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Research Article

Hexavalent Chromium Reduction of Artificial Waste Using Resin Immobilized Photocatalyst TiO_2

Reduksi Krom Heksavalen Limbah Artifisial menggunakan Resin Immobilized Photocatalyst TiO_2

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Abstract

Photocatalysis is a process that can be used to reduce hexavalent chromium in wastewater. Therefore, this study aimed to analyze the effect of a semiconductor in the form of Resin Immobilized Photocatalyst (RIP)-TiO_2 on the reduction of Cr (VI), as well as the effect of pH and catalyst mass. In the process, RIP-TiO_2 was produced using rutile crystal TiO_2 and cation resin. The study was conducted in a column bed with continuous flow and UV lamp irradiation. Sampling was performed every 5, 15, 45, and 60 minutes, as well as the use of 30 and 40 g of RIP-TiO_2. The statistical results from a Two-Way Analysis of Variance (ANOVA) showed no significant differences in pH variation and catalyst mass. However, the best operating conditions were obtained at pH 5 and a catalyst mass of 40 g with a removal rate of 21.32%. These results suggested that pH adjustment had no significant effect on the reduction of Cr(VI) to Cr(III) using RIP-TiO_2 catalyst in the photocatalytic process. Further studies are needed to evaluate other factors, such as UV light intensity, contact time, and physical characteristics of the catalyst, capable of improving the efficiency of the RIP-TiO_2 system.

Keywords hexavalent chromium; photocatalyst; reduction; resin immobilized

Abstrak

Fotokatalis menjadi salah satu proses yang dapat digunakan untuk mereduksi krom heksavalen dalam air limbah. Penelitian ini bertujuan untuk menganalisis pengaruh semikonduktor berupa Resin Immobilized Photocatalyst (RIP)-TiO_2 pada reduksi Cr (VI) serta pengaruh kondisi pH dan massa katalis pada reduksi Cr (VI). Pembuatan RIP-TiO_2 menggunakan TiO_2 dengan kristal rutuil dan resin kation. Penelitian dilakukan pada bed kolom dengan aliran kontinyu dan penyinaran lampu UV yang dilakukan sampling setiap 5, 15, 45, dan 60 menit serta penggunaan RIP-TiO_2 sebanyak 30 dan 40 g. Dari penelitian ini diperoleh hasil statistik Two Way ANOVA bahwa tidak terdapat perbedaan signifikan pada variasi pH dan massa katalis. Namun, secara tren data kondisi operasi terbaik pada penelitian ini diperoleh pada pH 5 dan massa katalis 40 gram dengan tingkat removal sebesar 21,32%. Hasil ini menunjukkan bahwa pengaturan pH tidak memberikan pengaruh signifikan terhadap reduksi Cr(VI) menjadi Cr(III) menggunakan katalis RIP–TiO_2 pada proses fotokatalis, sehingga penelitian lanjutan diperlukan untuk mengevaluasi faktor lain seperti intensitas sinar UV, waktu kontak, serta karakteristik fisik katalis yang berpotensi meningkatkan efisiensi sistem RIP–TiO_2.

***Kata kunci**: fotokatalis; krom heksavalen; reduksi; resin immobilized photocatalyst TiO_2*

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1. Introduction

Water pollution is a persistent concern given the growing human population and the increasing number of industries. Heavy metals are a significant concern in water pollution due to the inherent resistance to natural degradation by living organisms [1]. Among the types of heavy metals is chromium in the form of hexavalent chromium (Cr(VI)). The Environmental Protection Agency (EPA) stated that Cr(VI) is toxic and requires increased attention [2]. According to Tezcan *et al.* [3], metal plating industrial waste can contain approximately 1000 mg/L of Cr(VI). Compounds containing this element are highly soluble in water, which affirms the potential to contaminate both surface and groundwater [4].

In the environment, chromium occurs more safely in the form of Cr(III), typically present as $Cr(OH)_3$, which readily precipitates [5]. The reduction of Cr(VI) to Cr(III) is achieved through various processes, such as chemical precipitation [6], adsorption [7], electrocoagulation [8], and ion exchange [9]. However, the processes are expensive and produce residual chemicals [10]. Currently, the most widely studied are Advanced Oxidation Processes (AOPs), such as photocatalysis. These reactions occur in semiconductors upon exposure to light, typically UV, and result in the production of residual chemicals and other byproducts, including sludge and rejected water [11].

Photocatalysis using semiconductors can produce electron (e^-) and hole (h^+) pairs. In this context, the resulting electrons play a role in the reduction of Cr(VI) in waste [12]. Various semiconductors have been tested and adopted in photocatalysis. However, a commonly applied type is TiO_2, which has excellent pollutant reduction rates [11]. According to Song *et al.* [12], a challenge experienced when using pure TiO_2 semiconductors in a suspended form is operational constraints. Several studies, such as Hidayah *et al.* [13], have developed innovations to overcome the obstacles, including immobilizing the compound on resin. This facilitates the separation of TiO_2 semiconductors in the final process. The innovation is largely focused on the removal of organic pollutants. Reports on heavy metal pollutants, particularly Cr(VI), remain limited. Therefore, this study examines the potential of resin-immobilized TiO_2 as a photocatalytic semiconductor in Cr(VI) reduction.

pH of wastewater is a consideration during the study. This is because the ability to alter the form of Cr(VI) in the sample, thereby enabling different levels of reduction during photocatalysis. pH can also affect the semiconductor used, specifically its isoelectric point, which influences the TiO_2's state in photocatalysis [14].

This study aimed to determine the effect of a resin-immobilized TiO_2 semiconductor catalyst in the reduction of Cr(VI). Furthermore, the optimal pH conditions and catalyst mass for the reduction of Cr(VI) to Cr(III) were analyzed.

2. Research Methods

2.1 Tools and Materials

The equipment used comprises a continuous-flow column-bed reactor equipped with a 15-watt UV-C lamp and a UV-Vis spectrophotometer (UBI-600) for Cr(VI) analysis. The materials used in this study were potassium dichromate

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($K_2Cr_2O_7$) (p.a. ≥99% Merck), titanium dioxide (TiO_2) (rutile, c.p. ≥98%), sulfuric acid (for analysis, 95%–97% Merck), sodium hydroxide (for analysis, ≥99% Merck), and distilled water.

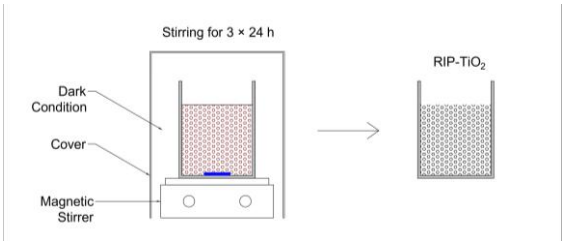


Figure 1. TiO_2 catalyst immobilization process on resin

2.1 TiO_2 Immobilization on Resin

The immobilization process was conducted by stirring the Dowex cation resin in a TiO_2 solution dissolved in distilled water. This includes the use of a magnetic stirrer in the dark (closed) for 3 × 24 hours [13]. After stirring, the resin was filtered and dried in an oven at 100°C for 10 minutes. The TiO_2 immobilization process on resin is shown in Figure 1.

2.2 Artificial Waste Preparation

Artificial waste containing Cr(VI) was prepared by dissolving Pro Analysis (PA) grade potassium dichromate ($K_2Cr_2O_7$) in distilled water. Potassium dichromate requirement was calculated based on equation 1. The target Cr(VI) concentration in this study was 85 mg/L, and the required artificial waste volume was 40 liters. Based on these data, the amount of compound required for the production was 9.61 g.

$$Mass_{K_2Cr_2O_7} = C_{Cr^{6+}} \times V_{solution} \times \frac{Mr(K_2Cr_2O_7)}{n \times Mr(Cr)} \quad \textbf{.(1)}$$

2.3 pH Conditioning

Artificial waste was prepared at two pH levels, namely 5 and 7. A pH of 5 represented the initial condition after potassium dichromate dissolution. Adjustment was performed using 0.1 N sulfuric acid (H_2SO_4) when the solution was over basic or 0.1 N sodium hydroxide (NaOH) when it was over acidic. The selected reagent was added gradually until the pH reached 7.

2.4 Photocatalysis

Photocatalysis was conducted in a column bed filled with Resin Immobilized Photocatalyst TiO_2 (RIP-TiO_2). The reactor consisted of two continuous-flow column beds, each containing 30 g and 40 g of catalyst, respectively. Samples were collected at 0 (initial waste sample), 5, 15, 45, and 60 minutes. Finally, a test was performed for Cr(VI) content using UV-Vis spectrophotometry in accordance with SNI 6989.71:2009.

3. Results and Discussion

3.1 Cr(VI) Reduction Using RIP-TiO_2

Artificial wastewater, prepared by dissolving potassium dichromate in distilled water, was characterized by a bright orange solution with a pH of 5 and an initial turbidity of 4.03 NTU. Since the initial pH was 5, in subsequent variations, NaOH was added gradually, increasing it to 7. Data obtained from photocatalysis using RIP-TiO_2 catalyst are presented in Table 1.

The data in Table 1 represent Cr(VI) measurements using a UV-Vis Spectrophotometer. A normality test was performed to assess whether the reduction data followed a normal distribution using Minitab 19. Figure 2 shows a P-value of

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0.067, which exceeds the 5% rejection region (α), suggesting a normal distribution. Based on the results, a parametric two-way Analysis of Variance (ANOVA) was used to test the mean differences among variables.

Figure 3 shows Cr(VI) removal concentration for all variations used, namely pH 5 and 7, as well as catalyst masses of 30 and 40 g. The highest removal percentage occurred at pH 5 and 40 g. However, the percentage removal across all variations used was not significantly different. Further analysis of the effect of each variation is needed.

3.2 Effect of Catalyst Mass and Waste pH on Cr(VI) Reduction

This study adopted two variables in the Cr(VI) reduction process, namely pH and catalyst mass. Each variable influenced the reduction process, but their interaction is also crucial for optimal performance. Therefore, a two-way ANOVA was conducted to evaluate the simultaneous effects of initial waste pH and catalyst mass, as well as the interaction on Cr(VI) concentration.

The results in Table 2 showed that the initial pH change of wastewater, the amount of catalyst mass, or the interaction between the two factors did not significantly affect Cr(VI) concentration. This is signified by the P-value for each factor exceeding the significance level (α = 5%). As a result, using 30 or 40 g of catalyst at initial pH 5 or 7 did not produce a statistically significant difference in Cr(VI) concentration.

Table 1. Cr(VI) reduction results using Resin Immobilized Photocatalyst TiO_2 (RIP-TiO_2)

Sampling Time (minutes)	pH	Cr(VI) Concentration (mg/L)		Cr(VI) Reduction (%)	
		30 g	40 g	30 g	40 g
0	5	85.94	85.94	0.00	0.00
5		76.30	73.48	11.22	14.49
15		75.41	70.39	12.25	18.09
45		69.14	69.51	19.54	19.12
60		69.10	67.62	19.59	21.32
0	7	85.94	85.94	0.00	0.00
5		84.05	77.62	2.20	9.68
15		79.07	76.38	7.99	11.13
45		74.37	69.87	13.46	18.70
60		70.35	67.94	18.14	20.94

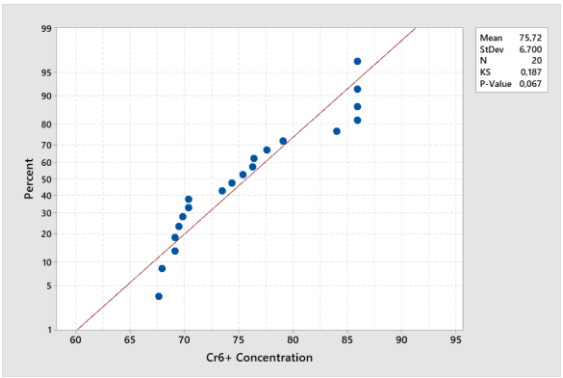


Figure 2. Normality test for Cr(VI) reduction results using Resin Immobilized Photocatalyst TiO_2 (RIP-TiO_2)

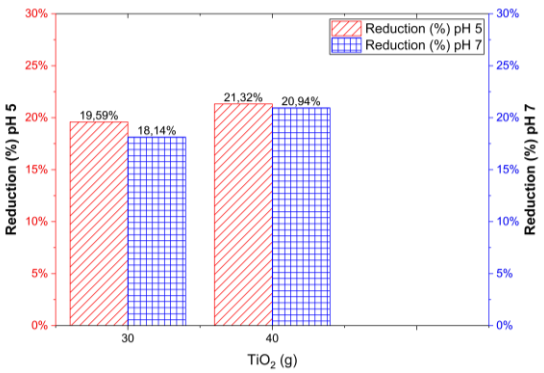


Figure 3. Percentage of Cr(VI) reduction with Resin Immobilized Photocatalyst TiO_2 (RIP-TiO_2)

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Further analysis using the Tukey post hoc test was presented in Table 3. All comparisons between variations were in the same group, confirming the absence of significant differences between treatment combinations. However, the test results showed that some combinations were more effective at reducing Cr(VI) concentration. Based on the average values recorded, the 40-g catalyst mass combination at initial pH 5 had the lowest Cr(VI) concentration compared to the other variations. This suggested that the conditions provided relatively better reduction performance, although the difference was not statistically significant.

According to Table 3, the 40 g catalyst mass variation performed better than the 30 g, as shown in Figure 4. Cr(VI) concentration decreased more significantly with the 40 g catalyst mass variation at both pH 5 and 7. This suggested that catalyst surface area increased with higher mass, enhancing the interaction between TiO_2 catalyst and Cr(VI) as well as accelerating the reduction process [15], [16].

Table 2. Two-Way ANOVA results of catalyst mass and initial pH of waste on Cr(VI) concentration

Source	Two-Way ANOVA				
	Degrees of Freedom	Sum of Squares	Mean Square	F-Count	P-Value
Catalyst Mass	1	31.225	31.225	0.64	0.435
Initial pH of Waste	1	41.145	41.145	0.85	0.371
Catalyst Mass*Initial pH of Waste	1	2.500	2.500	0.05	0.823
Error	16	777.999	48.625		
Total	19	852.869			

Table 3. Grouping results of average Cr(VI) concentrations based on catalyst mass and initial pH using the Tukey test

Catalyst Mass	Initial pH of Waste	Tukey Pairwise Comparisons		
		N	Average Concentration	Group
30	7	5	78.7545	A
40	7	5	75.5484	A
30	5	5	75.1788	A
40	5	5	73.3869	A

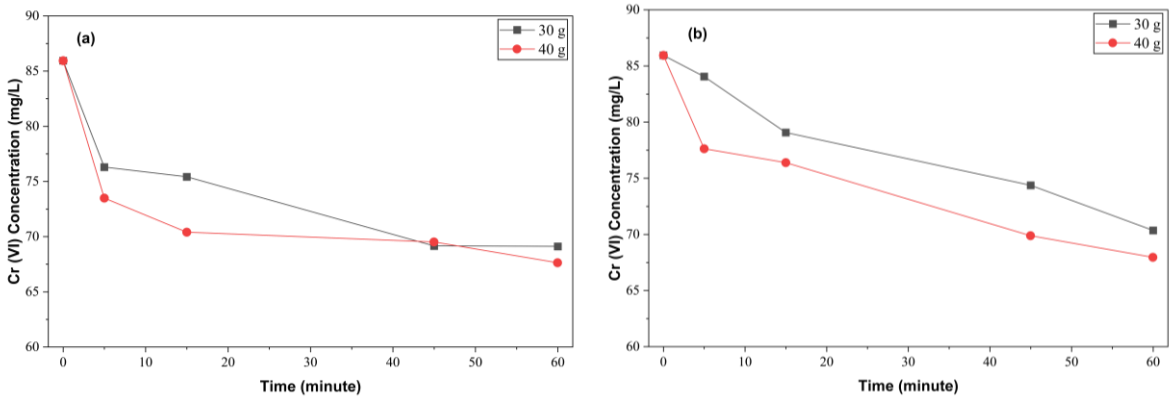


Figure 4. Effect of Resin Immobilized Photocatalyst TiO_2 (RIP-TiO_2) catalyst mass on Cr(VI) reduction at pH conditions: a) pH 5 and b) pH 7

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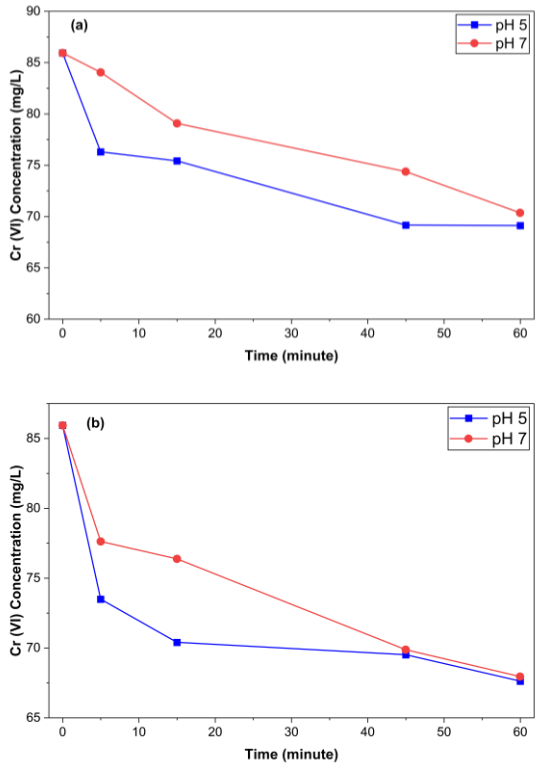


Figure 5. Effect of pH on Cr(VI) reduction with catalyst mass: a) 30 g and b) 40 g

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$

(at acidic) ..... **(2)**

$$CrO_4^{2-} + 8H^+ + 3e^- \rightarrow Cr^{3+} + 4H_2O$$

(at neutral) ..... **(3)**

Figure 5 showed that wastewater at pH 5 experienced a better reduction in Cr(VI) concentration compared to pH 7. However, the statistical difference between the two conditions was not significant. Acidic conditions (pH 5) had a higher reduction rate than neutral (pH 7) or basic conditions [17]. This is consistent with several studies on $NiCo_2S_4$/BiOBr-30 composite catalysts [18] and TiO_2 catalysts [19], where Cr(VI) reduction was more effective at acidic pH.

Reaction equations 2 and 3 showed the differences in Cr(VI) reduction reactions using photocatalytic processes at different pH conditions. Based on these equations, the reduction requires electrons generated by photocatalysis. A pH of 7 (neutral) was achieved by adding 0.1 N NaOH, thereby introducing Na^+ cations into the waste. According to Qin *et al* [18], the presence of cations in the sample can reduce the reduction rate. This occurs due to the potential competition between Cr(VI) cations for electrons [20].

4. Conclusion

In conclusion, a two-way ANOVA showed that variations in pH and catalyst mass did not produce a significant difference in Cr(VI) reduction efficiency. Based on the trend in the data, the performance was better at pH 5 and a mass of 40 g, with a removal rate of 21.32%. The results showed that adjusting these factors did not significantly affect the reduction of Cr(VI) to Cr(III) using RIP-TiO_2 catalyst in photocatalysis. Therefore, further studies are needed to evaluate other factors, such as UV light intensity, contact time, and catalyst physical characteristics that may increase the efficiency of the RIP-TiO_2 system.

References

[1] Yusron, M., & Asroul Jaza, M. (2021). Analisis Jenis dan Kelimpahan Mikroplastik serta Pencemaran Logam Berat pada Hulu Sungai Bengawan Solo. *Environmental Pollution Journal*, 1(1), 41–48. doi: 10.58954/epj.v1i1.6

[2] Gibbons, C. F., Sasso, A. F., Angrish, M. M., Arzuaga, X., Bateson, T. F., Christensen, K. Y., … Kaupas, G. (2024). *IRIS Toxicological Review of Hexavalent Chromium [Cr(VI)] CASRN 18540-29-9*. Washington (DC): U.S. Environmental Protection Agency.

[3] Tezcan, U., Eroglu, S., & Ozel, E. (2017). The treatment of chromium-containing wastewater using electrocoagulation and the production of ceramic pigments from the resulting sludge. *Journal of Environmental Management*, 200, 196–203. doi: 10.1016/j.jenvman.2017.05.075

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[4] Kangralkar, M. V., Manjanna, J., Momin, N., Rane, K. S., Nayaka, G. P., & Kangralkar, V. A. (2021). Photocatalytic Degradation Of Hexavalent Chromium And Different Staining Dyes By Zno In Aqueous Medium Under UV Light. *Environmental Nanotechnology, Monitoring & Management*, 16(April), 100508. doi: 10.1016/j.enmm.2021.100508

[5] Wang, N., Zhang, F., Mei, Q., Wu, R., & Wang, W. (2020). Photocatalytic TiO2/rGO/CuO Composite for Wastewater Treatment of Cr(VI) Under Visible Light. *Water, Air, and Soil Pollution*, 231(5). doi: 10.1007/s11270-020-04609-8

[6] Minas, F., Singh, B., & Leta, S. (2017). Chemical precipitation method for chromium removal and its recovery from tannery wastewater in Ethiopia, 3(4), 291–305.

[7] Assefa, H., Singh, S., Olu, F. E., Dhanjal, D. S., Mani, D., Khan, N. A., … Ramamurthy, P. C. (2024). Advances in adsorption technologies for hexavalent chromium removal_ Mechanisms, materials, and optimization strategies. *Desalination and Water Treatment*, 319(June), 100576. doi: 10.1016/j.dwt.2024.100576

[8] Kabdaşlı, I., & Tünay, O. (2023). Hexavalent Chromium Removal from Water and Wastewaters by Electrochemical Processes: Review. *Molecules*. doi: 10.3390/molecules28052411

[9] Wang, H., Song, X., Zhang, H., Tan, P., & Kong, F. (2020). Removal of hexavalent chromium in dual-chamber microbial fuel cells separated by different ion exchange membranes. *Journal of hazardous materials*, 384, 121459.

[10] Gao, X., & Meng, X. (2021). Photocatalysis For Heavy Metal Treatment: A Review. *Processes*, 9(10). doi: 10.3390/pr9101729

[11] Navidpour, A. H., Abbasi, S., Li, D., Mojiri, A., & Zhou, J. L. (2023). Investigation of Advanced Oxidation Process in the Presence of TiO2 Semiconductor as Photocatalyst: Property, Principle, Kinetic Analysis, and Photocatalytic Activity. *Catalysts*, 13(2). doi: 10.3390/catal13020232

[12] Song, Y., Lu, X., Liu, Z., Liu, W., Gai, L., Gao, X., & Ma, H. (2022). Efficient Removal of Cr(VI) by TiO2-Based Micro-Nano Reactor via the Synergy of Adsorption and Photocatalysis. *Nanomaterials*, 12(2), 1–15. doi: 10.3390/nano12020291

[13] Hidayah, E. N., Pachwarya, R. B., & Cahyonugroho, O. H. (2022). Immobilization Of Resin Photocatalyst In Removal Of Soluble Effluent Organic Matter and Potential For Disinfection By-Products. *Global Journal of Environmental Science and Management*, 8(3), 437–448. doi: 10.22034/gjesm.2022.03.10

[14] Al-Nuaim, M. A., Alwasiti, A. A., & Shnain, Z. Y. (2023). The Photocatalytic Process In The Treatment of Polluted Water. *Chemical Papers*. Versita. doi: 10.1007/s11696-022-02468-7

[15] Sato, M., Furukawa, M., Tateishi, I., Katsumata, H., & Kaneco, S. (2025). Development of Photocatalytic Reduction Method of Cr (VI) with Modified g-C3N4. *Chemistry Proceedings*, 17(1), 3. doi: 10.3390/chemproc2025017003

[16] Lu, W., Wang, C., Bai, Y., Xie, C., Zhang, Z., Song, W., & Wang, J. (2024). A novel covalent organic framework for efficient photocatalytic reduction of Cr(VI) and synergistic removal of organic pollutants under visible light irradiation. *Environmental Science: Nano*, 11(1), 229–240. doi: 10.1039/D3EN00734K

[17] Djellabi, R., Su, P., Elimian, E. A., Poliukhova, V., Nouacer, S., Abdelhafeez, I. A., … Contreras, S. (2022). Advances In Photocatalytic Reduction Of Hexavalent Chromium: From Fundamental Concepts to Materials Design and Technology Challenges. *Journal of Water Process Engineering*, 50(August 2022). doi: 10.1016/j.jwpe.2022.103301

[18] Qin, S., Xu, R., Jin, Q., Wang, S., Ren, Y., Huang, Y., … He, Z. (2024). Efficient Photocatalytic Reduction of Hexavalent Chromium by NiCo2S4/BiOBr Heterogeneous Photocatalysts. *Coatings*, 14(12). doi: 10.3390/coatings14121492

[19] Zhao, B., Zhang, K., Huang, Y., Wang, Q., Xu, H., Wang, Y., … Liu, J. (2021). A novel visible light-driven TiO2 photocatalytic reduction for hexavalent chromium wastewater and mechanism. *Water Science and Technology*, 83(9), 2135–2145. doi: 10.2166/wst.2021.116

[20] Jie, X., Shiu, B.-C., Wu, H., Zhang, Y., Ye, Y., Lin, C., & Fang, R. (2023). Adsorption and Recovery of Cr(VI) From Wastewater by Chitosan–Urushiol Composite Nanofiber Membrane. *e-Polymers*, 23(1). doi: doi:10.1515/epoly-2023-0157

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