Journal of the Serbian Chemical Society
JSCS-info@shd.org.rs • www.shd.org.rs/JSCS

ACCEPTED MANUSCRIPT

Journal of the Serbian Chemical Society
JSCS-info@shd.org.rs • www.shd.org.rs/JSCS
J. Serb. Chem. Soc. **00(0)** 1-9 (2024)
JSCS–12719
Original scientific paper
Published DD MM, 2024

Efficiency of physical-chemical treatment of wastewater of the paper and cardboard factory

LARYSA SABLII[1], OLEKSANDR OBODOVYCH[2], VITALII SYDORENKO[2]*

[1]*Department of Bioenergy, Bioinformatics and Environmental biotechnology, National Technical University of Ukraine "Igor Sikorsky Kyiv Polytechnic Institute", Prospect Beresteiskyi 37, 03056, Kyiv, Ukraine, and* [2]*Department of Heat and Mass Transfer in Disperse Systems, Institute of Engineering Thermophysics of NAS of Ukraine, Akademika Bulakhovskoho 2, 03164 Kyiv, Ukraine*

(Received 6 December 2023; revised 25 January 2024; accepted 19 February 2024)

Abstract: The purpose of the work is to study the wastewater treatment of a cardboard and paper factory in the Khmelnytskyi region using physico-chemical methods, namely, coagulation and oxidation, to increase the efficiency of removing organic pollutants according to COD and BOD indicators. The use of coagulation and chlorination methods before biological treatment in aeration tanks was proposed. Alumofloc 18 % was used as a coagulant, PAA was used as a flocculant, and sodium hydroxide was used as an alkalizing reagent. The study was conducted on a mixture of industrial and sewage wastewater with COD and BOD5 - 3200 and 1575 mg/L, respectively, and on industrial wastewater with COD and BOD5 - 4480 and 1960 mg/L, respectively. The effects of reducing COD and BOD5 indicators in the first case after coagulation were 30 and 40 %, after chlorination - 37.82 and 43.18 %, respectively, and in the second after coagulation - 28.58 and 47.25 %, respectively. The effects of wastewater treatment of a cardboard and paper factory using coagulation and oxidation methods will allow for a reduction in the concentration of organic substances according to COD and BOD indicators before the biological treatment of wastewater in aeration tanks and will ensure an increase in the efficiency of biological treatment.

Keywords: liquid waste, organic pollutants, coagulation, Alumofloc, chlorination.

INTRODUCTION

Wastewater from cardboard and paper factories make significant contributions to environment pollution and water body. Such waters are a stable colloid system. Organic substances presented in wastewater cause complex changes in water bodies.[1] They disrupt the established abiotic factors and are

*Corresponding author. E-mail: V.V.Sydorenko@nas.gov.ua
https://doi.org/10.2298/JSC231206014S

involved in chemical and biochemical processes. As a result, non-negotiable changes occur in the composition of biocenoses and the quality of water of the river decreases significantly. Wastewater contains cellulose fibers, paper, fillers, dyes, latexes, emulsions, adhesives, etc. They have a high content of suspended solids and organic substances, a specific smell. Sources of organic substances are products of cellulose destruction, formed during bleaching and processing. These are substances such as aliphatic (alcohols, amines, acids, aldehydes, etc.) and terpene hydrocarbons, aromatic hydrocarbons of the phenolic series, low molecular weight alcohols, fatty acids, etc.[2] Due to the significant content of organic substances, wastewater is characterized by high COD values ranging from 800 to 2000 mg/L and BOD5 values are within 500-800 mg/L. The BOD5/COD ratio has average values, which indicate the possibility of applying a biological method of wastewater treatment. BOD5/COD has a value in the range from 0.2 to 0.7. Suspended solids range from 900 to 3000 mg/L. Therefore, factory wastewater requires mechanical pretreatment, as a result of which coarse and suspended solids and some colloidal particles are removed.[3] The presence of low concentrations of phosphorus and nitrogen compounds in wastewater indicates that they should be added to water for biological processes.

Today, the most widespread methods of wastewater treatment in cardboard and paper factories are physico-chemical, namely reagent treatment, coagulation, flocculation, chemical, electrochemical oxidation,[4] and biological. The use of reagent methods requires the purchase of chemical reagents, namely, coagulants based on iron, aluminum, expensive flocculants or strong oxidizers as ozone,[5,6] hydrogen peroxide (Fenton method),[4] and does not ensure high purification efficiency in conditions of multicomponent pollution. Adsorption methods[7] can be used for wastewater treatment but require sophisticated equipment.

The most accessible and effective both from the point of view of high efficiency of the treatment, low costs for construction and operation, and the impact on the environment and natural water bodies is the biological method,[8-11] namely, the aerobic[12,13] and anaerobic[14-20] methods.

At a cardboard and paper factory in the Khmelnytskyi region, wastewater is treated at a wastewater treatment plant, which includes grit traps, primary radial sedimentation tanks, aeration tanks with activated sludge regenerators, secondary radial sedimentation tanks, and biponds (Fig.1).

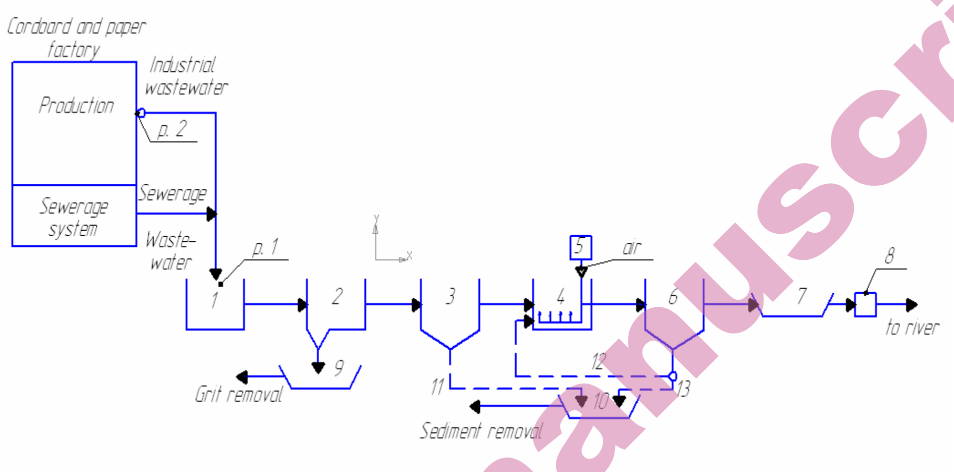

Fig. 1. Block diagram of waste water removal and treatment of cardboard and paper factory: 1 - inlet chamber; 2 - grit traps; 3 - primary sedimentation tanks; 4 - aeration tanks; 5 - air blower; 6 - secondary sedimentation tanks; 7 - biopounds; 8 - disinfection; 9 - grit beds; 10 - sludge beds; 11 - sediment; 12 - recirculated activated sludge; 13 - surplus activated sludge. p.1 - sampling site of the mixture of industrial and sewerage wastewater from the inlet chamber; p.2 - sampling site of industrial wastewater in the well at the outlet of industrial wastewater from the workshop

The productivity of the treatment plant is 7,000 m^3 per day. Aeration tanks are designed for 14 hours of aeration and 12 hours of regeneration. The main drawback of the treatment plant is the insufficient efficiency of wastewater treatment from organic pollutants according to COD and BOD indicators, which necessitated research to find and use methods of pretreatment of factory wastewater using physical and chemical treatment.

The purpose of the work is to study the wastewater treatment of a cardboard and paper factory using physico-chemical methods, namely, coagulation and oxidation, for increasing the efficiency of removing organic pollutants according to COD and BOD indicators.

EXPERIMENTAL

A series of samples of the following wastewater were selected for analysis:

- a mixture of industrial and sewage wastewater from the inlet chamber of the wastewater treatment plant of the cardboard and paper factory (Table I);
- wastewater directly from production (Table II).

Samples were taken at points p.1 and p.2, shown in the block diagram shown in Fig. 1. Coagulation and chlorination of samples were carried out in laboratory conditions. Samples were taken at the indicated points three times: at 9 a.m., 2 p.m., and 7 p.m.

The analysis results of the samples taken at sampling site p.1 and p 2 were averaged according to the indicators. The average values are shown in the Tables 1 and 2.

In the first case (Table I), the following indicators were determined: pH, suspended solids, COD, BOD5 of untreated wastewater, water after coagulation, as well as chlorinated coagulated water.

In the second case (Table II), the same indicators were determined for the untreated and water after coagulation.

Reagents with the following doses were used for the study:

- for coagulation:
- Alumofloc 18 % – 0.6 mL/L;
- sodium hydroxide – 55 mg/L;
- PAA flocculant – 2 mg/L.

The volume of sediment after coagulation and settling for 2 hours was 20 %.

- for chlorination:
- active chlorine – 42 mg/L.

The duration of settling after coagulation and chlorination was 2 hours.

Coagulation was successful in both cases. In the water obtained after settling, in the first case suspended solids decreased from 127 to 15 mg/L, and in the second - from 162 to 20 mg/L.

The results of the conducted analyses according to average values are summarized in Tables I and II.

The dissolved oxygen concentration in both cases was close to zero (0-0.1 mg/L), so the oxidation of water impurities with the participation of dissolved oxygen was not considered.

The error of the results of experimental measurements was no more than 5%.

To increase the efficiency of removing pollutants from waste water of a cardboard and paper factory during primary sedimentation, it is possible to apply pre-reagent treatment of waste water with the help of a coagulant, for example Alumofloc. This reagent forms colloidal particles of aluminum hydroxide in water, capable of coagulation and forming flakes. Suspended particles (cellulose fibers, paper particles, fillers, etc.) colloidal and dissolved organic substances (hydrocarbons, fatty acids, etc.) contained in wastewater are adsorbed on the surface of the flakes, thus forming aggregates that settle in sedimentation tanks. As a result of coagulation, the concentration of suspended substances in wastewater and the concentration of organic substances according to COD and BOD5 indicators are reduced to a greater extent than with simple settling.

In order to increase the efficiency of removal of organic substances from wastewater, the chlorination was used for pretreatment. The action of active chlorine consists in the chemical oxidation of organic substances, which are contained in large quantities in waste water of the cardboard and paper factory, namely aliphatic (alcohols, amines, acids, aldehydes, ketones, etc.) and terpene hydrocarbons, aromatic hydrocarbons of the phenolic series, low molecular weight alcohols , fatty acids, etc.

These substances are determined by COD and BOD5 indicators. Moreover, most of these substances are difficult to oxidize biologically (during wastewater treatment in aeration tanks), so pretreatment is needed.

The purpose of oxidation is to decompose hard-to-oxidize substances into biodegradable substances for microorganisms in the biological treatment. When oxidized with chlorine, simpler compounds are formed. For example, acids or ketones are formed when alcohols are oxidized, and acids are formed when aldehydes are oxidized. The formed reaction products are biologically degradable with the participation of active sludge of aeration tanks, which increases the efficiency of biological wastewater treatment. For example, when ketones are oxidized with chlorine, mixtures of organic acids are formed, which are easily decomposed by activated sludge microorganisms.

When ketones are oxidized, C-C bonds between the carbon atoms of the carbonyl group and the carbon radical are broken with the formation, for example, of a mixture of formic, acetic, propionic, or other biodegradable acids.

RESULTS AND DISCUSSION

Rows 5 to 10 of Tables I and II show the results of some calculations that characterize the efficiency of wastewater treatment using the applied coagulation and chlorination methods.

Studies of the wastewater treatment in the factory using the coagulation method showed the following.

In a case of an industrial and sewage wastewater mixture (Table I) in the mixture of wastewater from the inlet chamber of the wastewater treatment plant, after coagulation, BOD5 decreases by 40 %, and COD by 30 %. The BOD5/COD ratio for the next biological treatment in the aeration tanks of the wastewater treatment plant should be greater than 0.5. In this case, as the results showed, coagulation worsened the ratio from 0.49 to 0.42.

The difference between COD and BOD5 ("pure" COD) is:

$$3200 – 1575 = 1625 \text{ mgO}_2\text{/L};$$
$$2240 – 945 = 1295 \text{ mgO}_2\text{/L}.$$

The difference of "pure" COD of wastewater from the inlet chamber of the wastewater treatment plant before and after coagulation is: 1625 - 1295 = 330 $\text{mgO}_2\text{/L}$.

The "pure" COD of wastewater (without taking into account its BOD5) after coagulation decreased by only 330 $\text{mgO}_2\text{/L}$ or 20.3 %.

As a result of chlorination, the following indicators were obtained.

After coagulation and chlorination, BOD5 decreases by 43.18 %, and COD - by 37.82 %, in wastewater from the inlet chamber of the wastewater treatment plant.

Chlorination (separately, after coagulation) decreased BOD5 by 3.18 %, and COD by 7.82 %.

Chlorination, in comparison with coagulation, additionally reduced BOD5 by 5.3 %, and COD by 11.17 %.

The BOD5/COD ratio in the case of using coagulation and chlorination decreased from 0.49 to 0.45.

"Pure" COD (minus BOD5) will be:

$$3200 – 1575 = 1625 \text{ mgO}_2\text{/L};$$
$$2240 – 945 = 1295 \text{ mgO}_2\text{/L};$$
$$1990 – 895 = 1095 \text{ mgO}_2\text{/L}.$$

The difference of "pure" COD of wastewater from the inlet chamber of the wastewater treatment plant before and after coagulation and chlorination will be:

$$1625 – 1095 = 530 \text{ mgO}_2\text{/L.}$$

TABLE I. Change in indicators of the mixture of industrial and sewage wastewater of the cardboard and paper factory after coagulation and chlorination

Ser. no	Indicator	Units	Value		
			initial	after coagulation	after coagulation and chloration
1	pH	-	6.3	7.1	7.25
2	Suspended solids	mg/L	127	15	15
3	COD	mgO$_2$/L	3200	2240	1990
4	BOD$_5$	mgO$_2$/L	1575	945	895
5	COD/BOD$_5$ ratio	-	2.03	2.37	2.22
6	BOD$_5$/COD ratio	-	0.49	0.42	0.45
7	COD – BOD$_5$ («pure» COD)	mgO$_2$/L	1625	1295	1095
8	decrease of the BOD$_5$	mgO$_2$/L		630 (40 %)	50 (43.18 %)
				680 (43.17 %)*	
9	decrease of the COD	mgO$_2$/L		960 (30 %)	250 (37.82 %)
				1210 (37.81 %)*	
10	decrease of the «pure» COD	mgO$_2$/L		330 (20.3 %)	200 (12.4 %)
				530 (32.62 %)*	

* estimated differences in the values of the indicators of the untreated wastewater and water after coagulation and chlorination.

After coagulation and chlorination, the "pure" COD of wastewater (excluding its BOD5) decreased by only 530 mgO$_2$/ L or 32.62 %.

The difference between "pure" COD of wastewater from the inlet chamber of the wastewater treatment plant before and after coagulation will be:

$$1625 – 1295 = 330 \text{ mgO}_2\text{/L.}$$

The "pure" COD of wastewater (without taking into account its BOD5) after coagulation decreased by only 330 mgO$_2$/L or by 20.3 %.

The difference between the "pure" COD of wastewater from the inlet chamber of the wastewater treatment plant between coagulated and chlorinated wastewater will be:

$$1295 – 1095 = 200 \text{ mgO}_2\text{/L.}$$

The "pure" COD of wastewater (excluding its BOD5) between coagulated and chlorinated wastewater decreased by only 200 mgO$_2$/L or 12.4 %.

TABLE II. Change in indicators of industrial wastewater cardboard and paper factory after coagulation

Ser. no	Indicator	Units	Value	
			initial	after coagulation
1	pH	-	6.5	7.2
2	Suspended solids	mg/L	162	20
3	COD	mgO_2/L	4480	3200
4	BOD_5	mgO_2/L	1960	1034
5	COD/BOD_5 ratio	-	2.28	3.09
6	BOD_5/COD ratio	-	0.43	0.32
7	BOD – COD_5 («pure» COD)	mgO_2/L	2520	2166
8	decrease of the BOD_5	mgO_2/L	926 (47.25 %)	
9	decrease of the COD	mgO_2/L	1280 (28.58 %)	
10	decrease of the «pure» COD	mgO_2/L	354 (14.05 %)	

In the case of production wastewater from a cardboard and paper factory (Table 2), the BOD5 indicator after coagulation decreases by 47.25 % and the COD by 28.58 %. In this case, coagulation decreases the BOD5/COD ratio from 0.43 to 0.32.

"Pure" COD (minus BOD5) will be:

$$4480 – 1960 = 2520 \text{ mgO}_2\text{/L};$$

$$3200 – 1034 = 2166 \text{ mgO}_2\text{/L}.$$

The difference of "pure" COD of industrial wastewater before and after coagulation will be:

$$2520 – 2166 = 354 \text{ mgO}_2\text{/L}.$$

The "pure" COD (excluding BOD5) decreased by only 354 mgO_2/L or 14.05 % after coagulation.

As can be seen from Tables I and II (rows 7, and 8), the coagulation and settling allow a reduction of BOD5 in the first and second cases by 40 (Table I) and 47.25 % (Table II), and COD by 30 % (Table I) and 28.58 % (Table II), respectively. These indicators indirectly indicate how many percentages of organic pollutants (according to BOD5) and the total amount of organic matter (according to COD) are in wastewater in suspended and colloidal states. At the same time, it is worth noting that coagulation reduces BOD5 more effectively than COD, which indicates that most of the hard-to-oxidize compounds are dissolved.

CONCLUSION

As a result of studies of the coagulation process for the treatment of wastewater from a cardboard and paper factory, a decrease in the indicators of suspended solids, COD, and BOD was obtained.

The BOD5/COD ratio was less than 0.5, and this must be taken into account when adjusting the composition of wastewater (by changing the ratio of easily and hard-oxidizing substances due to the detection and reduction of chemical components coming from production).

It was determined that 60-70 % of organic substances according to the COD indicator in a dissolved state.

During the coagulation of wastewater, the efficiency of purification according to the BOD5 indicator was determined to be 40-47 %.

It has been determined that as a result of chlorination, the maximum reduction of "pure" COD is achieved; therefore, the possibility and expediency of chlorination of water after the secondary settling tank in increased doses should be considered in the wastewater treatment technology of the cardboard and paper factory.

It should be noted that the use of reagents in the doses adopted in the study is unlikely to be economically justified, but it will be advisable to arrange an oxidizer-biocoagulator in front of the primary settling tank, in which activated sludge is used instead of reagents.

И З В О Д

ЕФИКАСНОСТ ФИЗЧКО-ХЕМИЈСКИХ МЕТОДА У ПРЕЧИШЋАВАЊУ ОТПАДНИХ ВОДА ФАБРИКЕ КАРТОНА И ПАПИРА

LARYSA SABLII[1], OLEKSANDR OBODOVYCH[2], VITALII SYDORENKO[2*]

[1]*Department of Bioenergy, Bioinformatics and Environmental biotechnology, National Technical University of Ukraine "Igor Sikorsky Kyiv Polytechnic Institute", Prospect Beresteiskyi 37, 03056, Kyiv, Ukraine, and* [2]*Department of Heat and Mass Transfer in Disperse Systems, Institute of Engineering Thermophysics of NAS of Ukraine, Akademika Bulakhovskoho 2, 03164 Kyiv, Ukraine*

Сврха рада је проучавање пречишћавања отпадних вода фабрике картона и папира у Khmelnytskyi региону коришћењем физичко-хемијских метода, односно коагулације и оксидације, како би се повећала ефикасност уклањања органских загађивача према ХПК и БПК индикаторима. Предложена је употреба метода коагулације и хлорисања пре биолошког третмана у аерационим резервоарима. Алумофлок 18 % је коришћен као коагулант, ПАА је коришћен као флокулант, а натријум хидроксид је коришћен као алкализирајући реагенс. Студија је спроведена на мешавини индустријских и канализационих отпадних вода са ХПК и БПК5 - 3200 и 1575 mg/L, респективно, и на индустријским отпадним водама са ХПК и БПК5 - 4480 и 1960 mg/L, респективно. Ефекти смањења ХПК и БПК5 индикатора у првом случају након коагулације били су 30 и 40 %, након хлорисања - 37,82 и 43,18 %, респективно, а у другом случају након коагулације - 28,58 и 47,25 %, респективно. Ефекти пречишћавања отпадних вода из фабрике картона и папира методама коагулације и оксидације омогућиће смањење концентрације органских материја према ХПК и БПК индикаторима пре биолошког третмана у аерационим резервоарима и обезбедиће повећање ефикасности. биолошког третмана.

(Примљено 6. децембра 2023; ревидирано 25. јануара 2024; прихваћено 19. фебруара 2024.)

REFERENCES

1. *The "Global Paper Packaging Market: Growth, Trends, Competitive Landscape, and Forecasts" report* , GLOBE NEWSWIRE, Dublin, Ireland, 2020.
2. M. A. Hubbe, J. R. Metts, D. Hermosilla, M. A. Blanco, L. Yerushalmi, F. Haghighat, P. Lindholm-Lehto, Z. Khodaparast, M. Kamali, A. Elliott, *BioRes*. **11** (2016) 7953 (https://doi.org/10.15376/biores.11.3.Hubbe)
3. O. Ashrafi, L. Yerushalmi, F. Haghighat, *J. Environ. Manage.* **158** (2015) 146 (https://doi.org/10.1016/j.jenvman.2015.05.010)
4. K. Eskelinen, H. Särkkä, N. A. Kurniawan, M. E. T. Sillanpää, *Desalination* **255** (2010) 179 (https://doi.org/10.1016/j.desal.2009.12.024)
5. N. Kishimoto, T. Nakagawa, H. Okada, H. Mizutani, *J. Water Environ. Technol.* **8** (2010) 99 (https://doi.org/10.2965/jwet.2010.99)
6. W. De los Santos Ramosa, T. Poznyaka, I. Chairez, I. Córdova, *J. Hazard. Mater.* **169** (2009) 428 (https://doi.org/10.1016/j.jhazmat.2009.03.152)
7. S. Kakkar, A. Malik, S. Gupta, *J. Appl. Nat. Sci.* **10** (2018) 695 (https://doi.org/10.31018/jans.v10i2.1769)
8. C. Ram, P. Rani, K.A. Gebru, *Phys. Sci. Rev.* **5** (2020) 8 (https://doi.org/10.1515/psr-2019-0050)
9. P. Singh, A. Srivastava, *Int. J. Pharm. Bio. Sci.* **5** (2014) 773 (https://api.semanticscholar.org/CorpusID:98160371)
10. M. Cabrera, A. Zaki , *Pulp Mill Wastewater: Characteristics and Treatment*, in *Biological Wastewater Treatment and Resource Recovery*, F. Robina, A. Zaki, (Eds), InTech, 2017, p. 256 (https://doi.org/10.5772/62795)
11. A. Schnell, P. V. Hodson, P. Steel, H. Melcer, J. H. Carey, *Water Research* **34** (2000) 501 (https://doi.org/10.1016/S0043-1354(99)00161-X)
12. C. W. Bryant, *Water Sci. Technol.* **62** (2010) 1248 (https://doi.org/10.2166/wst.2010.934)
13. C. V. Dubeski, R. M. Branion, K. V. Lo, *J. Environ. Sci. Health*. **36** (2001) 1245 (https://doi.org/10.1081/ese-100104875)
14. M. Tielbaard, T. Wilson, E. Feldbaumer, W. Driessen, *Full-scale anaerobic treatment experiences with pulp mill evaporator condensates*, in *TAPPI International Environmental Conference*, (2002), TAPPI Press, Atlanta, 2002, p. 621-634
15. L. Habets, W. Driessen, *Water Sci. Technol*. **55** (2007) 223 (https://doi.org/10.2166/wst.2007.232)
16. N. B. Golub, M. V. Potapova, Yu. V. Karpenko, *IBB* **3** (2019) 96 (https://doi.org/10.20535/ibb.2019.3.2.166429)
17. N.B. Golub, M.V. Shinkarchuk, O.A. Kozlovets, B. V. Morgun, O. R. Lakhneko, A. I. Stepanenko, M. V. Borisjuk, *Water Air Soil Pollut*. **231** (2020) 445 (https://doi.org/10.1007/s11270-020-04805-6)
18. R. Chhotu, R. Pushpa, G. A. Kibrom, M. G. M. Abrha, ,*Phys. Sci. Rev.* **5** (2020) 20190050 (https://doi.org/10.1515/psr-2019-0050)
19. M. A. Hubbe, J. R. Metts, D. Hermosilla, M. A. Blanco, L. Yerushalmi, F. Haghighat, P. Lindholm – Lehto, Z. Khodaparast, M. Kamali, A. Elliott, *BioRes.* **11** (2016) 7953 (https://doi.org/10.15376/biores.11.3.hubbe)
20. S. R. Hassan, N. Q. Zaman, I. Dahlan, *Prep. Biochem. Biotechnol*. **50** (2019) 234 https://doi.org/10.1080/10826068.2019.1692214).