IOSR Journal of Applied Chemistry (IOSR-JAC)
e-ISSN: 2278-5736.Volume 12, Issue 2 Ser. II (February. 2019), PP 54-61
www.iosrjournals.org

Removal of Methylene Blue Dye from Wastewater using Zeolite Synthesized from Coal Fly Ash

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Abstract: *Zeolite was synthesized from coal fly ash by direct hydrothermal treatment with sodium hydroxide at different concentration ratios at temperature 550 °C and activation time of 4 hrs. Characterization of coal fly ash and synthesized zeolite was done using XRD, SEM and FTIR. It was used as a low cost adsorbent for the removal of Methylene Blue dye from wastewater. Batch studies were carried out to study the effect of pH, adsorbent doses, adsorbate concentration, temperature and contact time. The results of batch studies revealed that the adsorption of Methylene Blue was strongly pH dependent and maximum Methylene Blue removal was observed at equilibrium pH of 8.0. Optimum adsorbent dose and contact time were found to be 5 g/l and 15 minutes respectively. Approx. 97 % of Methylene Blue was adsorbed at 50 mg/l at 30 °C. Kinetic studies have been performed to have an idea of the mechanistic aspects of the process. The results also show that adsorption increases with increase in temperature thereby showing the process endothermic in nature. Adsorption data have also been correlated with both Langmuir and Freundlich isotherm models.*

Keywords: *Methylene Blue, zeolite, adsorption, Langmuir, Freundlich isotherm.*

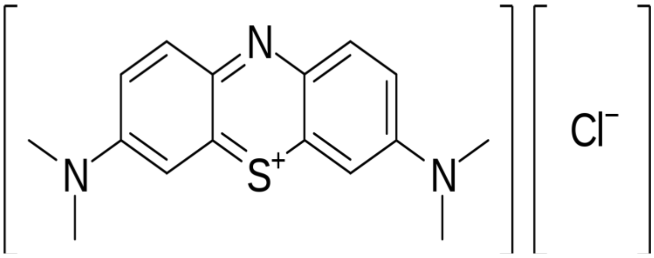
Date of Submission: 01-03-2019 Date of acceptance: 18-03-2019

I. Introduction

The discharge of synthetic dyes into wastewaters from the textile industries has raised much concern because of potential health hazards. Dyes are used in almost every industry from textile to food industries to color their products.Disposal of dyeing industry wastewater poses one of the major problems, because such effluents contain number of contaminants, odour, and colour[1].Removal of many dyes by conventional waste treatment methods is difficult since these are stable to light and oxidizing agents and are resistant to aerobic digestion.There are number of methods of dye removal from textile effluents include chemical oxidation, froth flotation, adsorption, coagulation etc. Out of these adsorption is the best suitable method for the treatment. Due to high cost of activated carbon, the feasibility of cheap, commercially available materials have been investigated. Such materials range from industrial waste products such as waste tyres, baggasse blast furnace slag, fly ash, zeolites and lignin to agricultural products such as wool, rice husk, coconut husk, saw dust, peat moss etc. [2-11]. A number of low-cost adsorbents such as activated carbon prepared from various wastes [12-15], diatomaceous earth [16], industrial waste products [17], bagasse fly ash [18], clay mineral [19], biodegradable waste [20], hydrotalcite [21], coffee grounds [22], dusts [23], kudzu [24], 'waste' metal hydroxide sludge [25], agricultural waste [26], dolomitic sorbents [27], charcoal from extracted residue of coffee beans [28], bentonite and polyaluminum hydroxide [29] have been studied for adsorption of different dyes from solutions.

Many industrial solid wastes, such as fly ash and bottom ash contain silicon in abundance therefore these raw materials have been utilized for the production of mesoporoussilicas[30].However, scanty work has been reported the fly ash-derived mesoporous silica materialsfor the removal of dye from aqueous solution. Zhou and coworkers synthesized spherical Al containing MCM-41 materialsfrom coal fly ash and further evaluated their adsorption performance for methyleneblue [31].Very recently adsorptiveremoval ofmethylene blue fromaqueous solution using coalfly ash-derived mesoporoussilica material was reported by NingYaun and coworkers[32]. In spite of the exemplary work, the adsorption capacity of fly ash-derived mesoporous silica materials needs tobe further enhanced for the practical application in industry.

The purpose of this study is to prepare Zeolite material for the removal of methylene blue from wastewater. Zeolite material was prepared from coal fly ash by hydrothermal treatment process. Batch experiments were designed for the sorption process and the effects of temperature, pH value, initial concentrations of methylene blue and adsorbent dosages on adsorption were evaluated. The optimum condition was also discussed for methylene blue removal.



Scheme 1:Methylene blue

II. Materials And Methods

2.1 Methylene Blue dye

Methylene blue is cationic dye having chemical formula$C_{16}H_{18}ClN_3S$; MW, 319.85 g/mol g·mol^{-1}; IUPAC name as 3,9-bisdimethyl-aminophenazo thionium chloride). A stock solution 1000ml was prepared by dissolving a weighed amount (1.0g) of Methylene blue in one liter distilled water. Different concentrations were prepared by diluting the stock solution with suitable volume of distilled water and the natural pH of the stock solution was around 8.0 All the reagents used were of analytical grade. The concentration of dye was measured with a 1cm-path-length cell at a wave length (λ_{max}) of 630 nm.

2.2 Fly Ash Collection and Adsorbent Development

A representative sample of the fly ash was collected from H.E.G. Thermal Power Station, Mandideep, Bhopal, India. The fly ash was in the form of small, spherical grayish black particles. The collected sample was sieved to a desired particle size ranges (150 μm). Sample was washed with distilled water five times to remove the adhering organic materials and then dried in an oven at 110 °C for 24 h, and finally stored in vacuum desiccator.

2.3 Zeolite Synthesis

The direct hydrothermal method was used for the synthesis of zeolites since it is fast, economic and less involving than the other fusion and the microwave methods as reported by kumar P [33]. NaOH is added with coal zeolite in different ratios of 1:2, 1:1.5 and 1:1.2 and kept for fusion at 550^{o}C for 04 hours. After this fusion mixtures were washed with double distilled water and agitated for 15 hours on magnetic stirrer to wash off excess of alkali, filtered on whatmann filter paper and dried in oven for 04 hours at 100^{o}C and stored in desiccator before use.

2.4 Adsorption Studies

The adsorption was performed using the batch method. The equilibrium adsorption uptake and percentage removal of methylene blue from the aqueous solution q_e (mg/g) was calculated using the following relationship:

Amount adsorbed $q_e = \frac{(Co - Ce)V}{W}$(mgg^{-1}) (1)

% Removal $q_e = \frac{100\,(Co - Ce)}{Co}$ (2)

Where C_o is initial adsorbate concentration (mg L^{-1}),Ce is equilibrium adsorbate concentration (mg L^{-1}),V is the volume of solution (L), W is the mass of adsorbent (g).

2.5 Adsorption Isotherms

The equilibrium data obtained in the present study were analyzed using Langmuir and Freundlich isotherm models. The rearranged Langmuir and Freundlich isotherm equations can be described as:

1/qe =1/qm+(1/bqm) (1/Ce) (3)

Logqe=log K_f+ 1/n log Ce (4)

2.6 Kinetic Studies

Intraparticle diffusion is the most common technique used for identifying the mechanism involved in adsorption process. In order to investigate the mechanism of the Methylene Blue adsorption onto zeolite adsorbent, intraparticle diffusion based mechanism was studied. Kinetic studies were carried out in batch at 5 mg/l of initial dye concentration with a fixed dose of adsorbent dose of 5g/l at 303 K and pH 5.0. After a fixed time interval the adsorbent was separated by filtration and the filtrate thus obtained was analyzed spectrophotometrically to determine the equilibrium concentration of the dye. The study of kinetics of adsorption describes the solute uptake rate at the solid-solution interface. The rate constant of adsorption of dyes on to zeolite, K_{ad} has been studied using the Lagergren first order rate equation:

$$\log (qe - qt) = \log qe - K_{ad}t / 2.303 \qquad (5)$$

where, qe is the amount of dye adsorbed at equilibrium, and qt is the amount of dye adsorbed at time t (both in mg/g).

III. Results and Discussion

3.1 Characterization of Adsorbent

The chemical composition of coal fly ash determined by X-ray fluorescence spectrometer is shown in Table 1. The result shows that the mineralogy of this CFA is very rich and it is class F fly ash. The sum of SiO_2, Al_2O_3 and Fe_2O_3 content in the CFA was found to be greater than 70%, while its CaO content was lower than 5%. Minor elements within the CFA were also identified by the XRF and the results reveal that trace elements like Sc, Ni, Cu, Sr, Rb, Zr, Nb are also present.

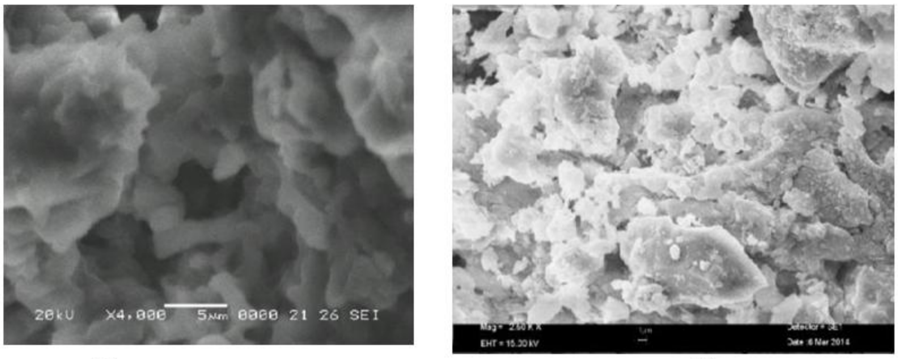
The results of SEM investigation of coal fly ash and zeolite are shown in Fig. 1 which reveals typical fly ash morphology and surface texture. Most of the particles present in the fly ash are sub angular and spherical in shape. The image also reveals that the particles present in the fly ash are covered with relatively smooth grains of quartz, clusters of iron (Fe-oxide). SEM image confirms various type of particles of fly ash in rawform as well alkali activated fly ash has resulted into a significant transition in morphology from lumps to crystalline form which is attributed to chemical reaction between Si^{4+}, Al^{3+}, and Na^{+} ions and their nucleation.

The diffractogram(Fig.2) shows the X-ray diffraction pattern of fly ash for particle size ≤ 45 μm. It is observed that the fly ash consists mostly of mullite, quartz, hematite and a small amount of hematite and calcium oxide with large characteristic peaks of quartz (SiO_2). The intensity of quartz is very strong with mullite forming a chemically stable and dense glassy surface layer. The low calcium oxide intensity is characteristic of low-Ca Class-F fly ash. It is observed that there is reduction in the silica and alumina contents associated with the crystalline particles of the fly ash due to its alkali activation. This can be attributed to the dissolution of the metal oxides and release of corresponding soluble ions Na^{+}.

The infrared spectrum of fly ash (Fig. 3) shows broad and weak peaks in the region of 4000-500 cm^{-1} associated with the functional groups that are on the surface of coal fly ash. The band appearing at 560 cm^{-1} is associated with octahedral aluminium present in mullite. In addition, bands appearing between 800-600 cm^{-1} are associated with tetrahedral vibrations formed which are known as secondary building units and fragments of alumino-silicate system. Band appearing at 2360 cm^{-1} could be attributed due to alkyl groups that are present in clay material of coal fly ash. Bands appearing at 800-1200 cm^{-1} and 450-550 cm^{-1} assign to asymmetric stretching mode and bending mode of T-O bond respectively. These bands are more or less dependent on the crystal structure. The mid infrared region of the spectrum contains the fundamental framework vibrations of $Si(Al)O_4$ groupings. Although some interference can be made about surface functional groups from IR spectra, the weak and broad bands do not provide any definitive information about the nature of the surface oxides. The data, however, indicate the presence of some surface groups on the adsorbent material. It is observed that there are significant changes in the intensities and the width of various bands due to interaction of fly ash with alkali. It can be noticed that there is an increase in intensity and broadness of the stretching frequency OH band at 3452 cm^{-1} after the treatment. This can be attributed to an increase in hydrated products due to the reaction between amorphous silicate and the alkali.

Table 1: Chemical constituents of the fly ash

Constituents	%Weight
SiO_2	55.26
Fe_2O_3	7.12
Al_2O_3	22.75
CaO	4.10
TiO_2	2.95
K_2O	2.14
P_2O_5	1.65
SO_3	1.58
Na_2O	1.23
MgO	0.63
LOI	4.10



(a) (b)

Fig. 1: SEM image of (a) Coal fly ash (b) Zeolite

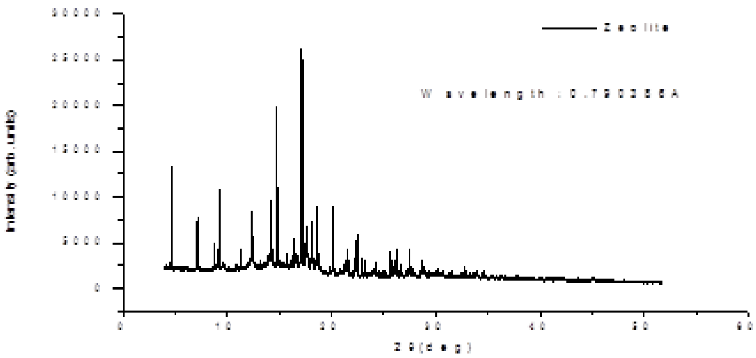


Fig. 2: X-ray diffraction pattern of coal fly ash

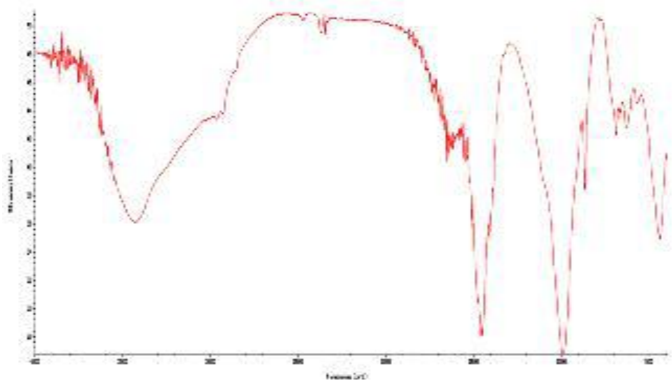
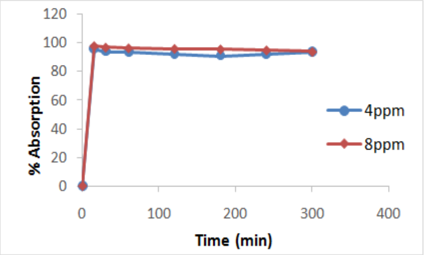


Fig.3: FTIR of coal fly ash

3.2 Batch Studies

3.2.1 Effect of Contact Time

The effect of contact time was studied at Methylene Blue concentrations of 4 and 8 ppm with a fixed adsorbent dose of 10 g/l at 30$\pm$1^{o}C. Perusal of Fig.4 shows that 96 % of the total amount of Methylene Blue uptake was found to occur in 180 minutes with 20 ppm dye concentration and thereafter no appreciable change occurred.



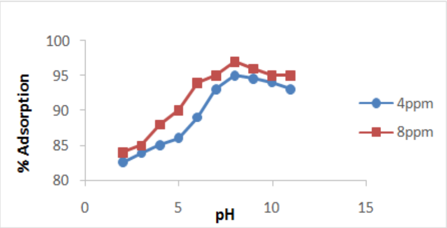


Fig.4: Effect of contact time on Methylene blue**Fig. 5:**Effect of pH on Methylene blue

3.2.2 Effect of pH

The pH of the solution was found to influence the adsorption of the adsorbate on adsorbent. The effect of pH on the adsorption of Methylene Blue was evaluated at 30°C at different pH values in the range of 2–9.pH was adjusted by adding either 0.1M HCl or 0.1M NaOH.Fig.5suggested that adsorbed amount increased with increasing pH value and an appreciable amount of adsorption occurred at pH 8.

3.2.3 Effect of amount of Adsorbent

In order to investigate the effect of mass of adsorbent on the adsorption of Methylene Blue, a series of adsorption experiments was carried out with different adsorbent dosage at initial concentrations of 4 and 8 ppm. The percentage removal of Methylene Blue increased with the increase in adsorbent initially from 5 g/l to 10, g/l. With the increase in the amount of adsorbent, the sites for adsorption increase initially. But on increasing it further the adsorption efficiency is reduced.Fig. 6 showed the effect of adsorbent dosage on the removal of methylene blue.

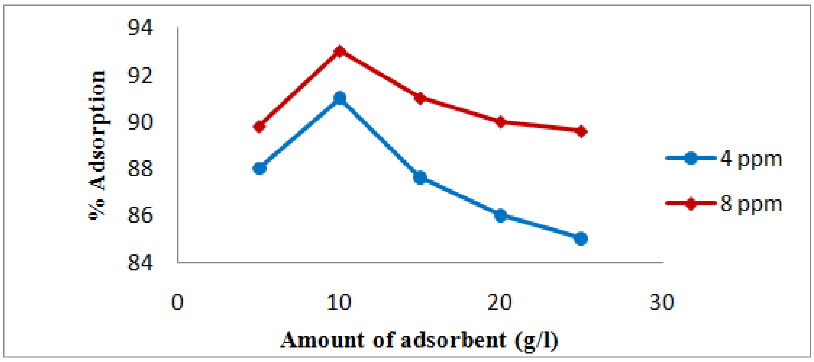


Fig. 6: Effect of adsorbent dosage on Methylene blue dye adsorption coal fly ash

3.2.4 Effect of Initial Adsorbate Concentration and Temperature:

The effect of initial adsorbate concentration on the removal efficiency was investigated at temperatures of 30°,40° and 50°C (Fig.7). The experiments were carried out with fixed adsorbent dose of 10 g/l of activated adsorbent at pH 8.0.Results indicating that uptake of methylene blue was favoured at high temperature.

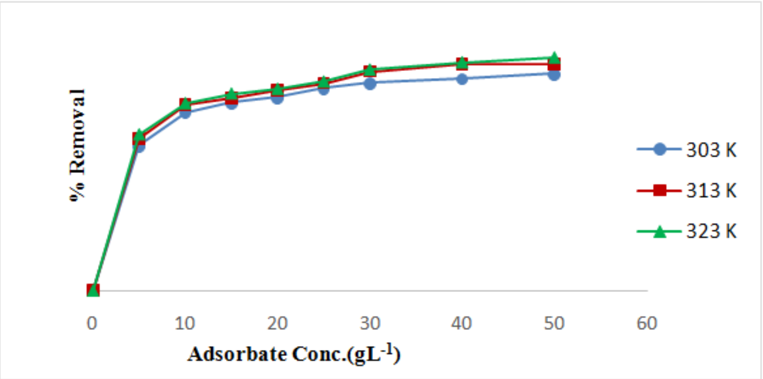


Fig. 7: Effect of adsorbate concentration and temperature on Methylene blue dye adsorption on coal fly ash

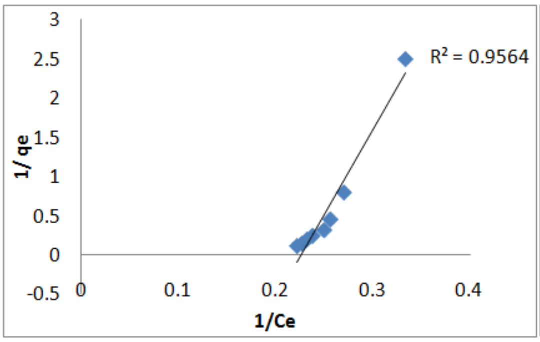
3.3 Adsorption Isotherms

The adsorption of Methylene blue dye at equilibrium with increases in initial dye concentration at 30°C has been fitted in Langmuir model and Freundlich isotherm. The results obtained on the adsorption of Methylene Blue were analyzed by the well-known models given by Langmuir and Freundlich.In Langmuir isotherm, values of 1/qe and 1/Ce were plotted for the adsorption of Methylene Blue (Fig. 8).The Langmuir constants, b and qm were calculated and the values of these were given in Table 2.

Table 2: Freundlich and Langmuir isotherm parameters at 30°C

Freundlich parameters			Langmuir parameters		
K_f (mg/g)	1/n	R^2	q_m (mg/g)	b	R^2
7.017	0.129	0.974	0.226	0.210	0.956

The equilibriumadsorption data has also been fitted in the linear form of Freundlich isotherm model. logqe against log Ce, values were plotted for the adsorption of methylene blue which clearly showed that the data is fitted very well to the Freundlich model (Fig. 9).The calculated value of 1/n is less than 1, which suggests the favorable adsorption of dye onto zeolite.The Freundlich constants, K_f and n were calculated from the best-fit lines and the values were given in Table 2.



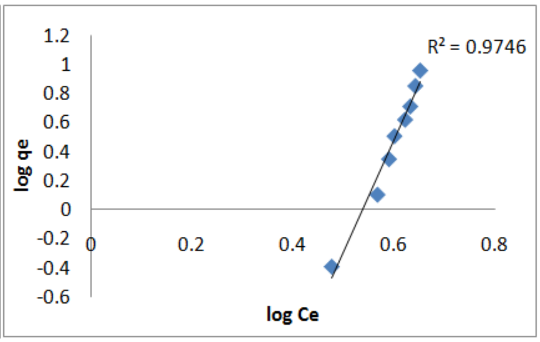


Fig. 8: Langmuir's plot of methylene blue dye**Fig. 9** Freundlich plot of methylene blue dye

3.4Thermodynamic Parameters

Thermodynamic parameters were evaluated by using the data obtained from the adsorption isotherms**.** The change in standard free energy (ΔG^0), Enthalpy (ΔH^0) and entropy (ΔS^0) of adsorption for methylene blue was calculated by known methods and the values are given in Table 3. The negative free energy value indicates the feasibility of the process and spontaneous nature of adsorption. Positive enthalpy value indicates the process is endothermic in nature. Positive entropy value supports the affinity of the adsorbent material and feasibility of the system under consideration.

Table 3: Thermodynamic Parameters of Methylene Blue

ΔG^0 (KJ mole^{-1})	ΔH^0 (KJ mole^{-1})	ΔS^0 (KJ mole^{-1} K^{-1})
-0.0123	87.759	0.2897

3.5 Kinetic Studies

The graph (Fig. 10) obtained for log(qe − qt) versus time (t) in minutes exhibits straight lines and confirm the adsorption process to follow first order rate kinetics in each case. The K_{ad} value calculated from slope of the plot (K_{ad}/2.303) is 0.02648 min^{-1}.

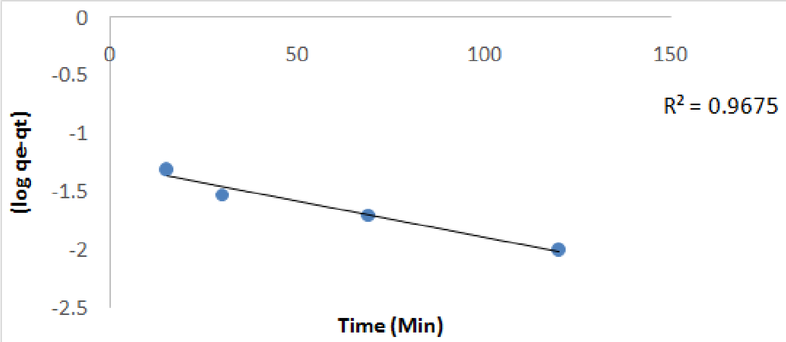


Fig. 10: Lagargren's plot of methylene blue dye adsorption on coal fly ash

Table 3: Thermodynamic Parameters of Methylene Blue

ΔG^0 (KJ mole^{-1})	ΔH^0 (KJ mole^{-1})	ΔS^0 (KJ mole^{-1} K^{-1})
-0.0123	87.759	0.2897

IV. Conclusion

The studies revealed that zeolite synthesized from coal fly ash can be fruitfully employed as adsorbent for the removal of Methylene Blue dye.The adsorption process was of first order; physical and endothermic in nature. The adsorption data was analyzed by Langmuir and Freundlichmodels.The value of regression coefficient indicates that the data satisfactorily follow both Langmuir and Freundlich models but Freundlich isotherm fits the experimental data better. The developed adsorbent is quite cheaper than commercially available activated carbon, while their performance is comparable.

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IOSR Journal of Applied Chemistry (IOSR-JAC) is UGC approved Journal with Sl. No. 4031, Journal no. 44190.

M. K. Dwivedi. "Removal of Methylene Blue Dye from Wastewater using Zeolite Synthesized from Coal Fly Ash." IOSR Journal of Applied Chemistry (IOSR-JAC) 12.2 (2019): 54-61.