Volume 1, Issue 2, Nov 2018

KOCAELI JOURNAL OF SCIENCE AND ENGINEERING

(2018)

http://dergipark.gov.tr/kojose
kojose@kocaeli.edu.tr

Owner

Prof. Dr. Sadettin HÜLAGÜ - (Kocaeli University)

Editor in Chief

Prof. Dr. K. Süleyman YİĞİT - (Kocaeli University)

Associate Editors

Prof. Dr. Murat HOŞÖZ - (Kocaeli University)
Assoc. Prof. Dr. H. Hakan GÜREL - (Kocaeli University)

Production Editor

Instructor Yusuf YAĞCI - (Kocaeli University)

Assistant Editors

R. A. Abdurrahman GÜN - (Kocaeli University)
R. A. Alp Eren ŞAHİN - (Kocaeli University)

Copy Editor (English)

Lecturer Ismail HakkēPASLI - (Kocaeli University)

Secretary

Durmuk KMAT - (Kocaeli University)

Section Editors

ALADAĞ Zerrin, (Prof. Dr.) - (Kocaeli University, TR)
ARIK Mehmet, (Prof. Dr.) - (Özyeğin University, TR)
ATUN Ata, (Prof. Dr.) - (Cyprus Science University, KKTC)
AZEVEDO Helena, (Dr.) - (Queen Mary University of London, ENG)
CASTILLO Oscar, (Prof. Dr.) - (Tijuana Institute of Technology, MEX)
CİVAN Mihriban, (Asst. Prof. Dr.) - (Kocaeli University, TR)
ÇANAKÇI Mustafa, (Prof. Dr.) - (Kocaeli University, TR)
DUNFORD Nurhan Turgut, (Prof. Dr.) - (Oklahoma State University, USA)
ENGİN Tahsin, (Prof. Dr.) - (Sakarya University, TR)
ERDEMLİ Yunus Emre, (Prof. Dr.) - (Kocaeli University, TR)
ERTUNÇ H. Metin, (Prof. Dr.) - (Kocaeli University, TR)
FIĞLALI Nilgün, (Prof. Dr.) - (Kocaeli University, TR)
GÖKTAŞ Recep Kaya, (Dr.) - (Kocaeli University, TR)
GÜLTEKİN Fatma, (Prof. Dr.) - (Karadeniz Technical University, TR)
GÜRAY Taygun, (Assoc. Prof. Dr.) - (Kocaeli University, TR)
KASIM Ufuk, (Assoc. Prof. Dr.) - (Kocaeli University, TR)
KİSHALİ Emre, (Asst. Prof. Dr.) - (Kocaeli University, TR)
ORUÇ Bülent, (Prof. Dr.) - (Kocaeli University, TR)
ÖZDEMİR Engin, (Prof. Dr.) - (Kocaeli University, TR)
ÖZTÜRK Günay, (Assoc. Prof. Dr.) - (Kocaeli University, TR)
PEKEY Beyhan, (Prof. Dr.) - (Kocaeli University, TR)
SAYAR Ahmet, (Assoc. Prof. Dr.) - (Kocaeli University, TR)
SINMAZÇELİK Tamer, (Prof. Dr.) - (Kocaeli University, TR)
SOPIAN Kamaruzzaman, (Prof. Dr.) - (The National University of Malaysia, MAL)
SOSTAKS Aleksandrs, (Prof. Dr.) - (University of Latvia, LV)
SÖZEN Adnan, (Prof. Dr.) - (Gazi University, TR)
STANASEL Iulian, (Assoc. Prof. Dr.) - (University of Oradea, RO)
ŞAHİN Ahmet Z., (Prof. Dr.) - (KFUPM, SA)
ŞAHİN Suhap, (Asst. Prof. Dr.) - (Kocaeli University, TR)

Advisory Board

AKIN Nilgün, (Prof. Dr.) - (Kocaeli University, TR)
ARI Ayşe Arzu, (Asst. Prof. Dr.) - (Kocaeli University, TR)
ARICI Müslüm, (Assoc. Prof. Dr.) - (Kocaeli University, TR)
ATAPEK Hakan, (Assoc. Prof. Dr.) - (Kocaeli University, TR)
BAYNAL Kasım, (Assoc. Prof. Dr.) - (Kocaeli University, TR)
ÇEPNİ Murat Selim, (Assoc. Prof. Dr.) - (Kocaeli University, TR)
ÇETKİN Vildan, (Asst. Prof. Dr.) - (Kocaeli University, TR)
ÇOBAN Onur, (Asst. Prof. Dr.) - (Kocaeli University, TR)
COŞKUN Safa Bozkurt, (Prof. Dr.) - (Kocaeli University, TR)
DEMİR Arif, (Prof. Dr.) - (Kocaeli University, TR)
ENGİN Şeref Naci, (Assoc. Prof. Dr.) - (Yıldız Technical University, TR)
EREN Canan Dilek, (Asst. Prof. Dr.) - (Kocaeli University, TR)
ERGÜL Halim Aytekin, (Assoc. Prof. Dr.) - (Kocaeli University, TR)
GENÇ Nevim, (Prof. Dr.) - (Kocaeli University, TR)
GÜNDOĞDU Özcan, (Prof. Dr.) - (Kocaeli University, TR)
İPLİKÇİ Serdar, (Prof. Dr.) - (Pamukkale University, TR)
KANDEMİR İlyas, (Assoc. Prof. Dr.) - (Gebze Technical University, TR)
KARAKAŞ Ahmet, (Assoc. Prof. Dr.) - (Kocaeli University, TR)
KASIM Rezzan, (Prof. Dr.) - (Kocaeli University, TR)
KILIÇARSLAN Ali, (Prof. Dr.) - (Hitit University, TR)
KÖKER Raşit, (Prof. Dr.) - (Sakarya University, TR)
KUYUMCU Feriha Erfan, (Prof. Dr.) - (Kocaeli University, TR)
KÜRÜM Hasan, (Prof. Dr.) - (Fırat University, TR)
ONAT Burcu, (Assoc. Prof. Dr.) - (Istanbul University, TR)
ÖZER Nil Pembe, (Prof. Dr.) - (Kocaeli University, TR)
SAYIN Cenk, (Prof. Dr.) - (Marmara University, TR)
SERTÇELİK Fadime, (Assoc. Prof. Dr.) - (Kocaeli University, TR)
SÜRMELİ Hikmet, (Assoc. Prof. Dr.) - (Mersin University, TR)
SÜRMEN Ali, (Prof. Dr.) - (Uludağ University, TR)
TOKAT Sezai, (Prof. Dr.) - (Pamukkale University, TR)
URHAN Oğuzhan, (Prof. Dr.) - (Kocaeli University, TR)
YILMAZ Mehmet, (Assoc. Prof. Dr.) - (Kocaeli University, TR)
YİĞİT Halil, (Assoc. Prof. Dr.) - (Kocaeli University, TR)

Printed By

Kocaeli University - Graduate School of Natural and Applied Sciences - Umuttepe Campus 41380, Kocaeli / TURKEY
Tel: +090 (262) 303 30 32 Fax: +090 (262) 303 30 33 E-mail: kojose@kocaeli.edu.tr

Kocaeli University

Kocaeli Journal of Science and Engineering (KOJOSE)

http://dergipark.gov.tr/kojose

Koc. J. Sci. Eng., 1(2): (2018) 21-27

Kocaeli University

Kocaeli Journal of Science and Engineering (KOJOSE)

http://dergipark.gov.tr/kojose

Placement of Products and Improvement of Order Picking Process through Association Analysis: A Case Study in Pharmaceutical Warehouse

Fatma DİNÇER [1,*], Alpaslan FIĞLALI[1]

[1] *Department of Industrial Engineering, Kocaeli University, Kocaeli, 41310, Turkey*

Article Info

Research paper

Received : *28/05/2018*
Accepted : *12/06/2018*

Keywords

Apriori Algorithm
Association Analysis
Data Mining
Order Picking

Abstract

While taking strategic decisions for the future in today's business world, which has a constantly changing and dynamic structure, several implications can be drawn with the information obtained from databases and the correct processing and analysis of this information. With regard to these implications, various decisions can be taken to improve the processes. Businesses can execute their processes more efficiently and they are able to make better decisions on the future by processing the data that will benefit by using the data mining techniques. In this study, the past orders of a pharmaceutical company were analyzed and an association analysis of the products in these orders was performed and a methodological framework has been presented based on the Apriori Algorithm results to ensure that the products are placed at the optimum level in the warehouse. Therefore, this study contributes to the improvement of order picking process.

1. Introduction

Warehouses and storage processes have become an integral part of production systems today. Being flexible and responsive to ever changing customer needs is essential in the dynamic business world. In order for the products to reach end users, raw materials, semi-finished products and products must be transported from one place to another. The products are kept in certain warehouses till customers demand them. Warehouses are not only the places where raw materials, semi-finished products and products are kept but also business units where goods are accepted, placed on shelves, orders are picked, replenishment, barcoding, packaging and shipment operations are carried out. When the processes from goods acceptance to shipment in warehouses are examined in detail, these may vary depending on the sector, the customer and the product, but it can also be said that basically many activities are common. In order to efficiently manage warehouse operations, it is very important that raw materials, semi-finished products and products are stored in the optimum way and can be prepared as soon as they are demanded by the customers. Delivering orders in a timely and accurate manner is an important criterion both for an efficient operation and for the image of the company. In the study by Van den Berg and Zijm, where the basic warehouse processes are addressed in four steps, it was determined that order picking costs accounted for more than 60% of the total cost of these four basic storage activities as seen in Fig. 1 [1]. When this data is evaluated, it can be said that order picking is the most costly process in warehouse operations.

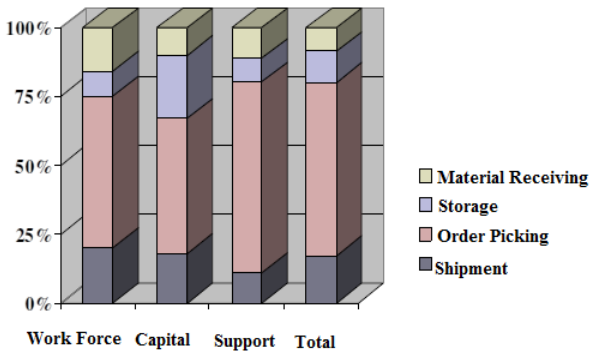


Figure 1. Storage costs according to activities.

* Corresponding Author: fatmatacar88@gmail.com

In this study, the products in a drug company's warehouse were placed according to the results of "Association Analysis", one of the most widely used methods in Data Mining, and the order picking process was improved. The possibility of products to be included in the orders was determined through "Apriori Algorithm" using past data stacks the layout of the products in the warehouse was rearranged in the direction of the data obtained from the analysis. Random orders were selected for products and the distances the products covered were calculated when the order picking process was performed according to the current layout. The measurements of the same orders were made again for the improved layout in the direction of the data obtained after the association analysis; the results were compared and the improvement rates were shared.

This study consists of five sections. The first section is the "Introduction" section and the second section is the "Literature" section. In the third section, "Association Analysis" and Apriori Algorithm which are data mining applications are explained and in the fourth section, data sets are analyzed. In the final section includes the results.

2. Literature Review

One of the processes that have the highest priority among the costs that must be met in warehouse management is the order picking [1]. Efficient warehouse processes and the efficient use of warehouse are among the biggest goals of the enterprises. The literature review revealed that generally the improvements made in the warehouse with the back to back shelf system are striking in the association analysis of the warehouses. The association analysis seems to be used in general to determine the tendency of customers to products. Liao and Chen proposed the product maps they obtained using the Apriori algorithm as a new product development source [2]. Yang and Lai compared the performance of decisions in product promotion based on the information obtained from online shopping behaviors [3]. Ay and Çil formed association rules in a retail chain operation [4]. They proposed the premises order in line with the data obtained from the association rules formed in the study. They worked on the use of data in layout planning. A study by Kılınç presented a method for the association analysis. The rules generated by the Apriori algorithm were eliminated and applied in the production and goods acceptance quality data in an electronics firm [5]. Koç et al. carried out research to examine the use of social networking by students of department computer teaching. Survey questions were asked to students to determine the extent to which social networks affected them and the association analysis was applied to the data obtained [6]. A study by Yurtay et al. aimed to determine why computer engineering students choose technical elective courses [7]. Doğan et al. conducted an association analysis on a data set related to the customers of an insurance company in their study. At the end of the study, it is reported that the types of insurance that can be purchased together were determined and information that can guide the activities for marketing were obtained [8]. Doğrul et al. utilized association analysis rules to analyze the data on traffic accidents in their work. In this study, the places and times where the accidents often occurred were determined and it was stated that in such cases the accidents can be prevented by increasing the measures [9]. K. Kaur and Kang noted that the Apriori algorithm works on static data stacks that do not take the time into account and suggested a new algorithm for it. The algorithms they suggested take into account not only static properties but also time-varying properties [10]. Yener et al. used association analysis and genetic algorithm methods to solve the order stack problem. Due to the fact that there are orders covering similar products within the stacks formed by the combination of multiple orders, they tried to save time and distance lost during the order picking [11]. When we look at the literature, there are association analysis studies to determine the tendency of customers to buy in marketing and to make layout arrangements in this direction. No study was found in the literature review in which the association analysis was applied directly according to the order rate of the products and the products in the drug warehouse were placed with the Apriori Algorithm.

3. Method

3.1. Association Rules

Due to the continuous and rapid development of computer systems nowadays, data can be stored digitally for many years. With too much increase in the data stacks and the need to analyze these stacks and produce meaningful results from the data, the concept of data mining emerged. Innovative businesses throughout the world use data mining to assess customers' needs and complaints, reorganize their products, or reduce their losses to a minimum [12]. The purpose of data mining is to analyze the data in the forms of stacks and to reveal the relations and tendencies between these data with various algorithms and to interpret the data obtained as a result of these data to produce meaningful results for the future [13]. One of the methods that allows the generation of these meaningful results is "Association Analysis". Association rules analyze a business's retrospective sales

and orders so that the relationship between these orders is revealed and make forecasts for the future based on those results. This method was developed by Agrawal and Srikant at the IBM Almaden Research Center in 1994. There have been many studies carried out on this subject in recent years. Through the obtained associations, consumer-oriented activities such as shelf product designs, customer personal preferences, promotional arrangements can be done in a more orderly fashion [14]. Association rule algorithms are used in many areas such as economics, health, storage and banking. They are often used in areas where customer-based databases are available; they are also preferred to reveal a variety of relationships in communication systems where there is a lot of data [15].

Association rules were mathematically expressed by Agrawal and Srikant as follows [16]:

- $I = \{I_1, I_2, \ldots I_m\}$ represents an array-object set
- $T = \{ t_1, t_2, \ldots t_n \}$ represents the operations (order) in the database. The value for each t_k is 0 or 1. If $t_k = 0$, it means I_k was not purchased; if $t_k = 1$, it means I_k was purchased. There is a separate record in the database for each operation. The t_k value corresponding to each I_k in X is $t_k = 1$.

This association is expressed with its rule in the following way:

- $X \Rightarrow I_J$ is a sub-set of X, I. I_j is any element in the I and this element is covered by X. In order to say that $X \rightarrow I_J$, rule is appropriate for T, it is necessary to mention a certain level of confidence. That is, how many of all the X's obtained for T cover I_k should be expressed in terms of % c. In this case, the association rule with $0 \leq c \leq 1$ confidence level can be expressed as follows:
- $X \Rightarrow I_J \quad X \rightarrow I_J \mid c$

Confidence level refers to the power of a defined rule. The rule also has the concept of support level. The support level is a concept that indicates how much of the operations in T provide X. Revealing the association rules through analyzing the data in a database is the determination of rules with greater confidence and support levels than the smallest support level and the smallest confidence level that the user would give. The object sets that provide the smallest support level are called the large object set, while others are called the small object set [16].

The support criterion indicates how often an association is in the data and confidence value means by what probability a product is likely to be purchased along with another product. Each rule is expressed by a value of support and confidence [16]:

- $A \Rightarrow B$ [support = 3%, confidence = 70%]

The 3% support value for the association rule means that 3% of the entire shopping have A and B products sold together. A confidence level of 70% indicates that 70% of customers who bought product A also bought product B in the same shopping.

Various algorithms have been developed to make such relations and derive rules. The Apriori algorithm is one of them.

3.2. Apriori Algorithm

The Apriori algorithm, a simple and well-known algorithm for deriving association rules from data sets, was developed in 1994 by Agrawal et al. has been the most widely applied algorithm for deriving association rules in data mining [13]. With Apriori algorithm, it is ensured that association rules with support and confidence over a specified threshold value are derived [17].

It has a recursive nature and the database is scanned many times to identify frequently repeated data sets in the databases. In order for the association rules in large data sets to be analyzed quickly and correctly, Agrawal, Srikant, et al. developed the Apriori algorithm. With Apriori algorithm, association rules data mining is performed on real data. The Apriori algorithm provides an effective solution by eliminating some candidate object clusters without counting the support values of them [16].

Agrawal and Srikant explain the details of the operation of the algorithm as follows [16]:

- For the detection of large object clusters during the first scan of the data, all objects are counted.
- If the next scan is regarded as the kth scan, it consists of two steps;
- Apriori-gene function is used to construct C_k candidate object clusters with L_{k-1} object clusters obtained in the (k-1)th scan,
- The database is then scanned and the support of candidates in C_k is counted.
- For a quick count, candidates constituting C_k in a given I process must be well known.

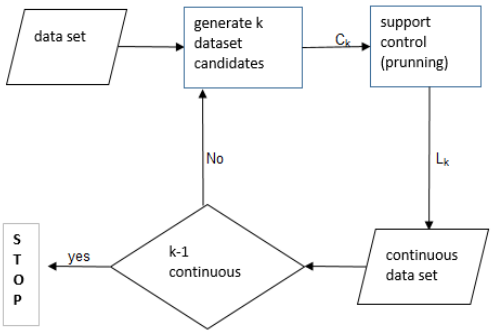


Figure 2. Apriori algorithm flow.

The apriori algorithm is often used to determine inter-product relationships in markets and to determine the future trends of customers' future decisions. Apriori

algorithm is used on many institutional resources in the world, and it is possible to find many examples in Turkey as well. The Apriori algorithm can also be used to identify associations to optimize layouts in warehouses.

4. Results and Discussion

4.1. Work Study

This study aims to analyze the past sales data of a pharmaceutical company and to place the products in the warehouse optimally according to the associations that will arise as a result of this analysis. As a result of this optimum placement, it is aimed to reduce distances while order picking is being carried out. The greatest factor affecting the order picking period is the distance between the products in the order. As the operators carrying out the order picking collect the products in the order list, the more distance between the products, the more they will be walking in the warehouse. For this reason, it is important to focus on placing the largest selling products near the exit, as well as the possibility of the products being ordered together in an order. If we place products that are likely to be ordered together in the same order close to each other, the distance operator will walk while performing the order picking process will be minimized. Sales order data was received from the SAP system and these orders were analyzed on an item basis. While doing this process, the data taken from the system was primarily analyzed on the order and product code basis on excel since it covers a significant amount of data. The "Association Analysis" method was utilized to calculate the likelihood of products being ordered together in the same order. As a result of this analysis, the likelihood of products being ordered in the same order was determined, and the products that were most likely to be ordered together were placed in close proximity to each other.

4.2. Modelling

The data from the last 3 years taken from SAP have been reviewed separately and made available for data processing in SPSS Clementine. In order to run the Apriori algorithm in SPSS Clementine, the data must be tabulated. Pivot tables were created to determine which products were ordered in which orders. The data obtained from these pivot tables was converted to tables. In the table format obtained in Excel, order numbers were used in the rows and product codes in the columns, and the data was made available for processing in the SPSS Clementine. The table has a section from the dataset converted to table format. It is not possible to list the entire dataset here. For this reason, a section has been presented in order to understand the data set.

Table 1. A section of the dataset to be processed in SPSS Clementine.

Order	A14000730	A14000984	A14000525	A14000533	A14000547	A14000697	A14002398	A14002699	…	A14003138	A14003151
1192543	0	0	1	0	0	0	1	1	…	1	0
1192545	1	0	0	0	0	0	0	0	…	0	0
1192550	0	0	0	0	0	0	0	0	…	0	0
…	…	…	…	…	…	…	…	…	…	…	…
1192551	0	0	0	0	0	0	0	1	…	0	0
1193587	0	0	0	0	0	1	0	0	…	0	0
1192588	1	0	0	0	0	0	0	0	…	0	0
1192589	0	1	0	0	0	0	0	0	…	0	0
1192590	1	0	0	0	0	0	0	0	…	0	0

In this study, Apriori algorithm, one of the algorithms used in association analysis, was utilized. The installation of the model in the SPSS Clementine module is shown in Fig. 3.

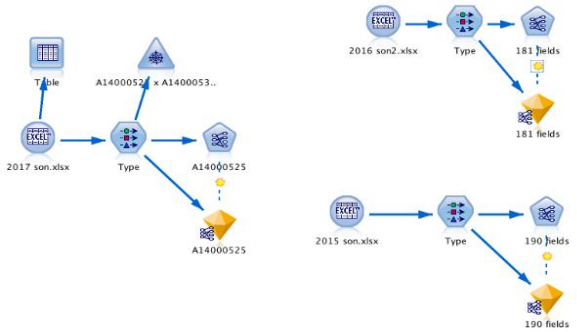
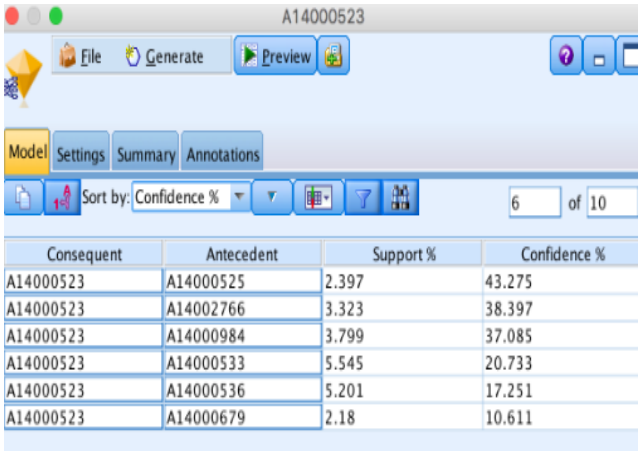


Figure 3. Installation of the model in SPSS.

Apriori algorithm was applied in SPSS by evaluating the data of the last 3 years drawn from SAP separately. There were 180 different products and the ratios of each of these products in total sales and the percentage of products in the order were determined and the average of these two values was found. According to these values, rates of 1.5% and above were taken and 27 different product codes

meeting this value were identified. Studies were carried out on these identified products. As a result of the examination of the data, the support value was determined as 2% and the confidence value as 10%.

When we examine the analysis conducted for the product coded A14000523; the possibility of customers who order this product to order products A14000525, A14002766, A14000984, A14000533 etc. in the same order is shown in Fig. 4. As a result of this analysis, the probability of the product coded A14000525 is being ordered in the order in which the product coded A14000523 ordered is 43.275%.



Consequent	Antecedent	Support %	Confidence %
A14000523	A14000525	2.397	43.275
A14000523	A14002766	3.323	38.397
A14000523	A14000984	3.799	37.085
A14000523	A14000533	5.545	20.733
A14000523	A14000536	5.201	17.251
A14000523	A14000679	2.18	10.611

Figure 4. Association analysis according to product code.

These operations were made separately for the 27 different products previously identified. Association analysis revealed that there were associations in products other than the previously identified 27 different products.

In the current lay out, the products are arranged as shown in Fig. 5. In this layout each color represents a different product.

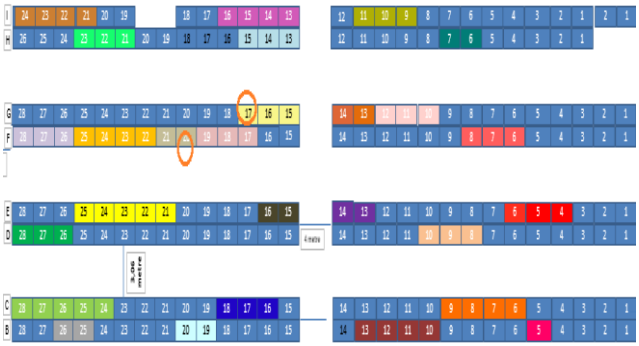


Figure 5. Current layout of products in warehouse.

Table 2 shows the walking distances for an order in the warehouse.

Table 2. Order picking by current layout.

S.N	Stages of Work	Distance (m)	Products on Order
1	Taking and controlling the order	****	
2	Controlling the location of products with RF handheld terminal	****	
3	Picker pick up	7.2	
4	Taking empty pallet	4.3	
5	Going to the product location -1 (F1028)	43.1	
	Picking the products on order	****	
	Going to the product location -2 (G1034)	7.5	1-Product A14000536 (300 Pcs)
	Picking the products on order	****	
6	Bringing the products to the closing area	35.8	2-Product A14000587 (120 Pcs)
7	Barcode reading process of products	****	
8	Labeling	****	
Total		**97.9**	

Then the products were ranked according to the support ratio and the first 4 products were identified. The association rules for some of these 27 products are shown in Fig. 5. The last 2, 3 and 4 digits of the product codes were taken in the visual.

Figure 6. Quadruple association analysis of products

Table 3 shows the walking distances measured for the corresponding order at the proposed layout.

Table 3. Order picking by layout after association analysis

S.N	Stages of Work	Distance (m)	Products on Order
1	Taking and controlling the order	****	
2	Controlling the location of products with RF handheld terminal	****	
3	Picker pick up	7.2	
4	Taking empty pallet	4.3	
5	Going to the product location -1 (G1012)	15.8	
	Picking the products on order	****	
	Going to the product location -2 (H1020)	6.3	1-Product A14000536 (300 Pcs)
	Picking the products on order	****	
6	Bringing the products to the closing area	28.3	2-Product A14000587 (120 Pcs)
7	Barcode reading process of products	****	
8	Labeling	****	
Total		**61.9**	

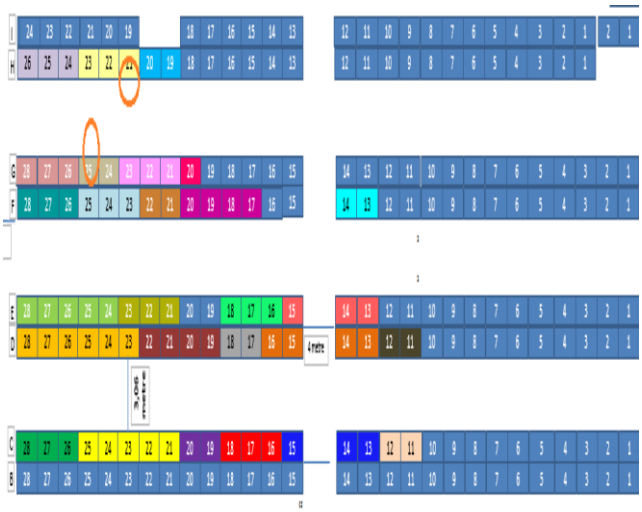


Figure 7. Proposed layout for the products

The layout of the products according to the association analysis is as shown in Fig. 6.

For 10 different orders, the distance covered during the order picking was measured primarily according to the current layout according to the layout created by the association analysis result. Then, the distance covered in the warehouse for these 10 different orders was measured. Table 4 shows the distance covered and the improvement rates according to the current layout and the improved layout. In current situation, it is necessary to walk more distance while collecting related orders. In proposed situation, the distance traveled when collecting the related order is reduced. The order picking processes has been improved.

Table 4. Improvement rates of the distances walked

	Total Walking Distance While Order Picking (m)		
Order	**Current Layout**	**Improved Layout**	**Improvement Rate**
1	160.9	121.5	24%
2	151.5	115.6	24%
3	97.9	61.9	36%
4	187.9	78.6	58%
5	151.5	50.1	67%
6	143.6	90.5	37%
7	122.2	111.0	9%
8	149.6	131.4	12%
9	196.9	156.4	21%
10	118.0	55.7	53%

5. Conclusions

Order picking is one of the processes that cause high costs in warehouse processes. It is important for the efficiency of the processes that the operators cover minimum levels of distances when orders are picked. Placing products that are likely to be in the same order close to each other ensures that the distance covered during the order picking operation is reduced to the minimum level; increasing the order picking efficiency. When Apriori algorithm is applied on the datasets that the company has, it has been observed that some product groups are in the same order. Association analysis ratios

were determined for product groups. In accordance with these association rules, the existing layout of the products was changed and the products were replaced according to the results obtained from the association analysis results. It was observed after this new layout that the distance the operator covered while picking orders was reduced at certain rates and that the order picking process was improved. This study is an important and fruitful study showing the effect of association analysis on the location of products. The work to be done on this subject can be extended.

References

[1] Van den Berg J. P., Zijm W. H. M., 1999. Models for warehouse management: Classification and examples. Int. J. Production Economics, **519**, 519–528.

[2] Chen M. C., Lin C. P.,2007. A Data Mining Approach to Product Assortment and Shelf Space Allocation. Expert Systems with Applications, **32**, 976-986.

[3] Yang T. C., Lai H., 2006. Comparison of Product Bundling Strategies on Different Online Shopping Behaviors. Electronic Commerce Research and Applications, **5**, 295-304.

[4] Ay D., Çil İ., 2008. Use of Association Rules in Layout Planning AT Migros Türk A.Ş. Journal of Industrial Engineering, **21**, 14-29.

[5] Kılınç Y., 2009. Mining Association Rules For Quality Related Data In An Electronics Company. Master's Thesis, Middle East Technical University, Industrial Engineering, 1-23.

[6] Koç M., Karabatak M., 2011. Investigation of the Effect of Social Networks on Students Using Data Mining. 5th International Computer & Instructional Technologies Symposium, Fırat University, Elazığ-Turkey, 22-24 September.

[7] Güngör E., Yalçın N., Yurtay N., 2013. Technical Elective Course Selection Analysis with Apriori Algorithm. National Distance Education and Technologies Symposium, Selçuk University, Konya,1-3 November, 114-119.

[8] Doğan B., Erol B., Buldu A., 2014. Usage of Association Rules for Customer Relationship Management in the Insurance Sector. Marmara Journal of Science, **3**, 105-114.

[9] Doğrul G., Akay D., Kurt M., 2015. Analysis of Traffic Accidents by Association Rules. Gazi Journal of Engineering Sciences, **1**, 265-284.

[10] Kaur M., Kang S., 2016. Market Basket Analysis: Identify The Changing Trends of Market Data Using Association Rule Mining. International Conference on Computational Modeling and Security, Procedia Computer Science, **85**, 78-85.

[11] Yener F., Yazgan H., Cömert S., Kır S., Kaya Y., 2016. Solution of Order Batching Problem with Association Rules and Genetic Algorithm: A Case Study in Pharmacy Warehouse. Journal of Transportation and Logistics, **1**, 130-142.

[12] Edelstein H. A., Edelstein H. C., 1997. Building, Using, and Managing the Data Warehouse. In: Data Warehousing Institute, 1st edn., Prentice Hall PTR, Englewood, Cliffs.

[13] Han J., Kamber M., 2006. Data Mining: Concepts and Techniques, 2rd edn., Morgan Kaufmann Publishers.

[14] Karaibrahimoğlu A., 2014. Analyzing Breast Cancer Data Using Association Rule Mining. Phd Thesis, Selçuk University, Graduate School of Natural Sciences, 1-126.

[15] Kotsiantis S., Kanellopoulos D., 2006. Association Rules Mining: A Recent Overwiev. GESTS Int'l Transactions on Computer Science and Engineering, **78**, 71-82.

[16] Agrawal R., Srikant R., 1994. Fast Algorithms for Mining Association Rules. Proceedings of the 20th VLDB Conferance, Santiago, Chile, 487-499.

[17] Bothorel G., Serrurier M., Hurter C., 2011. Using Visual Data Mining Tools to Explore a Set of Association Rules. IHM '11 23rd French Speaking Conference on Human-Computer Interaction, Sophia Antipolis, France, October 24-27.

Koc. J. Sci. Eng., 1(2): (2018) 28-32

Kocaeli University

Kocaeli Journal of Science and Engineering (KOJOSE)

http://dergipark.gov.tr/kojose

Antimicrobial Properties of Silk Fabrics Dyed with Green Walnut Shell (*Juglans regia* L.)

Hülya UZKUL[1, *], Rezan ALKAN[2,**]

[1] *Department of Biology, Graduate School of Natural and Applied Sciences, Kocaeli University, Kocaeli, 41310, Turkey*
[2] *Microbiology Laboratory, Kosekoy M.Y.O., Kocaeli University, Kocaeli, 41135, Turkey*

Article Info

Research paper

Received : 27/03/2018
Accepted : 05/06/2018

Keywords

E.coli
Green Walnut Shell
Natural Dye
S.aureus
Silk Fabric

Abstract

Natural dyes are obtained from plants, insects, lichens, fungus and molluscs which have been used since ancient times. These dyes have antimicrobial, anticarcinogenic and antihelmintic properties. Walnut (*Juglans regia* L.), a species of Juglandaceae family, is grown in Turkey. Green walnut shell has also antimicrobial functions due to its juglone components known as one of the strongest antimicrobial chemical compound. In this study, alum-mordanted and unmordanted silk fabrics were dyed with green walnut shell. Concentration was varied at 50, 100, 150 and 200 % owf (weight of fabric), in order to assess antimicrobial properties of green walnut shell. Pathogenic strains of *Staphylococcus aureus* subsp. *aureus* (ATCC 29213) and *Escherichia coli* (ATCC 25922) were used to test for fabrics' antimicrobial activities. Reductions of bacterial growth were determined using AATCC test methods. All the fabrics which were dyed with green walnut shell indicated antimicrobial effect on both bacteria species. Antimicrobial effect was increased from 50 to 200 % owf (weight of fabric) dye concentration. These results indicated that unmordanted silk fabrics dyed with green walnut shell had antimicrobial effect as high as alum-mordanted silk fabrics dyed with green walnut shell and *S.aureus* were more sensitive than *E.coli.*

1. Introduction

Formerly, wool and silk fibres were always dyed with natural dyes extracted from renewable sources such as plants, crops, animals and minerals in nature [1]. They were the primary colour source of textiles until mid-to late 19th century [2]. Nowadays natural dyes have attracted renewed attention because of their bio-degradability, sustainable production and uncommon, soothing shades [3]. Natural dyes are non-allergenic, non-toxic to the human body and eco-friendly in comparison with synthetic ones; hence the usage of natural dyes in textile dyeing is getting increased day by day [4].

Natural dyeing began in China and Central Asia, then it was technically developed by Egyptians [5]. In particular, natural dyes were improved in India. Mesoamerican civilizations such as Olmecs, Mayas, Aztecs and Teotihuacans used natural substances for the dyeing production. The Maya used natural dyes comprising both organism-derived (mainly from plants) and inorganic dyes [6]. In the Ottoman Empire, natural dyes and dyehouses were very important. Natural dyes especially, *Rubia tinctorum* L. (madder), *Crocus sativus* (crocus), *Reseda luteola* L. (weld) and *Rhamnus petiolaris* Boiss. (buckthorn) were used in natural dyeing. Madder and buckthorn were commercial dyes which were imported. *Reseda luteola* L. was used in the thirteenth-century Seljuk carpets and from the fifteenth to twentieth-century, it was used in Ottoman textiles for yellow and green colours. *Rubia tinctorum* L. was also used in the Ottoman dyehouses in the XVII. century [7,8].

The textile industry is one of the most polluted sectors in the world. It contributes a great deal to poor labour conditions, non-renewable energy and waste water, contamination and environmental impact [9]. Synthetic dyes are highly cytotoxic and carcinogenic to mammalian cells and act as a liver tumour promoter. They can also decrease the food intake capacity, growth and fertility

* Corresponding Author: hulyauzkul@gmail.com
** In memory of **Rezan Alkan**

rates, cause damage to liver, spleen, kidney and heart; inflict lesions on skin, eyes, lungs and bones [10]. Alternatively, dyes obtained from plants, insects/animals and minerals are proven to have bio-degradability, sustainability, eco-friendliness and generally higher compatibility with the environment [11].

People have used natural dyes since ancient times for dyeing carpets, rugs and clothings by using roots, stems, barks, leaves, berries and flowers of various dye plants [12]. These dyes are reported as potent antimicrobial agents owing to the presence of a large amount of compounds such as anthraquinones, flavonoids, tannins, naphthoquinones etc. which possess strong antimicrobial properties [13].

Textile materials are often prone to attacked by microorganisms, as these provide basic requirements such as moisture, oxygen, nutrients and temperature for microbial growth and multiplication [14]. Antimicrobial finishes prevent the growth of microorganisms on fabrics used in wide variety of apparel, home furnishing, commercial and industrial products. Fabrics will have a longer life when treated with some type of antimicrobial finishes that reduce or prevent damage from microorganisms [15].

In the previous dyeing studies, wool, cotton and polyamide fabrics [16], wool fabrics [17] and polyamide fabrics [18] were used. In the present study, we used silk fabrics in the dyeing process. Silk fabrics were dyed with green walnut (*Juglans regia* L.) shell (Fig. 1) presence and absence alum mordant. *Juglans regia* L., among the large numbers of plants grown over the world, which is cultivated throughout southern Europe, northern Africa, eastern Asia, USA and western South America [16]. The parts of a walnut tree such as leaves, husk and shell are tested as potential dyeing materials for different textile substrates. Textile materials dyed with aqueous green walnut shell extracts yield brown colour shades.

The aim of this study is to assess antimicrobial activity of silk fabrics dyed with green walnut shell against pathogenic strains of *Staphylococcus aureus* subsp. *aureus* and *Escherichia coli*.

Figure 1. Green walnut shell is used as a natural dyestuff

2. Materials and Methods

2.1. Materials

Commercially silk fabrics were provided by Armaggan Company. Green walnut shell was collected from Dardanos, Çanakkale in Turkey, by TCF-Armaggan, Cultural Heritage Preservation and Natural Dyes Laboratory. Alum mordant [$KAl(SO_4)_2.12H2O$], Nutrient Agar and Nutrient Broth were purchased from Merck (Germany).

To investigate antimicrobial activity of green walnut shell on alum mordanted and unmordanted silk fabrics, Gram-positive bacteria *Staphylococcus aureus* subsp. *aureus* (ATCC 29213), which is a clinical isolate that is obtained from wounds and Gram-negative bacteria *Escherichia coli* (ATCC 25922), which is a member of gut microbiota that cause urinary tract infections, were used for evaluation. Antimicrobial activities were tested according to AATCC (American Association of Textile Chemists and Colorists) Standards.

2.2. Mordanting and Dyeing Process

The silk fabrics were cut in 30 x 30 cm^2 size for five alum-mordanted fabrics and five unmordanted fabrics. Potassium aluminium sulphate (alum) [KAl(SO4)2.12H2O] was used as a mordant. Five of silk fabrics were treated with 10 % alum, at 65 °C at 4.5 pH for 1 hour in a water bath. Then fabrics left in mordant solutions for overnight. After this stage, fabrics were taken into dyeing bath.

Dried green walnut shell rinds were used at 50, 100, 150 and 200 % owf (weight of fabric) for dyeing. Green walnut shell aqueous extracts were obtained at 80 °C. Mordanted and unmordanted silk fabrics were dyed at 65 °C at 1:100 (material liquor ratio) at 6.0 pH and were stirred well for 60 min. After dyeing method, silk fabrics were washed with cold water and dried.

Several test methods have been developed to evaluate the antimicrobial activities of textiles. These methods fall into two categories: qualitative and quantitative test methods [19].

In Parallel Streak Method (AATCC Test Method 147-2004), broth cultures of *S.aureus* and *E.coli* were developed at 37 °C for 24 hours. 1 loop of culture was inoculated sterilized agar plates by making 7.5 cm five parallel streak and then sterilized fabrics which were cut in 25 x 50 mm, were pressed onto the agar plates. After incubation at 37 ± 2°C for 18-24 hours, a clear zone of interrupted growth around and underneath of the testfabrics were indicated antibacterial activity of green walnut shell.

In Antimicrobial Finishes on Textile Material (AATCC Test Method 100-2012) Method, *S.aureus* and *E.coli* test microorganisms were incubated on the Nutrient Agar Medium at 37 °C for 24 hours and then bacterial suspensions which containing 106 CFU/ml, were prepared in saline buffer. The circular fabric samples were cut 480 mm in diameter, placed in containers and sterilized at 121°C for 20 min. After the sterilization, 1 ml bacterial suspension were dropped centre of the sterilized fabrics. Then neutralization broth were added onto the fabrics and containers were shaken well with vortex for 1 min. Serial dilutions were made. 100 µL were taken from the solution and inoculated onto the Nutrient Agar Medium plates. The Petri plates were incubated at 37 ± 2°C for 18-24 hours. After the incubation viable colonies were counted (according to 104 dilutions) and expressed as a percentage reduction according to the Eq. (1) below:

$$\% \text{ Reduction} = [(B-A)/ B] \times 100 \quad (1)$$

Where, A is the number of bacteria colonies of treated fabrics, and B is the number of bacteria colonies of untreated fabrics.

3. Results and Discussion

In the present study, according to Parallel Streak Test Method, clear zones of interrupted growth underneath of the test fabrics had been obtained. All the fabrics (mordanted and unmordanted) which were dyed with green walnut shell concentration was varied at 50, 100, 150 and 200 % owf (weight of fabric), indicated antimicrobial effect to both of bacteria. Antimicrobial effect were increased from 50 to 200 % owf dye concentration. Unmordanted silk fabrics had between 89.68 and 99.81 % antimicrobial activities against *S.aureus* (Fig. 2) and between 70.37 and 93.85 % antimicrobial activities against *E.coli* (Fig. 3).

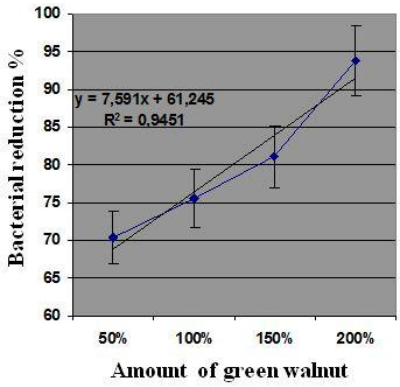


Figure 2. Amount of green walnut shell and *S.aureus* reduction (%) on mordanted silk fabric

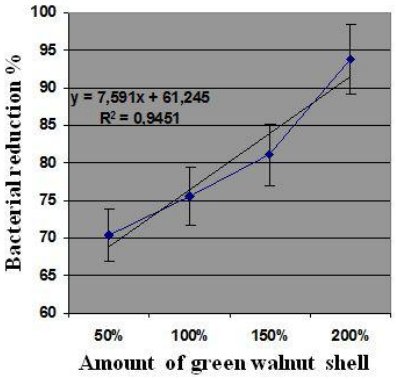


Figure 3. Amount of green walnut shell and *E.coli* reduction (%) on unmordanted silk fabric

Antimicrobial activities against *S.aureus* alum-mordanted silk fabrics range from 90.87 to 99.43 % (Fig. 4) and antimicrobial activities against *E.coli* of alum-mordanted silk fabrics range from 69.30 to 82.56 % (Fig. 5).

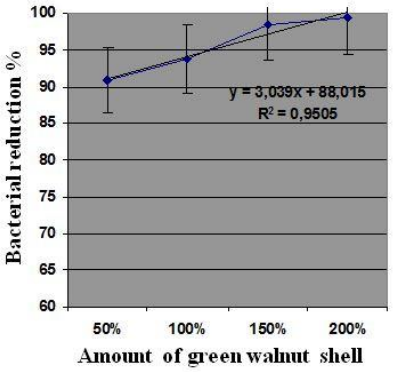


Figure 4. Amount of green walnut shell and *S.aureus* reduction (%) on mordanted silk fabric

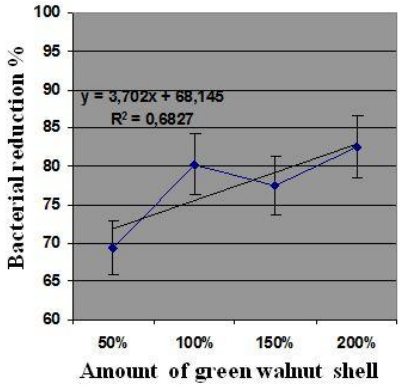


Figure 5. Amount of green walnut shell and *E.coli* reduction (%) on mordanted silk fabric

These results indicated that unmordanted silk fabrics had antimicrobial effect as high as alum-mordanted silk fabrics and *S.aureus* were more sensitive than *E.coli* against green walnut shell extract.

Ghaheh et al. reported similar results using walnut shell extract and pomegranate. Unmordanted and mordanted with chrome, copper (II) sulphate, iron (II) sulphate, iron (III) sulphate, aluminium sulphate, tin (II) chloride, potassium dichromate and tannic acid wool fabrics dyed with walnut shell extract and pomegranate showed antibacterial properties against *S.aureus, E.coli* and *P.aeruginosa* [17]. In the present study, alum-mordanted and unmordanted silk fabrics dyed with green walnut shell extract showed antibacterial activities against *S.aureus* and *E.coli*. Mirjalili et al. screened that polyamide fabrics with 1, 3, 5 and 10 % owf were dyed with green walnut shell showed better efficiency against *E.coli* in comparison with *S.aureus. S.aureus* had better antibacterial activity with using mordant. The present study indicated that unmordanted silk fabrics dyed with green walnut shell had antimicrobial effect as high as alum-mordanted silk fabrics dyed with green walnut shell against *S.aureus*. The antibacterial activity of dyed fabrics was ranked as ferric sulphate > cupric sulphate > potassium aluminium sulphate > without mordant against *S.aureus* and cupric sulphate > ferric sulphate > potassium aluminium sulphate > without mordant against *E.coli* [18]. Jabli et al. examined antimicrobial potential of stem and leaves methanolic extracts of Tunisian *Juglans regia* L. (walnut). Wool, cotton and polyamide fabrics dyed with stem, leaves and their mixture were performed against Gram (+) bacteria, Gram (-) bacteria and mold using disc diffusion method. Results indicated that *Aspergillus niger* and *Salmonella arizonae* 1 were the most sensitive microorganisms showing the largest inhibition zones (18 < d <20 mm) [16]. Jabli et al. performed the walnut stem and leaves methanolic extracts, in the present study, green walnut shell aqueous extracts were examined against Gram (+) bacteria *S.aureus* and Gram (-) bacteria *E coli*.

4. Conclusion

Present results indicate that green walnut shell extract can be used for silk fabric dyeing with or without mordant. Also, it has an antimicrobial effect against *S.aureus* and *E.coli*. Further research is needed on antimicrobial textile products such as baby clothes, socks, underwears, bedclothes, bathrobes, towels, hospital materials (aprons, bonnets and surgical garments) etc. Moreover, patients have some diseases such as skin allergy, eczema, psoriasis, fungal infectious disease, heat rash and acne. Therefore they can use textiles dyed with green walnut shell extract rather than synthetic dyed textiles. We can suggest green walnut shell extract as a dyeing material. It can be an alternative natural source for health and the environment.

Acknowledgment

The authors thank E. Torgan, C. Aydın and Prof. Dr. R. Karadag for their interest. They are indebted the TCF-Armaggan, Cultural Heritage Preservation and Natural Dyes Laboratory for the help of dyeing studies. The authors also thank to Assoc. Prof. Dr. H. A. Ergul for his notable comment on the manuscript.

References

[1] Alkan R., Torgan E., Aydın C., Karadag R., 2015. Determination of antimicrobial activity of the dyed silk fabrics with some natural dyes. Journal of Textiles and Engineer, **22**(97), 37-43.

[2] Erkan G., Sengül K., Kaya S., 2011. Dyeing of white and indigo dyed cotton fabrics with *Mimosa Tenuiflora* extract. Journal of Saudi Chemical Society, **18**, 139-148.

[3] Deveoglu O., Erkan G., Torgan E., Karadag R., 2013. The evaluation of procedures for dyeing silk with buckthorn and walloon oak on the basis of colour changes and fastness characteristics. Color. Technol., **129**, 223–231.

[4] Tutak M., Acar G., Akman O., 2014. Natural dyeing properties of wool fabrics by pomegranate (*punica granatum*) Peel. Tekstil ve Konfeksiyon, **24**(1), 81-85.

[5] Kilinc M., Canbolat S., Merdan N., Dayioğlu H., Akin F., 2015. Investigation of the color, fastness and antimicrobial properties of wool fabrics dyed with the natural dye extracted from the cone of *chamaecyparis lawsoniana*. Procedia-Social and Behavioral Sciences, **195**, 2152-2159.

[6] Chan-Bacab M. J., Sanmartin P., Camacho-Chab J. C., Palomo-Ascanio K. B., Huitz-Quime H. E., Ortega-Morales B. O., 2015. Characterization and dyeing potential of colorant-bearing plants of the Mayan area in Yucatan Peninsula, Mexico. Journal of Cleaner Production, **91**, 191-200.

[7] Inalcik H., Goyunç N., Lowry Heath W., Erunsal I., Kreiser K., Senturk A. A., 1998. The Journal of Ottoman Studies XVIII, **18**, 89-104.

[8] Deveoglu O., Torgan E., Karadag R., 2012. High-performance liquid chromatography of some natural dyes: analysis of plant extracts and dyed textiles, society of dyers and colourists. Color. Technol., **128**, 1-6.

[9] Carvalho C., Santos G., 2016. Sustainability and

biotechnology-natural or bio dyes resources in textiles. Journal of Textile Science & Engineering, **6**(239), 1-5.

[10] Sinha K., Saha P. D., Data S., 2012. Extraction of natural dye from petals of flame of forest (*Butea monosperma*) flower: process optimization using Response Surface Methodology (RSM). Dyes and Pigments, **94**, 212-216.

[11] Yusuf M., Mohammad F., Shabbir M., 2016. Eco-friendly and effective dyeing of wool with anthraquinone colorants extracted from *rubia cordifolia* roots: optimization, colorimetric and fastness assay. Journal of King Saud University Sci., http://dx.doi.org/10.2016/j.jksus.2016.06.005

[12] Yusuf M., Shahid M., Khan M. I., Khan S. A., Khan M. A., Mohammad F., 2015. Dyeing studies with henna and madder: a research on effect of tin (II) chloride mordant. Journal of Saudi Chemical Society, **19**, 64-72.

[13] Baliarsingh S., Panda A. K., Jena J., Das T., Das N. B., 2012. Exploring sustainable technique on natural dye extraction from native plants for textile: identification of colorants, colourants, colourimetric analysis of cyed yarns and their antimicrobial evaluation. Journal of Cleaner Production, **37**, 257-264.

[14] Khan M. I., Ahmad A., Khan S. A., Yusuf M., Shahid M., Manzoor N., Mohammad F., 2011. Assesment of antimicrobial activity of catechu and its dyed substrate. Journal of Cleaner Production, **19**, 1385-1394.

[15] Hashem M., Ibrahim N. A., El-Sayed W. A., El-Husseiny S., El-Enany E., 2009. Enhancing antimicrobial properties of dyed and finished cotton fabrics. Carbohydrate Polymers, **78**, 502-510.

[16] Jabli M., Sebeia N., Boulares M., Faidi K., 2017. Chemical analysis of the characteristics of Tunisian *juglans regia* L. fractions: antibacterial potential, gas chromatography-mass spectroscopy and a full investigation of their dyeing properties. Industrial Crops & Products, **108**, 690-699.

[17] Ghaheh F. S., Nateri A. S., Mortazavi S. M., Abedi D., Mokhtari J., 2012. The effect of mordant salts on antibacterial activity of wool fabric dyed with pomegranate and walnut shell extracts. Society of Dyers and Colourists, Color. Technol., **128**, 473-478.

[18] Mirjalili M., Karimi L., 2013. Extraction and characterization of natural dye from green walnut shells and its use in dyeing polyamide: focus on antibacterial properties. Journal of Chemistry, **2013**, Article ID 375352, 1-9.

[19] Varesano A., Vineis C., Aluigi A., Rombaldoni F., 2011. Antimicrobial polymers for textile products. Formatex, **1**, 99-110.

Koc. J. Sci. Eng., 1(2): (2018) 33-41

Kocaeli University

Kocaeli Journal of Science and Engineering (KOJOSE)

http://dergipark.gov.tr/kojose

Planning for Peace; Introduction of Transboundary Conservation Areas

Sahar POUYA [1], Sima POUYA[2,*]

[1] *Department of Architecture, Faculty of Urban and Regional Planning, University of Istanbul Technical University, Turkey*
[2] *Department of Landscape Architecture, Karadeniz Technical University,Turkey*

Article Info

Review paper

Received : 17/03/2018
Accepted : 22/05/2018

Keywords

Environment Conservation
Peace Park
Political Border
Resource Management
Transboundary Conservation Areas(TBCA)

Abstract

The idea of conserving borderlands has been founded to mitigate the issues around the political borders. Similarly, "Transboundary Conserved Area" or "Peace Park" has been created to protect the environmental resources and precious biodiversity over the political borders as well as enhancing international cooperation through harmonizing resource management approaches. There are various forms of the peace parks created all around the world especially in Africa. Even though various kinds of these parks are created, the subject seems interesting and new in Asian and Middle East countries. Thus, this research aims to provide a comprehensive view of the subject that can be practical for the urban and environmental planners. Trying to determine their functions; this research explains seven operated projects as examples of Transboundary Conserved Area. To gain information, desk research is used, which collects secondary data from the available sources. Regarding data analysis, it shows how these parks contribute to the ecological improvement and other political, economic, and cultural benefits. The results of the cases' surveys demonstrate a tangible consideration on ecosystem conservation, while other functions defined to the peace parks and peacemaking have been underestimated and partially ignored.

1. Introduction

Ecological areas are not in coordination with the international borders and they create a series of disjunction and environmental problems among political borders. Most of the geopolitical boundaries cut the natural habitats (both marine and terrestrial) and in some cases, it extends thousands of kilometers in fish, birds, and insect habitats. It is noticeable that many political boundaries are crossed by animals to access their needs and sources for survival. However, there are some human borders that completely block the way of species by the physical obstacles like fences. These obstacles make fragmentation in the natural landscape and ecosystems [1].

These markers of the human borders may cause an impervious road to the plants and animal species and limit their populations' access and migration through a landscape [2].

As a result, the political borders are associated with various environmental issues including the biodiversity reduction, the ecosystem fragmentation, the habitat destruction through human construction, road services, and other military operations over the border areas [3]. In these situations, a good solution can be to remove the limitation and obstacles in order to create a corridor for facilitating the species interaction and animal movements.

However, borderland conservation solutions have been used more extensively. According to Griffiths and Westing [4], the international borders contain biologically intact ecosystems that are mostly placed in distant and unkind regions. Therefore, environmental conservation of the border regions has been developed as an idea and later it was called Transboundary Conservation Areas (TBCA's) or/and Transboundary Peace Parks. Two other categories of transboundary areas have been also introduced besides TBCA's. Table 1 quantifies all three typologies.

TBCA's and Peace parks address various ecological deterioration and contribute with national and international cooperation across geopolitical boundaries [2]. These types

* Corresponding Author: sima_pouya2002@yahoo.com

Table 1. Typologies of Conservation Transboundary Areas [4].

Transboundary Conservation Areas	Areas that span well-defined borders, within precise and linear concepts of international borders [4]. Aim: To conserve the biodiversity, cultural heritage and economic benefits
Transfrontier Conservation Areas	Areas that span regions where boundaries have not been agreed upon [4]. Aim: The same as with TBCA's. Instead; to ameliorate tensions related to disputed borderlands
International Peace Parks	Areas that have definite political objectives and are largely symbolic in nature. Aim: To confirm, strengthen, or re-establish good relations with a neighboring state(s); prevent escalation of border disputes; and safeguard biodiversity

of cross-border actions can be practical in uniting artificially-separated ecosystems and lead to conservation achievements.

Other benefits of creating a peace park over borders include increased economic and tourism opportunities, better political relationships among countries, and the cooperation of local communities in the border areas conservation resulting in local benefits [2].

2. Materials and Methods

In this research, in order to get information about TBCAs projects executed in various countries (especially in African countries), desk method is used to collect secondary data from internal sources, the internet (project websites), libraries, government documents and published reports and documents.

Examples of transboundary protected areas are numerous and include international conserved areas, international marine protected areas, and the interstate parks mainly in the United States. In this research, some of best-known transboundary conserved areas have been selected and explained in order to determine their roles in protecting ecologically important border-lands all around the world. Although peace parks can be found in various ecoregions of the world, in this research they are categorized in two groups based on their location; terrestrial and marine conserved areas [1]. In this essay, Waterton-Glacier International Peace Park, the Great Limpopo Transfrontier Park, "W" Transborder Parks, Kavango-Zambezi Transfrontier Conservation Area have been chosen as the terrestrial cases; Binational Red Sea Marine Peace Park, Mnazi Bay-Ruvuma Estuary Marine Park, and Iona-Skeleton Coast Transfrontier Conservation Area have been studied as the Marine cases.

2.1. Waterton-Glacier International Peace Park (Between America and Canada)

Major features: Waterton-Glacier International Peace Park is the first International Peace Park in the world considered as a World Heritage Site established in 1995 (Fig. 1). It is a combination of two individual parks including Glacier National Park in Montana Waterton and Waterton Lakes National Park in Alberta. Each park is responsible for their own management and protection strategies. They manage their administrations and budgets separately. However, these two parks make attempt to cooperate on common projects that affect the whole area such as research projects, park publications, and interpretive activities. Unlike many peace parks of the world, the Waterton-Glacier is located between two countries that have experienced a long history of cooperation before the idea of park formation was mentioned [5].

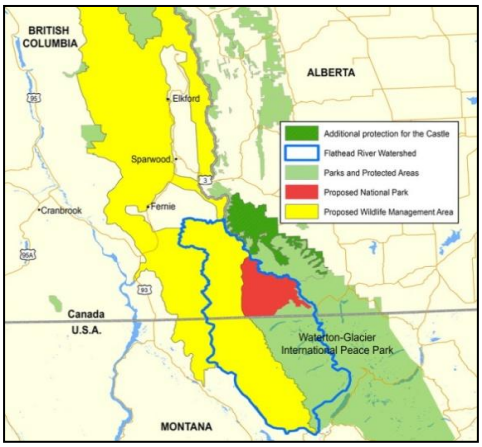


Figure 1. Conservation Plan of Waterton-Glacier International Peace Park [6].

Ecological Functions: The park is composed of forest, prairie, glacial and alpine attributes as well as mammals and plant species [7]. It is placed on the western part of the Interior Great Plains of North America and includes precious elements of Great Plain's plants. The park combines forest belts, great glacial lakes, huge mountains, deep canyons, and prairie grasslands, and rivers in the vast protected region. Therefore, by conserving the nature, the park consolidates the relationships between peace and nature.

2.2. The Great Limpopo Transfrontier Park (Among Mozambique, South Africa, and Zimbabwe)

Major features: The huge park consists of national reserves and parks, sanctuaries, private and communal land considered among three countries of Mozambique, Zimbabwe, and South Africa [8]. South Africa's Kruger National Park, Mozambique's Gaza Province, and Zimbabwe's Gonarezhou National Park are the main and largest parts of combination. The Great Limpopo as the largest cross-border park in Africa aims to facilitate the elephant's migration in particular to huge ecological zones as well as improving tourism opportunity through removing the borders between Mozambique and South Africa [9] (Fig. 2).

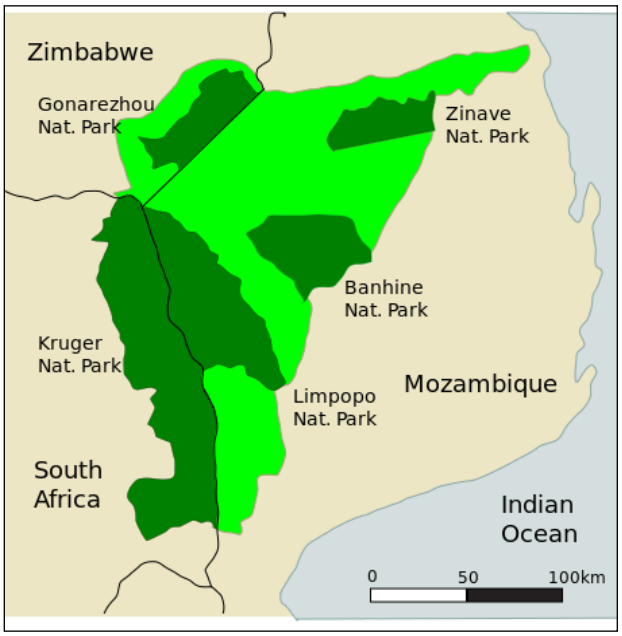


Figure 2. Sketch map of Great Limpopo Transfrontier Park [10].

Ecological Features: The Great Limpopo Transfrontier Park includes four main landscape categories of river valleys, granite plateau, lowland plain, and mountain range in a generally dry landscape. There are five major rivers flowing from west to east in this region. In general, the park has an ecosystem of lowland savannah divided by the Lebombo Mountains extending along the border between Mozambique and South Africa, with mild temperatures and minimal rainfall over year [11].

The conflict salvation increases the wildlife health by enhancing genetic diversity within populations and a general improvement in food resources and ecological habitats [9].

2.3. "W" Transborder Parks (among Benin, Burkina Faso, and Niger)

Main features: The W Park is a huge international protected area, including 1 million hectares of a surface coverage shared among three countries of Burkina Faso and Niger, Benin. The park takes its name "W" from a geometrical figure made by the Niger River between the mouth of the Me´krou River in Benin and the Tapoa River in Burkina Faso.

The World Heritage Convention registered the park as UNESCO World Heritage area in 1996. Following year, in 2002, it was added as a Transboundary Biosphere Reserve by the Man and Biosphere Program [12].

Occurrence of human poverty in the area has required the W park periphery to have environmental and economic forces. Thus, transforming this natural reserve into a true peace park is a solution that could resolve conflicts engendered by prior management [5]. It would be regarded the park as a tool that belongs not only to the state and national officials, but to the border communities and populations regarding their rights and duties of the park management (Fig. 3).

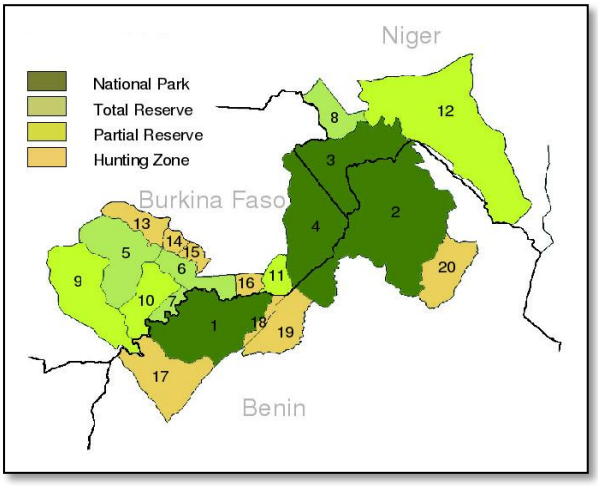


Figure 3. IUCN Protected areas of the WAP [13].

Ecological Features: The park is famous for its large animals and mammals and provides an accommodate for some wild African elephants. The National Park is also one of the last habitats for the cheetah population of Northwest Africa. At least, 15-25 animals of this rare cat are estimated in the park whose populations is obviously increasing.

Around 350 bird species are identified in the "W" park that includes particularly transitory migrating species. It has been recognized as an important bird region by the International Bird Life.

2.4. Kavango - Zambezi Transfrontier Conservation Area (KAZA) (among Namibia, Angola, Zambia)

Main features: KAZA is located in a site where the political borders of five countries meet. It is composed of a large part of the Okavango Basin and Delta and the Upper Zambezi basin. This ecological region consists of southwestern Zambia, the northern wildlands of Botswana, western Zimbabwe, the Caprivi Strip of Namibia, and the southeastern corner of Angola [14]. It aims to conserve and organize the biodiversity and the common cultural and natural resources of the KAZA Transfrontier Conserved Area to protect viable and healthy communities of wild species (Fig. 4).

Figure 4. Kavango - Zambezi Transfrontier Conservation Area [15].

Ecological Features: Hwange National Park, the Okavango Delta in Botswana, Chobe National Park and the Victoria Falls are the sites included in the park. The confluence of Zambezi River and the Chobe River are located in the center of the site where the borders of Zimbabwe, Botswana, Zambia, and Namibia meet.

Vulnerable population of cheetah, 250,000 of African elephant, African wild dog and Wattled Crane and Nile crocodile are the animal species of the area [16].

2.5. Binational Red Sea Marine Peace Park (between Israel and Jordan)

Main Features: The Red Sea Marine Peace Park belongs to Israel and Jordan. Israel and Jordan have round 41 kms of shared shoreline located along the northern Gulf of Aqaba. This park connects Israel's Coral Reef Reserve in Eliot and Jordan's Aqaba Marine Park (Fig. 5).

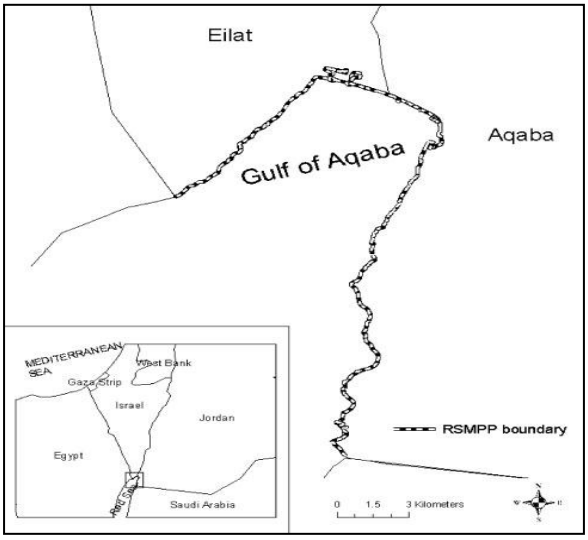


Figure 5. Locus map of the Red Sea Marine Peace Park [17].

Realization of the spectacular and unique nature of the Gulf has caused that each country takes steps for protecting the environment of coral reef [18]. Israel and Jordan have agreed to cooperate together unlike their political separation. The two countries clearly felt that the region will rapidly become a dead zone and a degraded area without correct management and pollution controls. The main objectives of the creation of this park are to protect the shared marine ecosystem and costal resources and to foster coordination and peace between the two countries [19].

Ecological Function: The Gulf of Aqaba with 180 kms length and 20 kms width is a semi-enclosed sea enlarged in northern part of the Red Sea. In the past, the Red Sea was famous for its exceptional corals, varieties of fish and its marine life that many of them were unique in the area. However, now, the coral reefs in the region are depredating particularly because of their isolation from the oceanic process of flushing and circulation, and also

extensive pressure of fishing, tourism, and land use development. The proposed marine peace park has been considered between the shores and the surrounding towns of Eliot and Aqaba in the northernmost stretch of the Aqaba Gulf [20].

2.6. Iona - Skeleton Coast Transfrontier Conservation Area (shared in Angola, Namibia)

Main Features: There is an agreement between Namibia and Angola to cooperate together in order to develop a transfrontier park. Main components of these parks are four areas that include Namibia Partial Reserve in Angola, the Iona National Park in Angola, Erongo Region known as the North West People's Conservation Area, The Skeleton Coast National Park (Namibia), and a suggested conservation zone in Namibia involving native communities in the Kunene. The youngest component was established more than 35 years ago, while the others show a longer history. After Angolan civil war, the park got damaged due to the infrastructure destruction and illegal poaching. So, some restorative activities were required to be implemented by the government over the park [20].

Ecological Feature: The Iona National Park and the Skeleton Coast National Park both emerge in a desert zone including the Namib Desert. The Iona National Park is known for its impressive rock structures and incredible mountains, however the Skeleton Coast National Park is rich in substances like diamonds and other gemstones.

The Atlantic Ocean in the western border of the Skeleton Coast National Park has brought much more diversity to the zone by the cold-oceanic current of Benguela (Fig. 6). The Namib Desert extending northwards of Iona has similar marine species to those which are found in Namibia Skeleton Coast Park and the adjacent areas. The black-faced impala and the Welwitschia mirabilis plant are the examples of the area species.

Figure 6. Otarie Del Capo, Skeleton Coast National Park /Namibia [21].

2.7. Mnazi Bay-Ruvuma Estuary Marine Park (in southern Tanzania, on the Mozambique border)

Main Features: The park is placed in the Mtwara region of Southeast Tanzania and covers the whole district towards the border of Mozambique. The area has extensive biodiversity values covering 33% of the land's biodiversity. The park enlarges from the northern part of the Ruvuma Estuary to Mnazi Bay which includes the headland of Ras Msangamkuu.

The park has embedded 11 villages and 8 small towns. Around 30,000 individuals whose livelihood depends on marine resources, live in the park. Poverty is one of the main challenges that limits the areas' development [22].

Ecological Features: The main environmental features located in the park include salt pans, seagrass beds, rocky and sandy shoreline, mangroves, mudflats, fringing coral reefs, lagoonal patch reef, three islands of Namponda, Mongo, and Kisiwa Kidogo, and numerous small rocky islands.

In addition, the park is the the home of various populations of dolphins, turtles, whales, birds specifically Crab-plovers which led to the area designation to a significant bird area in 2001.

To the marine protected park, various goals are associated as well as global biodiversity protection (Fig. 7).

Figure 7. Mnazi Bay-Ruvuma Estuary Marine Biodiversity [23].

Another important and rare component in the park is incredible sand dunes of Msimbati channel with more than 15 m height, and around 3 km length extending along the coast [22].

3. Results and Discussion

Peace Park is a classification that integrates peace and cooperative management of ecosystems and cultural

resources across jurisdictional boundaries. Transboundary protected areas (TBPAs) seem that they can handle and mitigate the critical ecological issues associated with borderlands, while there are lots of complex issues such as international cooperation, ecological management, security and budget challenges which should be addressed and studied.

According to Anne Hammill and Besanc, transboundary conservation areas and peace parks have been contributed to peace and cooperation between countries and nations by:

- Building discussions among neighboring countries that have environmental, social, and economic interests in the zones over the political boundaries.
- Providing control and security over sources in the border land in benefitting of the real owners.
- Generating common opportunities for sustainable development, ecotourism, and so on.
- Creating a sustainable net of relationships between protected area's managers of the involved countries, government and local actors such as international NGOs [24].

However, in these regions with history and experience of conflict, the proposed peace parks can inadvertently exacerbate the condition. So, at first steps, it is essential to analyze the relation between conflict and protected areas.

Transboundary peace parks offer different benefits and results for different groups. For environmental conservationists, they are tools for improving and protecting biodiversity; for mining and oil companies, a source of income and revenue; for tourism actors, a potential for ecotourism development; for military, a place of refuge in period violent and war; and for neighboring local communities, the peace parks can limit accessibility to the natural sources [24].

The main assumption of environmental peacemaking is that how protecting environment can lead to cooperation among the countries. TBCAs deal with different social, cultural and economic forces and interaction at work. They may lead to unexpected results such as destitution, social discrimination, dispute over resource rights, or ethnic contention.

Therefore, a series of approaches were established to integrate the dispute perspective into management and planning of the development projects. The Peace and Conflict Impact Assessment (PCIA), occurred in the mid-1990s by the work by Ken Bush and Luc Reychler is one of the approaches for assessing the effect of those projects and parks [25-26].

The Peace and Conflict Impact Assessment contains the following features and steps:

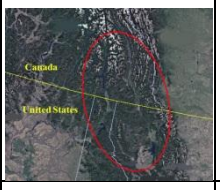
1. Mapping of conflicts which analyze the dynamics and causes of a dispute on a specific development program.
2. Mapping of the project that reviews the initial objectives, sub-structural purposes, location, stakeholders, timing, personnel, beneficiaries, operational partners, financial and physical needs.
3. Determining the effect of conflict on the program to examine how the conflict has impacted on intervention management.
4. Defining the effect of program on the conflict to examine how various aspects of the interference have contributed to make peace in the area.
5. Recommending according to the all done above to modify the intervention so that it meets the goals.

To create a transboundary protected area, 5 main steps are suggested: The first step is to analyze natural environment; cultural heritage; socio-cultural economic environment; agriculture systems; and environmental quality problems. The second step is to determine the

Table 2. Summary of four cases characteristics as Terrestrial Transboundary Conservation Areas.

Name	Location	Year	Area	Included Sites	Main Objective
W" Transborder Parks		1954	10,000 km^2	W National Parks, Arly Reserves, Pendjari national Park	Resolve of conflicts engendered by prior management approach; Increase of the wildlife number; Control of the poaching and divagation of the cattle, bush fires, ecotourism and tourism hunting
Kavango - Zambezi Transfrontier Conservation Area (KAZA)		2011	444,000 km^2	the Caprivi Strip of Namibia, the southeastern corner of Angola, southwestern Zambia, the northern wildlands of Botswana and western Zimbabwe	Maintenance of the shared natural and cultural heritage resources and biodiversity

Table 2.(Cont.) Summary of four cases characteristics as Terrestrial Transboundary Conservation Areas.

Name	Location	Year	Area	Included Sites	Main Objective
Waterton-Glacier International Peace Park		1932	457,614 ha	Waterton Lakes National Park in Alberta and Glacier National Park in Montana	Management of the land, wildlife and resource uses, including riparian zone management, old-growth forest management areas, and wildlife connectivity.
The Great Limpopo Transfrontier Park		2000	37 572 km²	Kruger National Park in South Africa, Gonarezhou, National Park in Zimbabwe, Limpopo National Park in Mozambique	Facilitation of the wildlife migration; promotion of tourism activates through loosening of the borders; Development of the eco-tourism to the area

planning approaches such as environment-sustainable development approach, community participation approach. The third one is to produce plans and suggestions related to management plans including base maps for the selected site. The fourth is zoning the area that defines areas with special protection, areas with potential for tourism and recreation and so on. The last one is to integrated monitoring after plan prepared and observing the situation conflicting with the objective to do necessary arrangement and feedback [1].

Table 3. Summary of three cases characteristics as Coast Transboundary Conservation Areas.

Name	Location	Year	Area	Included Sites	Main Objective
Binational Red Sea Marine Peace Park		1999	11 km of shoreline	Jordan's Aqaba Marine Park and Israel's Coral Reef Reserve in Eliot	Protection of the two countries' shared marine resources while fostering peace and coordination
Iona – Skeleton Coast Transfrontier Conservation Area		2003	19,600 Km^2	the Iona National Park (Angola), Namibia Partial Reserve (Angola), the Skeleton Coast National Park (Namibia) and a proposed contractual conservation area (Namibia)	Restoration and control over parks against illegal poaching and destruction of infrastructure; Protection of the marine life
Mnazi Bay-Ruvuma Estuary Marine Park		2000	650 km² (220 km^2 is terrestrial and 430 km^2 is aquatic)	The northern portion of the Ruvuma Estuary to Mnazi Bay, including the headland of Ras Msangamkuu	Protection of the wild life serving as reproductive and nursery grounds for many finfish and crustaceans

4. Conclusion

According to the cases surveyed in this research, some important achievements of peace parks or TBPAs are summarized here are:

- improving natural processes and enhancing the ecosystem integrity through coordinating the management approaches of natural resources;

- consolidating the coordination of the biological and cultural resource management and reinforce economic, social and other cooperation between stakeholders and governments;

- encouraging international collaboration and partnership in establishing a common management of natural and cultural sources;

- generating plans and strategies so that the local communities can utilize and receive advantage from peace parks;

- developing tourism opportunities over borderland in order to generate economic and social development in the region.

With no doubt, ignoring borders and military infrastructures in the peace parks can act effectively in terms of biodiversity and migratory species. However, their functions in dealing with the various challenges to provide peace do not seem clear. Regarding IUCN definition, international peace parks possess great potential for sustainable development and livelihood creation, while it seems that the conversational plans have been considered more than other criteria.

Even though various projects were done in some African countries over the last decades, the issue of peacemaking by environmental planning is completely initial in some other countries such as Asian and Middle East which are suffering from environmental issues over their international borders and need more scientific studies that cover general and specific issues of the subject.

References

[1] Pouya S., Özkul D. B., 2017. Creating peace park between Turkey and Georgia, The Journal of International Social Research, **10** (53). 510-526.

[2] Laverty F. M., Gibbs P. J., 2007. Ecosystem Loss and Fragmentation: Synthesis: Lessons in Conservation, 1, 72-96.

[3] Cunningham H., 2012. Companion to Border Studies: Permeabilities, Ecology and Geopolitical Boundaries, Blackwell `Publishing Ltd. Published 2012 by Blackwell Publishing Ltd., chapter 21, 372-384.

[4] Singh J., 1999. Study on the Development of Transboundary Natural Resource Management Areas in Southern Africa-Global Review: Lessons Learned, Biodiversity Support Programme, Washington D. C.

[5] Ali S. H., 2007. Peace Parks: Conservation and conflict resolution, MA: MIT Press, Cambridge.

[6] http://voices.nationalgeographic.com (2017, January).

[7] Dingwall R. P. (IUCN/WCPA) And Rao K., (UNESCO World Heritage Centre SEPTEMBER, 2009. Waterton-Glacier International Peace Park (Canada And Usa) Report Of The Reactive Monitoring Mission.

[8] Duffy R., 1997. The environmental challenge to the nation-state: superparks and national parks policy in Zimbabwe. Journal of Southern African Studies **23**(3). 441-451.

[9] King B., Wilcox S., 2008. Peace Parks and jaguar trails: transboundary conservation in a globalizing world, GeoJournal, Springer Science+Business Media B.V.

[10] https://en.wikipedia.org/wiki/Great_Limpopo_Transfrontier_Park, (2017, January).

[11] Carruthers J., 1995. The Kruger National Park: A social and political history. University of Natal Press, Pietermaritzburg.

[12] Eco guides of WAP, Parks Tapoa Association of Ecoquides and Ecosystem Protection (AEGT/PE), BIALA, the tourism association of Tapoa Province, (2010) Received from : http://www.ecoguides-wap.net/w.html

[13] http://wikitravel.org/en/W_National_Park (2017, January).

[14] Cumming, D. H., 2008. Large Scale Conservation Planning and Priorities for the Kavango-Zambezi Transfrontier Conservation Area, A report prepared for Conservation Internationa, Large scale conservation planning , Kaza Tfca.

[15] https://en.wikipedia.org/wiki/Kavango%E2%80%93Zambezi_Transfrontier_Conservation_Area (2017, January).

[16] Peace Parks Foundation, The global Solutions, Received from: http://www.peaceparks.org/index.php

[17] Israel Ministry of Foreign Affairs, 1997. Binational Red Sea Marine Peace Park, Israel Environment Bulletin, **20** (4), 1997-5758.

[18] Davis B. J., 2008. Marine Peace Parks: Establishing Transboundary MPAs to Improve International Relations and Conservation, International News and Analysis on Marine Protected Areas, **9**(9).

[19] Portman E. M., 2007. Zoning design for cross-border marine protected areas: The Red Sea Marine Peace Park case study, Elsevier, Journal of Ocean & Coastal Management, **50**, 499–522.

[20] Ministry of Environment & Tourism Namibia, Iona-Skeleton Coast Transfrontier Park, received from http://www.met.gov.na/national-parks/iona-skeleton-coast-transfrontier-park/298/

[21] http://www.travelrevolution.com/tours/namibia-inliberta/ (2017, January).

[22] Ministry of Natural Resources and Tourism, Tanzania Marine Parks and Reserves Unit; General Management Plan, Board of Trustees for Marine Parks and Reserves, The United Republic of Tanzania (2005).

[23] http://www.tfcaportal.org/content/MQTMCA (2017, January).

[24] Hammill A., Besanc C., 2007, Measuring Peace Park Performance: Definitions and Experiences, chapter 1, Peace parks : conservation and conflict resolution / edited by Saleem H. Ali., 2007 Massachusetts Institute of Technology, 23-4.

[25] Bush K., 1998. A measure of peace: Peace and conflict impact assessment (PCIA) of development projects in conflict zones. Working Paper 1.The Peacebuilding and Reconstruction Programme Initiative and The Evaluation Unit, IDRC.

[26] Reychler L., 1999. The Conflict Impact Assessment System (CIAS): A Method for Designing and Evaluating Development Policies and Projects. CPN, Ebenhausen.

Koc. J. Sci. Eng., 1(2): (2018) 42-45

Kocaeli University

Kocaeli Journal of Science and Engineering (KOJOSE)

http://dergipark.gov.tr/kojose

Degradation of 2-Chlorophenol Present in Effluent Water by Advanced Electrochemical Method

M. Saeed ULLAH[1,*], Aziz Ur Rehman MAJID[1], Umair ZAHID[2], Ghulam ABBAS[3], Yusra SHAHID[2], Ayesha MAROOF[5]

[1] *Department of Chemical Engineering, Kocaeli University, Kocaeli, 41310, Turkey*
[2] *University of the Punjab, 54000, Lahore, Pakistan*
[3] *Department of Chemical Engineering, University of the Gujarat, 50700, Gujarat, Pakistan*
[4] *Istanbul Ticaret University, Küçükyalı, 34840, Istanbul, Turkey*

Article Info

Research paper

Received : 17/04/2018
Accepted : 24/10/2018

Keywords

Electrochemical Treatment
Electrodes
Harmful Chemicals
Phenolic Degradation
Treating Time
Voltages

Abstract

Water is an important of life. When it is polluted, it disturbs not only human but also aquatic life. There are no of chemicals that contaminate the water. Industries generate different types of chemicals, which pollute the water. Effluent from these industries contains heavy metals, BOD, COD and phenolic compounds. Water pollution is a very serious issue. Different ways are available to treat the waste water. Flocculation, sedimentation, coagulation, photolysis and electrochemical methods are used for treatment of waste water. Phenolic compounds are the most harmful chemicals present as contamination in waste water. Phenolic compound accompanied with chlorine can exist as mono-chlorophenol, di-chlorophenol and tri-chlorophenol. These compounds are very carcinogenic in nature so their presence is dangerous for human as well as aquatic life. In this research electrochemical method is used to treat *o*-chlorophenol. Effect of electrodes, voltages and treating times on the removal efficiency have been studied. Stander sample of 100ppm from stock material have been prepared as an analogues to the waste water of industries. HPLC/UV detector is used to analyze the treatment effects. Graphite electrode, 20 volts and 20 min operating time is the most effective parameters that removes about 60% of the initial concentration of 2-CP (ortho-chlorophenol).

1. Introduction

Water is a transparent, tasteless, odorless, and nearly colorless chemical substance that is the main constituent of Earth's streams, lakes, and oceans, and the fluids of most living organisms. It is usually polluted due to different industrial activities done by human beings [1]. For drinking purpose, water should be clean and free from contamination. It is the first and fundamental right of human beings and other organisms. For this purpose, we should not only install some technological equipment for the reuse of water, but also have to save our natural resources from contaminations. To make these efforts fruitful and serious collective efforts are being done all around the world. Basically if we treat our waste from pollutants which have been adverse effects on the naturally available water resources, we will be able to save our natural resources of water as well as aquatic lives [2]. It is necessary to eliminate or treat different contaminants present in wastewater before drainage. Numbers of ways are available to treat the waste water. Flocculation, sedimentation, coagulation, photolysis, advance oxidation, ozonation and electrochemical methods are used for treatment of wastewater [3- 7].

Phenolic compounds are the most harmful chemicals present as contamination in wastewater. Phenolic compounds consist of mono-chlorophenol, di-chlorophenol and tri-chlorophenol. These compounds are very toxic and their presence is dangerous for human as well as aquatic life. These compounds are found in the wastewater of textile[8], pharmaceutical, petrochemicals, pesticides and synthetic fiber industries [9]. Environmental Protection Agency (EPA) has given the standards for the wastewater. To reduce the quantities of phenolic compounds

* Corresponding Author: engrsaeed147@gmail.com

in the exhausted water a number of treatments are available [8,10].

In Pakistan, most common method to treat the toxic compounds is the biological method [11]. In which microbial activities have been done to decompose or degrade the toxic organic components of the wastewater [12]. In this scenario the activity of biological sludge is the most important, which is usually decreased due to the varying concentrations of phenolic compounds. As well as it is due to the toxic in nature, sometimes these methods seem inefficient. Secondly, the biological treatment requires a type of pond and due to high rates of commercial land, this procedure feels to be high initial cost. Other drawback of this method is the disposal of bio sludge [13].

Other method is the chemical treatment in which different chemicals are used to maintain the pH and other parameters of the wastewater. Sometimes oxidation process is also used for this purpose. Some highly reactive oxidizing agents are used like ozone [14]. The nascent oxygen liberated reacts with different chemical compounds to oxidize them. In case of phenolic compounds oxygen reacts with benzene ring and it converts into the aliphatic straight chain carboxylic acids. When industrialist calculate the comical effect it seems too much high [15].

On considering these drawbacks, some sorts of solution required more effective from these conventional methods and the operating should be lower. Electro chemical oxidation process is one of the best fits in this situation, a continuous running channel can be made with the wall of factory, [16-17] which can save the space and land.

2. Materials and Methods

For the preparation of 100 ppm solution of 2-CP, 0.1 g of 2-CP have been taken and mixed with 1000 ml of distilled water. Solubility of 2-CP is low in water. To increase the solubility of ortho chlorophenol 0.2 ml of 1 ppm NaOH, solution has been added into the sample. After 30 min of stirring, neutralize the pH of the solution by using phosphoric acid. For electrolysis process some ions should be available in the sample so that electricity can pass through the solution and degrade the 2-CP in to aliphatic hydrocarbon. To obtain required results, 2 drops of 1 ppm solution of NaCl have been added into the standard solution. After that, 20 µl of solution have been taken for testing purpose on the HPLC and find the absorbance.

Electrochemical method is being used to treat *o*-chlorophenol and effect of different electrodes on the removal efficiency. The samples initially consist of 100 ppm solution *o*-chlorophenol. Samples treated for different timings as well as for same time at different voltages and the different electrodes, to study the removal efficiency in an electrolytic cell. Voltages are 5, 10, 15 and 20 volts. Electrolytic cell have made that it can contains 200 ml of sample water volume. Electrode dimensions are 0.0762 meter X 0.1016 meter. Time chosen for reaction is 5, 10, 15 and 20 minutes. 2 ml of 10 ppm salt solution is added for the conductance of electricity. HPLC / UV detector has been used for the quantitative analysis. Lambda max selected for Chlorophenol is 276 nm. With 1 ml/min flow rate of mobile phase (acetonitrile + water + methanol) with equal volume mixture the detection time is 11:35 min. Different concentrations of chlorophenol show different values of absorbance. Standard solutions of know concentration have been made and a reference calibration curve have been drawn to find the unknown concentrations of phenolic compound in treated water samples. By using Formula (1):

$$Y = m X + C \quad (1)$$

- $Y = 5.0107 x + 0.5714$
- Y = Absorbance (mAU) obtained the peak value
- m = Slope of line (5.0107)
- X = Value of concentration on X-axis (ppm of solution/ concentration of 2-CP in water)
- C = Y Intercept (0.5714)

Calibration curve helps to find the value of unknown concentration of solution. From these parameters one can calculate the degraded amount of 2-CP (2-Chloro Phenol) in water. Now subtract the reflected value from the standard value of master solution and again use the % age formula to calculate it.

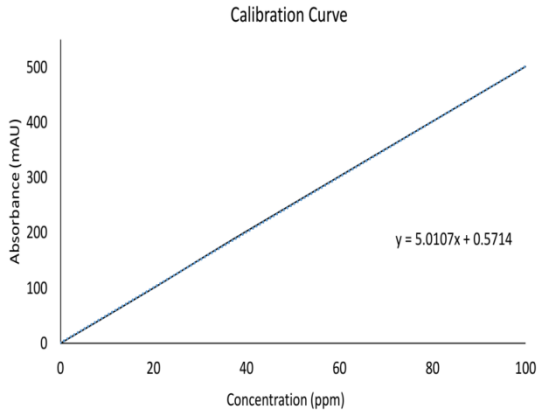


Figure1. Calibration curve for 2-cholorophenole.

3. Results and Discussion

In accordance with the parameters studied graphite electrodes shows higher removal efficiency (Fig. 2) as compared to copper (Fig. 3) and copper shows better efficiency from iron electrode (Fig. 4). Voltage has directly

proportional effect on the degradation of chlorophenol. As well as treated time & voltages have also direct relationship with efficiency. Iron electrode shows a different trend up to 7 min 10, 15 and 20 volts shows a similar efficiency and after that all trend lines show their liability separately (Fig. 4). 20 volts and 20 min operating time are the best conditions for degradation of 2-CP. Graphite & copper electrode (Fig. 2,3) shows less effective region 10-15 min operating time (other than 10 volts) in this time period, some side reactions start and the effectiveness of the process decreases. Iron electrode shows that a different trend in starting a steep line indicates the degradation reaction moving very fast (other than 5 volts).

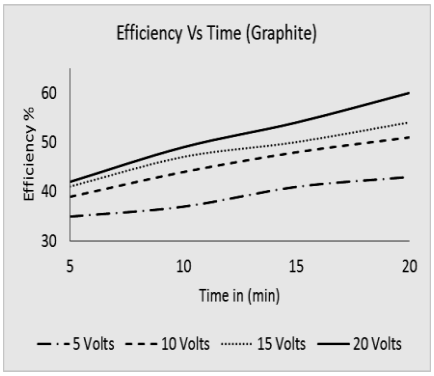


Figure 2. Graphite Electrode.

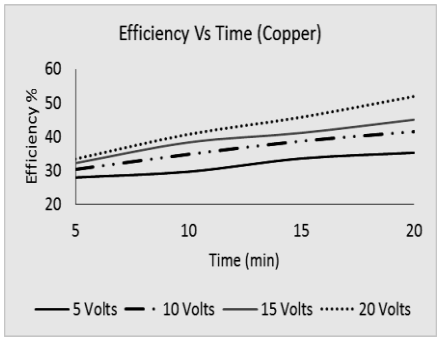


Figure 3. Copper Electrode Efficiency.

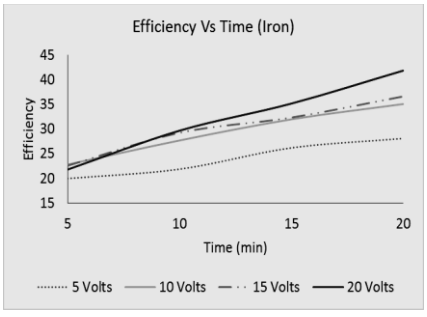


Figure 4. Iron Electrode Efficiency.

4. Conclusions

Trends of graphs of experiments show that treated time and voltages have a direct relationship with the degradation of 2-CP. As time increases, the efficiency of this process increases. Same as voltage increase will show good results on the gradation up to 20 volts. Nature of electrodes has been also studied. As graphite is inert and semiconductor in nature, so its efficiency is much higher than copper and iron electrodes. Iron is a cheaper one, but its efficiency remains between the limit of 20% to 41.90% that is lesser than copper and graphite electrodes. Graphite electrode efficiency remains between the range of 35% to 60%. This means that graphite can show better results on lower voltages even 5 volts, 35% efficiency is greater than both copper & iron. Ultimately at 20 min and 20 volts the efficiency of the process goes to 60%. Copper electrodes show its efficiency in the limit of 28% to 51.85%. These results show that in a short time period for treatment and lower voltage the efficiency of copper electrode remains ineffective as compared to graphite electrodes for the industrial point of view. Copper has a higher market value as compared to iron. On the other hand the upper limit of the process shows the comparable results with respect to graphite electrodes. At 20 min of treatment time and 20 volts, the process shows its efficiency at 51.85%. The similar meaning of these results is on using 20 min residence time and 20 volts potential difference in process will remove 50% of the 2-CP from waste water. Iron electrodes when operated on 5 min and 5 volts the efficiency of the process comes about 20%.

While residence time increased up to 20 min as well as volts up to 20, the process shows its efficiency 41.9%. When we compare copper and iron electrodes from an industrial point of view copper rates in market ranges from 450 PRs/kg while iron rate is only 60 PRs/kg, which makes the maintenance and initial cost of the plant 86% cheaper than copper electrode plant. While on the efficiency basis, we can see there is only difference of 26%. This drawback can be covered by using 26% more iron electrodes in the process. Cost effect of these extra electrodes will be negligible. While using these type of arrangements we get the results of up to 51.85% degradation of 2-CP from the exhaust water of the industry. For optimized conditions and industrial solution combination of electrodes has to be used. 1st install Iron electrode and use 20 volts for 20 min treating time which shows about 41.9% removal of total concentration. Then use graphite electrode voltage 20 and treating time 20 min which shows the efficiency of 60%. This means that total 76.76% removal can be obtained within 40 min of residence time.

In this research work degradation of 2-chlorophenol has been studied. There are many parameters which affect the degradation reaction or support the side reactions. The effects of three parameters have been studied here. Parameters are given below;

- Treating Time
- Voltage
- Nature of Electrodes

Each parameter has a significant effect on the degradation process. But there are other parameters that are missing here; surface area, consequently the electric current density and concentration. The combination of these parameters along with above given three parameters can give the most optimal solution in the industry. Through these results we can reduce the operating time and operation cost as well. We can use alternate electrodes and their combinations. These arrangements can help us to reduce the reactor volume, installation and maintenance cost. Surface area and current densities should be studied with respect to the time, voltage and electrodes. The surface area can be increased by using perforated electrodes that not only reduce the pressure drop but also increase the degradation efficiency.

References

[1] Chen G., Electrochemical technologies in wastewater treatment, 2004. Sep. Purif. Technol., **38**(1), pp. 11–41.

[2] Nguyen T. A., Juang R. S., 2013. Treatment of waters and wastewaters containing sulfur dyes: A review. Chem. Eng. J., **219**, pp. 109–117.

[3] Lin S. H., Chen M. L., 1997. Treatment of textile wastewater by chemical methods for reuse. Water Res., **31**(4), pp. 868–876.

[4] Sripriya R., Chandrasekaran M., Subramanian K., Asokan K., Noel M., 2007. Electrochemical destruction of p-chlorophenol and p-nitro phenol - Influence of surfactants and anode materials. Chemosphere, **69**(2), pp. 254–61.

[5] Sala M., Gutiérrez-Bouzán M. C., 2014. Electrochemical treatment of industrial wastewater and effluent reuse at laboratory and semi-industrial scale. J. Clean. Prod., **65**, pp. 458–464.

[6] Körbahti B. K., Tanyolaç A., 2003. Continuous electrochemical treatment of phenolic wastewater in a tubular reactor. Water Res., **37**(7), pp. 1505–1514.

[7] Cañizares P., Paz R., Sáez C., Rodrigo M. A., 2009. Costs of the electrochemical oxidation of wastewaters: A comparison with ozonation and Fenton oxidation processes. J. Environ. Manage, **90**(1), pp. 410–420.

[8] Article, P. A. N. A. T. of Contents, P. D. of A. 4-C. by S.-I. Polyoxometalates. Bin Yue S. J., Zhou Y., Xu J., Wu Z., Zhang X., Zou Y., , 2002. Department of Chemistry, Fudan University, Shanghai 200433, Photocatalytic Degradation of Aqueous 4-Chlorophenol by Silica-Immobilized Polyoxometalates, pp. Environ. Sci. Technol., **36** (6), pp. 1325–1329.

[9] Zhang W., Qu Z., Li X., Wang Y., Wu J., 2012. Je Sc Sc, **24**(3), pp. 520–528.

[10] Yoon J. H., Shim Y. B., Lee B. S., Choi S., Won M. S., 2012. Electrochemical degradation of phenol and 2-chlorophenol using Pt/Ti and boron-doped diamond electrodes. Bull. Korean Chem. Soc., **33**(7), pp. 2274–2278.

[11] Zhang F., Feng C., Li W., Cui J., 2014 . Indirect Electrochemical Oxidation of Dye Wastewater Containing Acid Orange 7 Using Ti / RuO 2 -Pt Electrode. Int. J. Electrochem. Sci., **9**, pp. 943–954.

[12] Jara C. C., Martínez-Huitle C. A., Torres-Palma R. A., 2009. Distribution of Nitrogen Ions Generated in the Electrochemical Oxidation of Nitrogen Containing Organic Compounds. Port. Electrochim. Acta, **27**(3), pp. 203–213.

[13] Zhang R., Zhang C., Cheng X., Wang L., Wu Y., Guan Z., 2007. Kinetics of decolorization of azo dye by bipolar pulsed barrier discharge in a three-phase discharge plasma reactor. J. Hazard. Mater, **142**(1–2), pp. 105–10.

[14] Wang H., Wang J., 2007. Electrochemical degradation of 4-chlorophenol using a novel Pd/C gas-diffusion electrode, Appl. Catal. B Environ., **77**(1–2), pp. 58–65.

[15] Jamil T. S., Ghaly M. Y., El-Seesy I. E., Souaya E. R., Nasr R. A., 2011. A comparative study among different photochemical oxidation processes to enhance the biodegradability of paper mill wastewater. Hazard. Mater, **185**(1), 353-8.

[16] Polcaro A. M., Palmas S., Renoldi F., Mascia M.,1999. On the performance of Ti/SnO2 and Ti/PbO2 anodesin electrochemical degradation of 2-chlorophenolfor wastewater treatment. J. Appl. Electrochem., **29**(2), pp. 147–151.

[17] Torres R. A., Lovell T., Noodleman L., Case D. A., 2003. Density functional and reduction potential calculations of Fe4S4 clusters. J. Am. Chem. Soc., **125**(7), pp. 1923–36.


KOCAELI UNIVERSITY
1992