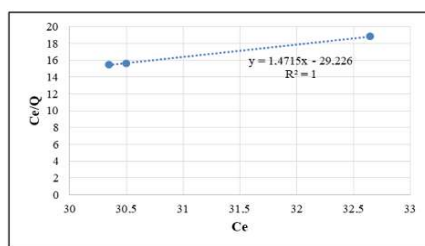


Fig.-5: Langmuir Isothermal Adsorption Model Graph Flow Rate Variation

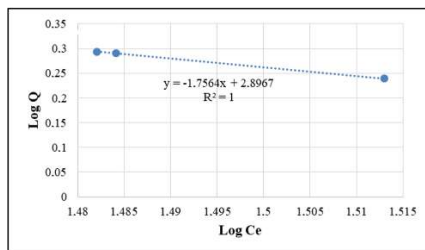


Fig.-6: Freundlich Isothermal Adsorption Model Graph of Flow Rate Variation

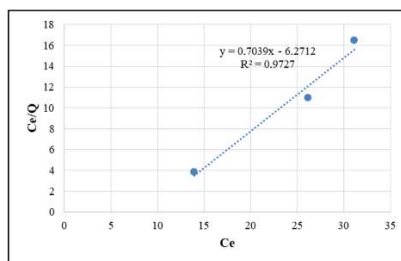


Fig.-7: Langmuir Isothermal Adsorption Model Graph pH Variation

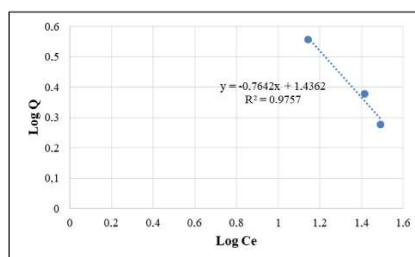


Fig-8: Graph of Freundlich Isothermal Adsorption Model pH Variation

The isotherms of adsorption was used to investigate the adsorption mechanism of solid-liquid phase adsorption, generally used the Langmuir and Freundlich isotherm model. The bond between metal molecules (adsorbate) and the surface of the adsorbent pore can occur by chemisorption and physisorption.

Cd Metal Ion Removal

Activated Carbon (PPAc) Performance

Cd metal ion reduction from 50 ppm Cd solution was performed using H₃PO₄ 30% activated PPAc based on flowrate in Fig.-9 and pH in Fig.-10. Fig.-9 shows that the 4 mL/s flow rate system has the lowest Cd removal (34.7%) while the 3 mL/s has the highest (39.3%), indicating 3 mL/s is the optimum flow rate. Low flow rate caused in longer contact time of Cd ions with activated carbon and removed more of Cd ions³⁴. On the other hand, Fig.-10 shows Cd removal of 37.8%; 47.7%; and 72.2% at pH = 4; pH = 5, and pH = 6 respectively, indicating the linearity of ion adsorption throught the pH increament. Low pH provides protonation at the surface of PPAc particles and reduces the attractive interaction with Cd ions.

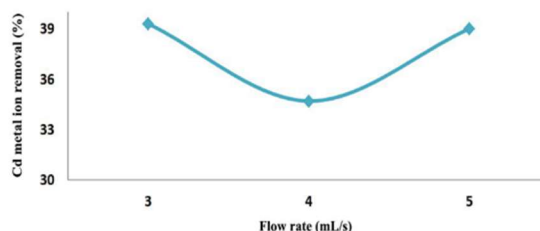


Fig.-9: Cd Metal Ion Removal Based on Flowrate

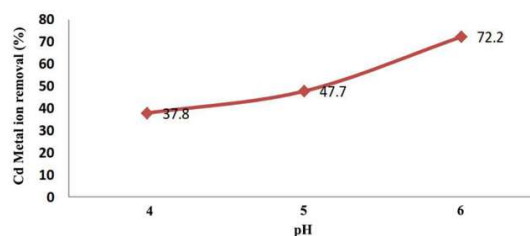


Fig.-10: Cd Metal Ion Removal Based on pH

Activated carbon and chitosan based composite (PPAcCh) performance

Fig.-11 shows the difference in Cd metal ion removal using PPAcCh composites with different chitosan concentrations. The addition of 2%-4% chitosan to the composite caused a significant increase in the absorption of Cd metal ions. However, the addition of 5% chitosan decreased the adsorption drastically and then slightly increased by addition of 6% chitosan. Increasing the concentration of chitosan provides more amine groups thus increasing the adsorption of the PPAcCh composite for Cd(II) metal ions. However by adding too much chitosan will reduce composite adsorption capacity due to chitosan particles can fill PPAc pores. When the equilibrium point has been reached, the composite surface is filled by adsorbate and reaches the saturation point of absorption³⁵. The optimum chitosan composition for the composite of this study is 4% (PPAcCh3) by remove Cd(II) metal ion up to 67.56%.

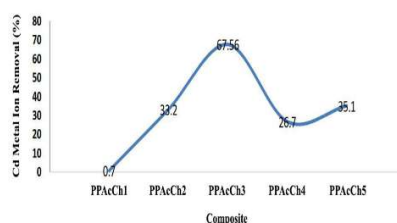


Fig.-11: Cd Metal Ion Removal Comparison Based on Chitosan Quantity of Composite: PPAcCh1; PPAcCh2; PPAcCh3; PPAcCh4; and PPAcCh5 (chitosan composition 2%;3%;4%;5%; and 6%)

CONCLUSION

Resultant activated carbon from papermill sludge waste (PPAc) exhibited high surface area and high total pore volume. The optimum flowrate and pH of PPAc activated carbon for Cd removal are at 3 mL/s and pH=6 respectively. Chitosan presence in activated-carbon composite (PPAcCh) successfully increased BET surface area and total pore volume, and removed Cd metal ion up to 67% from Cd(II) 50 ppm solution.

ACKNOWLEDGMENTS

The authors were grateful for the financial support provided by the Directorate of Research and Community Service, Ministry of Research, Technology, and Higher Education of the Republic of Indonesia. Directorate General Strengthen Research and Development, Financial Year 2019, The authors are grateful to the Postgraduate School, Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Sumatera Utara.

CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

CONTRIBUTION OF AUTHORS

All the authors contributed significantly to this manuscript, participated in reviewing/editing and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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REFERENCES

1. <https://www.kemenperin.go.id/artikel/16596/2017,-RI-Produsen-Kertas-Nomor-6-Terbesar-Dunia>
2. A. Demirbas, G. Edris, and W. M. Alalayah, *Energy Sources*, **39**(10), 999(2017), <https://doi.org/10.1080/15567036.2017.1283551>
3. A. Zawadzińska, A. P. Salachna, J. S. Nowak, W. Kowalczyk, R. Piechocki, Ł. Łopusiewicz, and A. Pietrak, *Agronomy*, **12**(1), 13(2022), <http://doi.org/10.3390/agronomy12010013>
4. Vaibhav R. Shirodkar, Nagaraj M. Naik, Ajay P. Naik, Dhanaraj Dessai, and Afran Shaikh, *International Journal for Research in Applied Science and Engineering Technology*, **7**, 1235(2019), <http://doi.org/10.22214/ijraset.2019.6212>
5. J. Prasetyo, K. Naruse, T. Kato, C. Boonchird, S. Harashima, and E.Y. Park, *Biotechnology for Biofuels and Bioproducts*, **4**, 35 (2011), <https://doi.org/10.1186/1754-6834-4-35>
6. M.O. Marín, C.F. González, A.M. García, and V.G. Serrano, *Applied Surface Science*, **252**, 5967(2006), <http://doi.org/10.1016/j.apsusc.2005.11.008>
7. M.Z.A. Zaimee, M.S. Sarjadi, and M.L. Rahman, *Water*, **13**(19), 2659(2021), <https://doi.org/10.3390/w13192659>
8. S. Mopoung, P. Moonsri, W. Palas, and S. Khumpai, *Scientific World Journal*, **2015**, 415961(2015), <http://doi.org/10.1155/2015/415961>
9. R.R. Pawar, Lalmunsiam, M. Kim, Jae-Gyu Kim, Seong-Min Hong, S.Y. Sawant, and S.M. Lee, *Applied Clay Science*, **162**, 339(2018), <http://doi.org/10.1016/j.clay.2018.06.014>
10. Z. Zhang, T. Wang, H. Zhang, Y. Liu, and B. Xing, *Science of The Total Environment*, **757**, 43910 (2021) <http://doi.org/10.1016/j.scitotenv.2020.143910>
11. M. Wang, G. Bera, K. Mitra, T.L. Wade, A.H. Knap, and T.D. Phillips, *Environmental Science and Pollution Research*, **28**, 6758(2021) <http://doi.org/10.1007/s11356-020-10973-z>
12. M. Hatamian, A.R. Nejad, M. Kafi, M.K. Souri, and K. Shahbazi, *Chemical and Biological Technologies in Agriculture*, **7**, 9(2020), <http://doi.org/10.1186/s40538-019-0173-0>
13. J. Sun, L. Liu, and F. Yang, *Journal of Hazardous Materials*, **394**, 122534(2020), <http://doi.org/10.1016/j.jhazmat.2020.122534>
14. B.S. Rath, and P.S. Kumar, *Environmental Pollution*, **280**, 116995(2021), <http://doi.org/10.1016/j.envpol.2021.116995>
15. Y.J. Yim, and B.J. Kim, *Polymers*, **15**(16), 3472(2023), <https://doi.org/10.3390/polym15163472>
16. W.S. Wan Ngah, L.C. Teong, and M.A.K.M. Hanafiah, *Carbohydrate Polymers*, **83**(4), 1446(2011), <https://doi.org/10.1016/j.carbpol.2010.11.004>
17. D. C. da Silva Alves, B. Healy, L.A. d. Pinto, T.R.S. Cadaval, and C.B. Breslin, *Molecules*, **26**(3), 594(2021), <https://doi.org/10.3390/molecules26030594>
18. S.M. Yakout, and G.Sharaf El-Deen, *Arabian Journal of Chemistry*, **9**, S1155(2016), <https://doi.org/10.1016/j.arabjc.2011.12.002>
19. G.A. Wardani, A.N. Octavia, M. Fathurohman, T. Hidayat, and E. Nofiyanti, *Jurnal Riset Kimia*, **8**(3), 280(2022), <https://doi.org/10.22487/kovalen.2022.v8.i3.16090>
20. D. Suwazan, and N. Nurhidayanti, *Jurnal Ilmu Lingkungan*, **20**, 37(2022), <https://doi.org/10.14710/jil.20.1.37-44>
21. M.A.H. Badsha, M. Khan, B. Wu, A. Kumar, and I.M.C. Lo, *Journal of Hazardous Materials*, **408**, 124463(2021), <https://doi.org/10.1016/j.jhazmat.2020.124463>
22. X Han, Z. Zheng, C. Yu, Y. Deng, Q. Ya, F. Niu, Q. Chen, W. Pan, and Y. Wang, *Carbohydrate Polymers*, **290**, 119490(2022), <https://doi.org/10.1016/j.carbpol.2022.119490>
23. M. A. Islam, M.K. Nazal, A.A. Akinpelu, M. Sajid, N.A. Alhussain, and M. Ilyas, *Journal of Analytical and Applied Pyrolysis* **180**, 106546(2024), <https://doi.org/10.1016/j.jaap.2024.106546>

24. M.S. Park, S.E. Lee, S. M. II. Kim, and Y.S. Lee, *Carbon Letters*, **16**, 45(2015), <https://doi.org/10.5714/CL.2015.16.1.045>
25. M.A. Khapre, S. Pandey, and R.M. Jugade, *International Journal of Biological Macromolecules*, **190**, 862(2021), <https://doi.org/10.1016/j.ijbiomac.2021.09.026>
26. F. Hisham, M.H. Maziati Akmal, F.B. Ahmad, and K. Ahmad, *Materials Today: Proceedings*, **42**, 2369(2021), <https://doi.org/10.1016/j.matpr.2020.12.329>
27. E.M. Mistar, T. Alfatah, and M.D. Supardan, *Journal of Materials Research and Technology*, **9(3)** 6276 (2020), <https://doi.org/10.1016/j.jmrt.2020.03.041>
28. K. Gong, X. Li, H. Liu, X. Cheng, D. Sun, Q. Shao, M. Dong, C. Liu, S. Wu, T. Ding, B. Qiu, and Z. Guo, *Carbon*, **156**, 320(2020), <https://doi.org/10.1016/j.carbon.2019.09.046>
29. J. Wang, W. Xu, W. Zhang, J. Da, L. Liu, X. Huang, C. Yang, Y. Zhan, H. Jin, Y. Li, and B. Zhang, *Carbohydrate Polymers*, **314**, 120926(2023), <https://doi.org/10.1016/j.carbpol.2023.120926>
30. Y.H. Li, F.m. Chang, B. Huang, Y.P. Song, H.Y. and Zhao, K. J. Wang, *Fuel*, **266**, 117053(2020), <https://doi.org/10.1016/j.fuel.2020.117053>
31. V.M. Monsalvo, A.F. Mohedano, and J.J. Rodriguez, *Desalination*, **277**, 377(2011), <https://doi.org/10.1016/j.desal.2011.04.059>
32. A. Setiawan, M.I.A. Bawafi, T.A. Ramadani, and I. Santiasih, *Teknik*, **42**, 316(2021), <https://doi.org/10.14710/teknik.v42i3.36031>
33. Z. Yi, J. Yao, M. Zhu, H. Chen, F. Wang, and X. Liu, *Springerplus*, **5**, 1160(2016), <https://doi.org/10.1186/s40064-016-2839-4>
34. J. L. Cervantes, D. I. S. Machado, R.G.S. Duarte, and M.A.C. Murrieta, *Adsorption Science & Technology*, **36**, 215(2018), <https://doi.org/10.1177/0263617416688021>
35. I. Nurhayati, J. Sutrisno, and M.S. Zainudin, *Jurnal Teknik UNIPA*, **16**, 62(2018), <https://doi.org/10.36456/waktu.v16i1.1491>

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