# EFFICIENCY OF COMBINED ELECTROCOAGULATION USING ALUMINUM ELECTRODES AND MAHOGANY PODS ACTIVATED CARBON IN THE REMOVAL OF COD AND DECOLORIZATION OF DYE-CONTAMINATED WASTEWATER

**Nathaniel E. Quimada[1,*], Jose R. Comia Jr[2], Sophy Beak[3], Allen Rhay R. Bayantong[1], Ferlyn V. Logronio[4]**

[1] University of Science and Technology of Southern Philippines – Claveria

[2] Nueva Vizcaya State University

[3] Deutsche Gesellschaft für Internationale Zusammenarbeit, Phnom Penh, Improved Service Delivery for Citizens in Cambodia, Cambodia

[4] Northwestern Mindanao State College of Science and Technology

Corresponding author: nathaniel.quimada@ustp.edu.ph

***ABSTRACT:*** *Treating wastewater is necessary to address the water shortage and the adverse effects on the environment and humans. Electrocoagulation and Adsorption are effective methods for removing COD and decolorizing dye-contaminated waters. This experiment aimed at the treatment of synthetic wastewater contaminated with dye using a combined electrocoagulation and adsorption process. The Response Surface Methodology's Central Composite Design (CCD) was employed to optimize operating parameters such as adsorbent dose, current density, and contact time to achieve maximum removal efficiency. The combined electrocoagulation and mahogany pods adsorbent had succeeded in efficiently removing the COD and dye in the aqueous solution. The dye removal efficiency in synthetic wastewater reached as much as 99.08%, and the COD removal was 93.08%. Fourier transform infrared spectroscopy (FTIR) for surface functional groups was done for surface morphology and found the presence of alcohols, phenols, carboxylic acids, and thiocyanates. The adsorption data fit in the Freundlich adsorption model, showing a multilayer of dye molecules at the outer surface of Mahogany pods' activated carbon.*

**Keywords**: adsorption, azo dye, electrocoagulation, current density

## 1. INTRODUCTION:

Synthetic dyes find extensive application across various industries; however, they are recognized as a major contributor to water pollution on a global scale [1]. Higher efficiency is required to treat dyeing effluents because even at low dye concentrations, discharge water is aesthetically displeasing and hinders light penetration, inhibiting light-dependent biological processes in natural water [2]. Dyes are toxic, and they greatly affect human health and other living organisms [3].

Effective treatment methods for dye and COD removal include chemical coagulation, electrocoagulation, oxidation, photo-catalyzed degradation, and adsorption. Adsorption and electrocoagulation are effective processes that remove dye and COD in the wastewater [1, 4-10] Adsorption, a physico-chemical process, is considered to be an effective treatment process for textile wastewater. It possesses several advantages by being cheap, sludge and can have very high removal efficiencies necessary for eliminating color from these effluents [11] On the other hand, electrochemical methods such as electro-oxidation and electrocoagulation have been widely used as attractive and suitable methods in the treatment of wastewater containing oils, colloids, surfactants, dye compounds and heavy metals. Electrocoagulation treatments of textile dye-containing solutions or wastewater samples have been conducted on a laboratory scale and good removal of COD, color, turbidity, and dissolved solids at varying operating conditions have been obtained [12, 13]. Many combined processes are suggested in these days to provide more efficient treatment systems for wastewater. Treatment of textile wastewater by application of combined chemical coagulation, electrocoagulation, and then adsorption processes was already performed [9].

However, no study was performed for simultaneous electrocoagulation and adsorption. Electrocoagulation can reduce the amount of sludge formation and significantly treat high organic loads. To reduce the amount of energy and increase the removal efficiency, adsorption is proposed to couple with electrocoagulation. Adsorption is not good for high organics since it easily fouls but is good at eliminating residual organics and color. The combined electrocoagulation and adsorption processes will take increase their efficiencies and lessen the challenges and disadvantages of the separate processes.

The study aims to treat textile wastewater by simultaneous electrocoagulation and adsorption. Based on various literature, both processes have their advantages and limitations. The simultaneous process intends to combine the advantages while reducing their downsides. Activated carbon to be used for adsorption will be from the pods of *Switenia macrophylla* commonly known as Mahogany. It is a waste material and a cheaper alternative to activated carbon. Also, there are no previous studies regarding the use of *S. Macrophylla* capsules for adsorption. On the other hand, for the electrocoagulation process, aluminum electrodes used cans of carbonated beverages or aluminum pans. Overall efficiency and cost reduction are aimed to be achieved. Since COD and color are the most common pollutants in textile wastewater, the study will be focused on reducing these two. Parameters to be considered in the conduct of the experiment are adsorbent dose, current density, and contact time.

## 2. METHODS

### Carbonization and Activation of Adsorbents

Mahogany pods were dried for 24 hours at 1050C to remove the moisture using a Thermo Scientific Heratherm oven. The adsorbents were then carbonized in the Thermo Scientific Thermolyne Eurotherm 2116 Furnace at 4000C for 1 hour and 30 minutes. After carbonization, the adsorbents were ground and prepared for activation. Sulfuric acid ($H_2SO_4$) from Labscan was used to prepare a concentration of 0.1 mol/liter solution used the activate the carbonized materials. The said

carbonized materials were then soaked for 24 hours at a 1:10 carbon-to-acid ratio. After which, the acid was decanted and the soaked carbon was washed with distilled water (Absolute brand) repeatedly until the pH was neutral. Drying for 24 hours was done next. After drying, further grinding was performed and the activated carbon was sieved into 800 µm particle sizes.

**Preparation of Simulated Textile Wastewater**

For the preliminary runs, 100 ppm of methylene blue was treated by separate adsorption and electrocoagulation with different parameters considered. Analytical grade Methylene Blue from Ajax FineChem was used in the study. For the optimization runs, wastewater was simulated using methylene blue for the color and potassium hydrogen phthalate (analytical grade, FineChem) for the Chemical Oxygen Demand (COD). From a 1000 mg/L methylene blue stock solution, 500 mL was mixed with dissolved 2.125g KHP and then diluted to 5 liters using distilled water. Simulated wastewater was only prepared once for uniform initial concentrations. Theoretically, KHP had a COD of 1.176 mg $O_2$/mg. The said reagent was dried for 12 hours at 1100C before it was dissolved in distilled water.

Determination of the Effect of Adsorbent Dose on Color Removal Different doses of activated carbon (0.25 g, 0.50 g, 0.75 g, 1.0 g, 1.25 g, 1.50 g, and 1.75 g) was mixed with 50 mL of 100 ppm methylene blue solution and stirred at 150 revolutions per minute (rpm). After 60 minutes, the effluent was filtered using Whatman filter paper. The remaining dye content of the effluents with varying doses of carbon was analyzed using Shimadzu UV mini - 1240 UV-VIS spectrophotometer.

**Determination of the Optimum Time in Electrocoagulation**

For the determination of optimum time, electrocoagulation was performed for 200 mL of 100 ppm methylene blue solution. The sacrificial electrode used was made of aluminum, which was taken from commercially available aluminum pans. The surface area of the electrode was maintained at 0.00285 $m^2$ for every run. The setup for electrocoagulation can be seen in the figure 1. At different intervals (10 min, 15 min, 20 min, 25 min, 30 min, 35 min, and 40 min), 3 ml of sample was taken, filtered, and analyzed for the dye concentration using a spectrophotometer. **Determination of the Effect of Varying Current Density**

The current was varied for the decolorization runs. Different currents from 0.05 A – 0.20 A which were set in the DC regulator were used to determine the effect of varying currents on the color removal. Each run with a different current/current density was processed until the optimum time was determined. The effluents were then filtered and analyzed using the spectrophotometer.

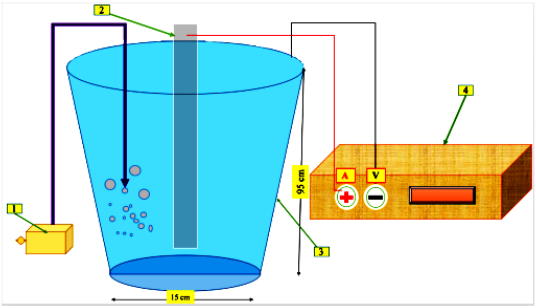


**Figure 1. Experimental set-up: 1-air pump, 2-anode (aluminum) 3, stainless steel (cathode) 4, power supply (DC).**

**Analysis of COD**

For the optimization runs, COD was determined using COD LR reagents from HACH. Two ml of the sample with a dilution factor of 7 was added to the LR reagent vial. Digestion was performed using a HACH DRB 200 COD reactor for 2 hours at 1500C. After digestion, the vials were cooled and COD values \were determined using the HACH DR/890 Colorimeter.

**Design of Experiment**

The design of the experiment was aided by Design Expert 7.0. Adsorption and electrocoagulation were done simultaneously to treat the simulated textile wastewater with known COD and color values. Stirring and formation of flocs were aided using an air pump, as shown in Figure 1. A stainless-steel container was used as the cathode, and a sheet of aluminum from an aluminum pan was used as the anode. The aluminum and stainless steel electrodes were connected to power sources from a Direct Current (DC). Optimization runs were provided by the software in terms of adsorbent dose, current density, and reaction time. Experimental runs were conducted based on the combination of parameters given by the software shown in Table 1. After every run, the stainless-steel container and aluminum were washed with 0.1 mol/ L of $H_2SO_4$ and then distilled water to avoid contamination. Color and COD were the parameters analyzed for each run.

## 3. RESULTS AND DISCUSSION

**Calibration Curve**

An initial calibration curve of absorbance versus concentration was constructed at the absorption maximum at a wavelength of λ=664 nm by the use of Beer-Lambert's Law which is shown in the following equation. A= εbc (1)

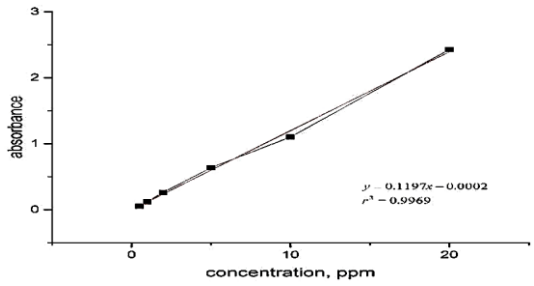


**Figure 2. Plot of concentration and adsorbent for methylene blue at 664 nm**

where A is the absorbance, $\varepsilon$ is the molar absorptivity, ($L\ mol^{-1}cm^{-1}$), **b** is the sample's path length (1 cm), and **c** is the concentration of the compound in solution ($mol\ L^{-1}$).

**Effect of Adsorbent Dose**

The adsorbent dose is one of the factors affecting adsorption efficiency. Figure 2 is a graphical representation of the effect of adsorbent dose on the removal of color by the activated carbon made from Mahogany capsules. The reduction of the color by the adsorbent increased as the adsorbent dosage increased from 0.25g to 1.75g, which can be attributed to the increase in active surface sites[11]. Activated carbon has a porous structure and a large internal surface area. Three consecutive mass transport steps are associated with solute adsorption from solution by porous adsorbent. First, the adsorbate migrates through the solution to the exterior surface of the adsorbent particles by molecular diffusion, followed by solute movement from the particle surface into the interior site by pore diffusion. Finally,

the adsorbate is adsorbed into the active sites at the interior of the adsorbent particle [2].

The optimum adsorbent dose range is at 0.75-1.25 g activated carbon per 50 mL of 100 ppm methylene blue solution for 1 hour. A higher dose beyond 1.25 g gave higher removal efficiency but there was no significant increase. This suggests that after a certain dose of adsorbent, the maximum adsorption is attained, and hence the amount of pollutants remains constant even with further addition of a dose of adsorbent[9].

**Functional groups of the activated carbon**

The Fourier Transform Infrared Spectroscopy (FTIR) is a significant way to examine the characteristics of the functional groups, which makes the adsorption behavior possible. The analysis was made using a Thermo Violet 6700 FTIR Spectrometer. The infrared spectrum of activated carbon from S. macrophylla capsule before adsorption was presented in Figure 3. The FTIR spectroscopic analysis showed a broad band at 3679.753 cm-1 corresponds to the O-H stretching vibration of alcohols, phenols, and carboxylic acids, thus showing the presence of free hydroxylic groups on the adsorbent surface [7]. The bands appearing at 2152.2, 1781.9, 1589.08, 1373.09, 1164.81, 910.25, 509. 12 cm-1 were assigned to -SCN thiocyanate, C-H stretching of acid halide in carbonyl compound group, N-H stretching of secondary amine, C-N stretching aromatic primary amine, C-N stretching of amine, C-H stretch of aromatic compound, C-I stretching aliphatic compounds, respectively. These show that conforming functional groups (-SCN, C-H, N-H, C-H, C-I) are involved in the mechanism of the removal of methylene blue.

**Adsorption isotherms**

The Langmuir and Freundlich isotherms were employed for the further interpretation of the adsorption data. Adsorption isotherms are important for the description of how adsorbates will interact with an adsorbent and are critical in optimizing the use of adsorbent [14]

**Langmuir Isotherm**

The Langmuir adsorption isotherm is based on monolayer, uniform, and finite adsorption site assumptions. Therefore, a saturation value is reached beyond which no further adsorption takes place. It also assumes that there is no interaction between the molecules adsorbed on neighboring sites. The Langmuir equation

$$q_e = K_F C_e^{\frac{1}{n}}$$

which is valid for monolayer adsorption onto a surface with a finite number of identical sites is given by:

$$q_e = \frac{q_{mon} K_L C_e}{1 + K_L C_e}$$

where $C_e$ is the concentration of the dye solution at equilibrium (mg/L), $q_e$ is the amount of dye adsorbed per unit mass of adsorbent (mg/g), and $K_L$ is the constant related to the free energy of adsorption (L/mg). $_{mon}$ is the maximum adsorption capacity. When linearized and plotted on a graph, the figure below illustrates the adsorption data following the Langmuir isotherm.

**Freundlich Isotherm**

The Freundlich isotherm model describes non-ideal sorption onto heterogeneous surfaces involving multilayer sorption. It is given by the equation: where KF is roughly an indicator of the adsorption capacity and 1/n is the adsorption intensity. The figure below is the plot of the adsorption data for the Freundlich isotherm.

Based on the two plots, it can be observed that the adsorption of methylene blue by Mahogany capsule-activated carbon follows the Freundlich Isotherm. The correlation coefficient is higher

with a value of 0.945. The data suggests the heterogeneous nature of the Mahogany capsules and demonstrates the favorable formation of multilayer coverage of the color at the surface of the adsorbent. Similar observations were reported for the adsorption of Methyl Orange, Congo Red, Methylene Blue, and Rhodamine B on waste banana peel [2, 15]. Adsorption of textile effluent by mahogany-activated carbon also followed the Freundlich model [11].

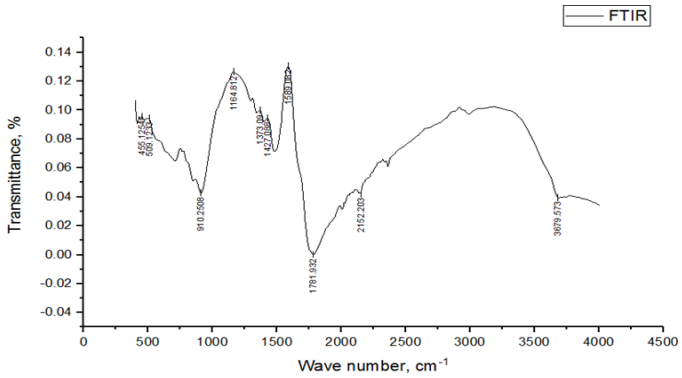


**Figure 3. FTIR Characterization of activated carbon from mahogany capsules before adsorption**

**Effect of Time** During electrolysis, one of the factors that affect pollutant removal is the contact time [16] Electrolysis time determines the production rate of Al3+ ions from aluminum electrodes. The color removal efficiency depends directly on the concentration of hydroxyl and metal ions produced on the electrodes [17]

As the reaction time for electrocoagulation is increased, removal also increases but until 30 minutes only. Removal

efficiency was almost constant in the succeeding minutes. This is due to the lack of dye materials to be removed after 30 mins of reaction. The current density for this run is at 35.1 A/m$^2$.

**Effect of Current Density on Color Removal**

Another factor that affects removal efficiency is the current intensity or current density. In all electrochemical processes, current density is the most important parameter for controlling the reaction rate within the reactor. Based on the general equation of electrocoagulation, the reaction in the anode is given by the equation:

$Al_{(s)} \rightarrow Al^{3+}_{(aq)} + 3e^-$ and at the cathode, $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

In the solution, the positively charged ions are attracted with the negatively charged hydroxides to produce ionic hydroxides that have a strong attraction towards dispersed particles as well as counter ions to cause coagulation [18]. These ions disrupt the stability of suspensions and emulsions and facilitate particle agglomeration and separation.

Based on Figure 4, it can be seen that the removal of dye increased with increased current/current density. This may be explained by the release of metal ions increasing with electrical potential. Therefore, there is an increase in floc production and, hence, an improvement in color removal efficiency. From a study, when current density was increased from 32 to 127.8 A/m2 for 6 minutes, the effectiveness would increase from 21% to 83.5% [19]. Conversely, the time required to achieve similar

efficiencies increases if the current density decreases. It is important to note that the current density has an impact on operating costs, so it is necessary to select a value of current density for efficient treatment and minimum cost. A similar result was observed in the electrocoagulation of carwash wastewater where the current density of 105 A/m2 from the range of 53-210 A/m2 is a reasonable compromise in the application because higher values show only small improvements [8]. The optimum range for current in his study is at 0.10-0.20A or 35.1-70.2 A/m2 for current density.

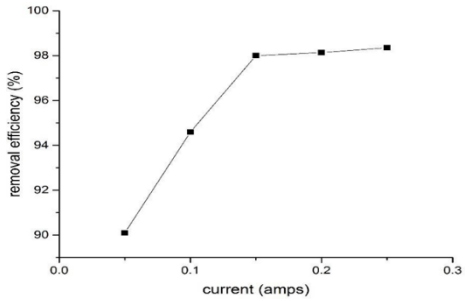


**Figure 4. Effect of increasing current on the removal of methylene blue, t=30 mins**

## 4. CONCLUSIONS

In this study, the potential of combined electrocoagulation and adsorption using activated carbon from S. Macrophylla capsule to decolorize and remove COD in the simulated textile wastewater was investigated. Fourier transform infrared spectroscopy (FTIR) for surface functional groups was done for surface morphology and found the presence of alcohols, phenols, carboxylic acids and thiocyanates. The adsorption data fit in the Freundlich model of adsorption, showing a multilayer of dye molecules at the outer surface of Mahogany capsule carbon.

Factors such as adsorbent dose, contact time, and current density were monitored and optimized. The maximum methylene blue removal was found to be at 93.12% based on the different combinations of the operating parameters generated by CCD which is 4.64 g activated carbon, 0.20 A, and 31 mins. On the other hand, a maximum of 78.54% of COD removal happened in the combined process.

## 5. REFERENCES

[1] N. E. Quimada, A. S. Sioson, F. Sutopo, and V. I. F. Mabayo, "Response surface optimization of the efficiency of ZnCl2-impregnated activated carbon from residual coffee grounds in the removal of Eriochrome Black T dye-contaminated wastewater," *Biomass Convers Biorefin*, 2023, doi: 10.1007/s13399-023-04090-3.

[2] P. K. Malik, "Dye removal from wastewater using activated carbon developed from sawdust: adsorption equilibrium and kinetics," *J Hazard Mater*, vol. 113, no. 1–3, pp. 81–88, 2004, doi: 10.1016/j.jhazmat.2004.05.022.

[3] B. Lellis, C. Z. Fávaro-Polonio, J. A. Pamphile, and J. C. Polonio, "Effects of textile dyes on health and the environment and bioremediation potential of living organisms," *Biotechnology Research and Innovation*, vol. 3, no. 2, pp. 275–290, Jul. 2019, doi: 10.1016/j.biori.2019.09.001.

[4] P. N. B, S. B. D, and R. J. P, "Studies on Removal of Dyes from wastewater using Electro-coagulation Process."

[5] A. H. Jawad, A. Saud Abdulhameed, L. D. Wilson, S. S. A. Syed-Hassan, Z. A. ALOthman, and M. Rizwan Khan, "High surface area and mesoporous activated carbon from KOH-activated dragon fruit peels for methylene blue dye adsorption: Optimization and mechanism study," *Chinese Journal of Chemical Engineering*, vol. 32. Materials China, pp. 281–290, Apr. 01, 2021. doi: 10.1016/j.cjche.2020.09.070.

[6] Yamin Yasin, Mohd Zobir Hussein, and Faujan Hj Ahmad, "Adsorption of Methylene Blue onto Treated Activated Carbon," *Malaysian Journal of Analytical Sciences*, vol. 11, no. 11, pp. 400–406, 2007, [Online]. Available: http://pkukmweb.ukm.my/~mjas/v11_n2/Yamin UITM.pdf

[7] D. Pathania, S. Sharma, and P. Singh, "Removal of methylene blue by adsorption onto activated carbon developed from Ficus carica bast," *Arabian Journal of Chemistry*, vol. 10, pp. S1445–S1451, 2017, doi: 10.1016/j.arabjc.2013.04.021.

[8] H. Rubí-Juárez, C. Barrera-Díaz, I. Linares-Hernández, C. Fall, and B. Bilyeu, "A Combined Electrocoagulation-Electrooxidation Process for Carwash Wastewater Reclamation," *Int J Electrochem Sci*, vol. 10, no. 8, pp. 6754–6767, 2015, doi: 10.1016/s1452-3981(23)06759-7.

[9] E. Bazrafshan, M. R. Alipour, and A. H. Mahvi,

"Textile wastewater treatment by application of combined chemical coagulation, electrocoagulation, and adsorption processes," *Desalination Water Treat*, vol. 57, no. 20, pp. 9203–9215, 2015, doi: 10.1080/19443994.2015.1027960.

[10] H. P. de Carvalho, J. Huang, M. Zhao, G. Liu, L. Dong, and X. Liu, "Improvement of Methylene Blue removal by electrocoagulation/banana peel adsorption coupling in a batch system," *Alexandria Engineering Journal*, vol. 54, no. 3, pp. 777–786, 2015, doi: 10.1016/j.aej.2015.04.003.

[11] A. H. Jawad, M. A. M. Ishak, A. M. Farhan, and K. Ismail, "Response surface methodology approach for optimization of color removal and COD reduction of methylene blue using microwave-induced NaOH activated carbon from biomass waste," *Desalination Water Treat*, vol. 62, pp. 208–220, Feb. 2017, doi: 10.5004/dwt.2017.20132.

[12] M. S. Mahmoud, J. Y. Farah, and T. E. Farrag, "Enhanced removal of Methylene Blue by electrocoagulation using iron electrodes," *Egyptian Journal of Petroleum*, vol. 22, no. 1, pp. 211–216, 2013, doi: 10.1016/j.ejpe.2012.09.013.

[13] N. E. Quimada, M. D. G. De Luna, A. C. Vilando, and M. C. Lu, "Competitive effect of copper and nickel recovery with carbonate in the fluidized-bed homogeneous granulation process," *Environmental Science and Pollution Research*, vol. 29, no. 9, pp. 12414–12426, Feb. 2022, doi: 10.1007/s11356-021-14733-5.

[14] Z. Shahryari, A. S. Goharrizi, and M. Azadi, "Experimental study of methylene blue adsorption from aqueous solutions onto carbon nano tubes," 2010. [Online]. Available: http://www.academicjournals.org/ijwree

[15] K. J. Ocholi, "Equilibrium Adsorption Studies Of Methylene Blue Onto Palm Kernel Shell-Based Activated Carbon," 2013. [Online]. Available: www.irjes.com

[16] A. S. Naje, S. Chelliapan, Z. Zakaria, and S. A. Abbas, "Treatment Performance of Textile Wastewater Using Electrocoagulation (EC) Process under Combined Electrical Connection of Electrodes," *Int J Electrochem Sci*, vol. 10, no. 7, pp. 5924–5941, 2015, doi: 10.1016/s1452-3981(23)17305-6.

[17] N. DANESHVAR, A. OLADEGARAGOZE, and N. DJAFARZADEH, "Decolorization of basic dye solutions by electrocoagulation: An investigation of the effect of operational parameters," *J Hazard Mater*, vol. 129, no. 1–3, pp. 116–122, 2006, doi: 10.1016/j.jhazmat.2005.08.033.

[18] A. Samir Naje and S. A. Abbas, "Electrocoagulation Technology in Wastewater Treatment: A Review of Methods and Applications", [Online]. Available: www.iiste.org

[19] K. Charoenlarp and W. Choyphan, "Reuse of dye wastewater through colour removal with electrocoagulation process TREATMENT OF DYE WASTEWATER BY ELECTROCOAGULATION PROCESS," 2009. [Online]. Available: https://www.researchgate.net/publication/284191353