

POLLUTION

THE IMPORTANCE OF MOBILE APPLICATION FOR REDUCING CARBON FOOTPRINT

Conflict of Interest

None declared.

Michael Siu², Rafis Abazov¹, Fatima Babazova^{1,*}

¹al-Farabi Kazakh National University, Almaty city, Kazakhstan, ²The Hong Kong Polytechnic University, Hong Kong, SAR of China

*To whom correspondence should be addressed

Associate editor: Alautdin Aliev

Received on 28 January 2017, revised on 02 February 2017, accepted on 15 February 2017.

Abstract

Motivation: Nowadays we face a problem of global warming. Global warming does not just mean that the Earth gets hotter, it means that the whole climate is changing. People can help to stop global warming that is why it is very important to know about level of their carbon footprint in order to conserve our nature. The purpose of this research was in collecting data of people's carbon footprint who are living in Hong Kong and in Almaty. That information helped us to understand how we need to work in order to try to show people their influences to the environment.

Results: We have asked through face-to-face survey and with using social network such as Facebook, Instagram, WhatsApp and V Kontakte in order to get to know people's knowledge about "carbon footprint" and total annual carbon emissions. After all, we have made diagrams. Survey proved that there is a lack of information about the ways to decreasing carbon footprint. As we expected nobody knows his or her percentage of influence to the nature. It means that we are in necessity of mobile application, which will give us knowledge about "carbon footprint". Mobile application should contain practical information about carbon footprint and calculator, which will help to people to calculate their carbon footprint. In addition, mobile application should have tips and advises which will help to reduce people's influence to the nature.

Keywords: global warming, carbon footprint, mobile application

Contact: babazova_fatima@mail.ru

1 Introduction

Nowadays we face a problem of global warming. Global warming does not just mean that the Earth gets hotter, it means that the whole climate is changing. Scientists are more than 95% certain that most of global warming is caused by increasing concentrations of greenhouse gases and other human caused (anthropogenic) activities. Certainly, people can help to stop global warming that is why it is very important to know about level of their carbon footprint in order to conserve our nature. We suppose that one third of world population know the meaning of carbon footprint, and they know that they can calculate their carbon footprints through the internet or by mobile applications. They should not only know how much percent is their carbon footprint but also know the ways to reduce it. We were looking for mobile applications, which have lots of necessary information about carbon footprint, but it was unsuccessful. Even if Appstore has such kind of application it will be paid application, and for sure, people not interested in that, because they need to pay.

Our study area is two cities: Hong Kong city and Almaty city. They are completely different. Hong Kong economically high-developed city in comparison with Almaty. As one of the world's leading international financial centers, Hong Kong has a major capitalist service economy characterized by low taxation and free trade. Almaty is the largest city in Kazakhstan, and it continues as the major commercial and cultural center of Kazakhstan.

The reason why we choose Hong Kong is that Hong Kong faces environmental changes. The changes in Hong Kong's climate in the 21st century may be summarized as follows:

- The number of very hot days and hot nights is projected to increase;
- The number of rain days is projected to decrease while the average rainfall intensity will increase;
- The frequency of extreme rainfall events is projected to increase;
- There will be more extremely wet years but the risk of extremely dry years will remain;

- Global sea level rise will lead to coastal changes all over the world, including in Hong Kong;
- The threat of storm surges associated with tropical cyclones will increase.

Over the past few decades, the world's Ecological Footprint – a measurement of humanity's demand for natural resources of our planet – has grown to alarming proportions. According to the Living Planet Report 2014, the global Ecological Footprint was 1.5 times what the planet could provide; meaning it would take 1.5 years for the Earth to regenerate the renewable resources which humanity uses in a year.

In Hong Kong today, the situation is even more severe. According to the latest research by WWF (World Wide Fund for Nature) and Global Footprint Network, on Hong Kong's Ecological Footprint, Hong Kong people are living beyond the Earth's limits. We need 3.1 Earths if everyone led the lifestyle of Hong Kong people.

The natural resources Hong Kong people use exceed what is available in the territory by an astounding 540 times. This difference, called "ecological deficit", is the largest in Asia. How has this happened? It all comes down to citizens' lifestyles. Over 60% of the total household Ecological Footprint comes from four categories: "Food", "Energy", "Transportation" and "Clothing".

We all need to urgently recognize the importance of living our lives within the boundaries of the Earth's finite natural resources. It is time for us to review our consumption practices and reduce the size of our Footprint. By changing the way of lifestyle, Hong Kong can become a much more sustainable city that drives positive changes in the region, and even to the world.

Massive increases in human population, urban development and consumption of renewable natural resources in the last century have created an imbalance in human's relationship with our planet. Since Hong Kong cannot provide the huge diversity and amount of natural resources, Hong Kong imports most of what citizens need.

The good news is that people do not have to be a scientist to save the planet. By making better choices in daily life, we can reduce their Ecological Footprint and conserve planet's valuable natural resources. Carbon footprint is a way of showing people's carbon emissions, compared to other people and other countries. It is people's impression on the planet. By carbon emissions, we mean greenhouse gases, including carbon dioxide, methane and nitrous oxide. Humans produce these gases in vast quantities by doing things like burning coal, oil and gas for energy and cutting down forests. Individual emissions are built up from the energy people use personally for electricity and travel, as well as the energy that is required to produce your food and all the other stuff people buy, whether it is made in your country or elsewhere in the world.

2 Methods

In order to see the average carbon emissions of Hong Kong and Almaty citizens we have used online and face-to-face survey. By using their answers, we count their carbon footprint with help of online calculator, which was created by WWF-UK (World Wide Fund for Nature). WWF was founded in 1961 by a group of passionate and committed individuals with the vision and determination to change the future – for good of the natural world and for all life on Earth. Today, WWF is one of the world's largest and most respected con-

servation organizations, with a network active in more than 100 countries. WWF is currently carrying out more than 1,300 conservation projects around the planet – from small-scale local conservation projects to large-scale species protection projects, which span all continents.

The calculator is divided into four sets of questions:

- 'Food' covers diet, food waste and buying habits.
- 'Home' covers energy type and usage in the house and the presence of energy-saving measures.
- 'Travel' covers personal and public transport usage for leisure and work, and flights.
- 'Stuff' covers the purchases of consumable items.

The results are an individual footprint in percentage, which we used for analyzing and making statistics.

Then, we decided get to know people's knowledge about "carbon footprint". We have asked through face-to-face survey and with using social network such as Facebook, Instagram, WhatsApp and V Kontakte.

3 Results

According to survey, we made some statistics and analyzed taken results. Questions were:

1. Do you know what does "carbon footprint" mean? Yes/ No
2. If "Yes", do you know the ways to reduce it? I know/ I don't know

We have asked 100 people: 50 Hong Kong citizens and 50 Almaty citizens, below you can see diagrams.

We have asked 50 Hong Kong citizens, mostly we questioned students. 84% of Hong Kong people (42 people) answered me that they know what does "carbon footprint mean" and explained me what they know, other 16 % (8 people) told me that they do not know or they have heard, but don not know what exactly does it mean (Fig.1).

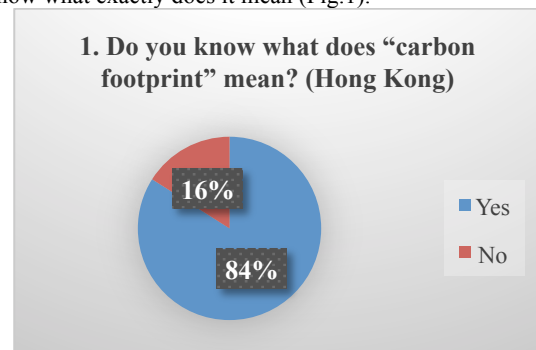


Fig. 1 – Percentages of people's knowledge about "carbon footprint" (Hong Kong)

When we were asking friends and relatives from Almaty, we were amazed that only 36 % (18 people) out of 100% (50 people) know what that terminology means, 64 % (32 people) people do not know, even they had not heard that word (Fig.2).

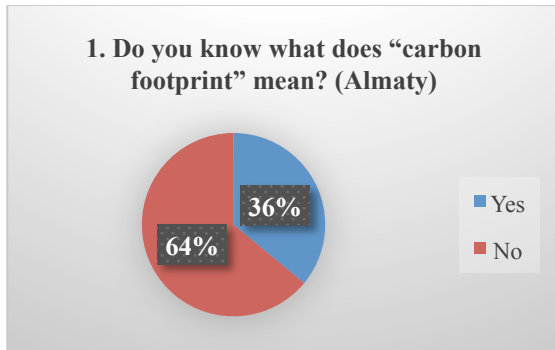


Fig. 2 - Percentages of people’s knowledge about “carbon footprint” (Almaty)

76 % (38 people) of Hong Kong students know the ways to reduce their carbon footprint, because at university, they had classes or they participated in different workshops and actions for preserving nature, another 24% (12 people) do not know exactly what to do (Fig.3).

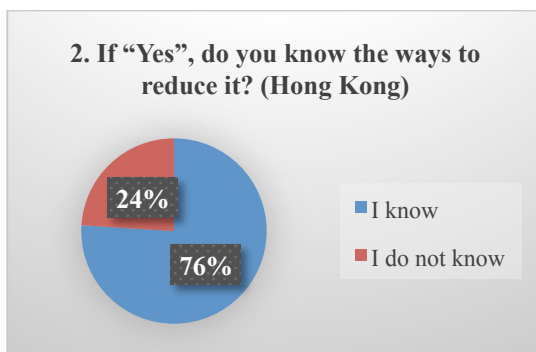


Fig. 3 - Percentages of people’s knowledge about the ways to reduce “carbon footprint” (Hong Kong)

20% (10 people) of Almaty citizens know how to reduce carbon footprint, because their specialty is connected to the ecology and they have heard from friends, others 80% (40 people) do not know (Fig.4).

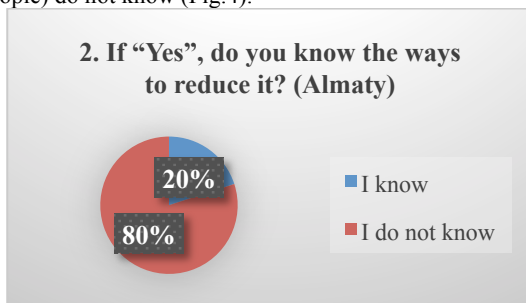


Fig. 4 - Percentages of people’s knowledge about the ways to reduce “carbon footprint” (Almaty)

Next step was collecting information about total annual carbon emissions. We have asked 100 people, 50 people from Hong Kong and 50 from Almaty city, we sent to people the links and we asked them to pass online survey. The link of that survey: <http://footprint.wwf.org.uk/>. In the end of the online survey they got results, below you can observe the diagram of results.

As you see from the graph, the average carbon emissions of Hong Kong citizens (16.6 tonnes) are bigger than Almaty’s citizens (10.7 tonnes). Anyway, both of the cities have big impact to the environment because the average worldwide carbon emission is 4 tonnes, worldwide target is 2 tonnes per person (Fig.5).

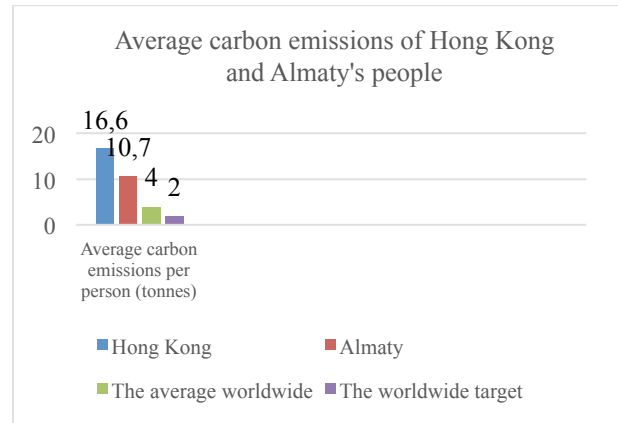


Fig. 5 - Average carbon emissions of Hong Kong and Almaty's people

The reason is that Hong Kong high-developed country, people earn a big amount of money according to GDP per capita. That is the reason why people can afford traveling, not only for business trip but also for leisure. In addition, Hong Kong people buy imported products. Almaty people mostly buy local produced products, because Almaty region one of the agriculture center of Kazakhstan. People’s from Almaty travel a lot as well, but not as much as Hong Kong people do.

In conclusion, we can examine that Hong Kong people know better about carbon footprint than Almaty people. Mostly of Hong Kong students know about carbon footprint and they know the ways to reduce it, a few Almaty students know about their carbon footprint, even if they know they are in the dark about how to minimize carbon footprint. Survey proved that there is a lack of information about the ways to decreasing carbon footprint. As we expected nobody knows his or her percentage of influence to the nature. It means that we are in necessity of mobile application, which will give us knowledge about “carbon footprint”.

The purpose of this research was in collecting data of people’s carbon footprint who are living in Hong Kong and in Almaty. That information helped us to understand how we need to work in order to try to show people their influences to the environment.

We did investigation in order to get more knowledge about carbon footprint. It was useful to make diagrams in order to show to people how it will be dangerous for future generations for the whole world if people do not reduce their carbon footprints. Mobile application should contain practical information about carbon footprint. People will have opportunity to calculate their carbon footprint. Mobile application should have tips and advises which will help to reduce people’s influence to the nature.

We hope that mobile application will increase people’s knowledge about carbon footprint. We expect that it will help to minimize carbon footprint of humanity, and people will pay

attention on what they eat and what they do in order to preserve environment.

References

RICHARD SMITH (2013). Global warming: Scientists “95% certain” humans are to blame for climate change. *Newspaper MIRROR.CO.UK is the online edition of The Daily Mirror*

WWF (2014). Living Planet Report 2014: Summary. [McLellan, R., Iyengar, L., Jeffries, B. and N. Oerlemans (Eds)]. WWF, Gland, Switzerland

Environment Bureau in collaboration with Development Bureau | Transport & Housing Bureau Commerce & Economic Development Bureau | Food & Health Bureau | Security Bureau (2015). Hong Kong Climate Change Report 2015.

WWF-UK (2016). Footprint calculator. <http://footprint.wwf.org.uk>

WWF-Hong Kong (2016). Sustainable City & Ecological Footprint. *World Wildlife Fund News* - www.wwf.org.hk

POLLUTION

CHELATE-ASSISTED PHYTOEXTRACTION OF HEAVY METALS FROM SUBSTRATUM, COMPOSED ON THE BASIS OF SEWAGE SLUDGE

Conflict of Interest

None declared.

Irina Avtukhovich^{1*}, Dmitry Postnikov¹

Russian Timiryazev State Agrarian University, Moscow, Russia, 127550, Moscow, Timiryazevskaya street, 49

*To whom correspondence should be addressed.

Abstract

The three-year field experiment was conducted on treatment facilities of town Istra to test chelate-assisted phytoextraction of Cd, Cu and Zn using EDTA and safflower dyeing (*Carthamus tinctorius L.*) on substratum, composed on the basis of sewage sludge. Chelating agent EDTA applied in rates accordingly 1; 3 and 6 mmol/kg once and annually according to the scheme of experiment. EDTA, applied in rates 1 and 3 mmol/kg of substratum improves parameters of plants' productivity. In all investigated application rates EDTA increases bioavailability of metals in the substratum and raises accumulation and uptake of pollutants by plants from substratum. In variants with annual application of EDTA in rates 1 and 3 mmol/kg the highest accumulation and removal of pollutants by plants are registered.

Keywords: sewage sludge, heavy metals, EDTA, phytoextraction, plants, rhizosphere, substratum (ground)

Contact: irina_avt@mail.ru

1 Introduction

Large quantity of sewage sludge is being amassed inside treatment facilities in Russia and the CIS countries. This liquid concentrated waste at overflow of sludge lagoon, drying bed and sludge pond is dumped in the nearest lowlands and is source of pollution for water reservoirs (Zubko et al, 2010).

Sewage sludge is expedient for applying in agriculture and forestry, in gardening and other spheres of human activity as cheap agrochemical filling agent and as a nutritious substratum when mixing with soil. However, the maximum use of sewage sludge by increase its share as a part of a substratum is hindered due to high concentrations of heavy metals.

Phytoextraction is innovative, novel and potentially inexpensive technology using higher plants for *in situ* decontamination of metal-polluted soils, sludge and sediments. By adding a chelating agent, e.g. EDTA, into the soil (substratum) under the plants with well developed biomass, the bioavailability of the heavy metals in soil (substratum) as well as their uptake by plants can be enhanced considerably (Wenzel, 2003).

2 Material and Methods

In 2010-2012 on a field site of Treatment Facilities of town Istra, Moscow region, the method of induced phytoextraction with application of chelate-forming agent EDTA was applied.

As a plant-accumulator of heavy metals was used Safflower dyeing (*Carthamus tinctorius L.*), which forms high biomass.

Chelating agent – (Na_2EDTA), disodium compound of ethylenediaminetetraacetic acid (further EDTA) - was applied in various rates according to the experiment scheme.

In experiment the vessels containing 6 kg of dry substratum (ground) were used, which were buried into the ground.

The investigated substratum was a sewage sludge mixed with wood sawdust (2:1). Properties of the substratum were as follows: total: N - 2,35%, P – 0,48% and K – 0,25%; pH=6,2; total: Pb – 19,30, Cd – 3,45, Co – 1,56, Cu – 164,6, Zn – 587,0, Al – 6260 and As – 1,57mg/kg.

The experiment consisted of 14 variants with four-multiple replication. EDTA in variants III - VIII, in rates accordingly 1; 3 and 6mmol/kg was applied once in summer 2010. In variants IX - XIV EDTA was applied in the same rates - annually (summer 2010, 2011 and 2012) according to the scheme of experiment. In 2012 the scheme of the experiment was: I – non-planted control 0 EDTA; II – planted control 0 EDTA; III – non-planted 1 EDTA; IV – planted 1 EDTA; V – non-planted 3 EDTA; VI – planted 3 EDTA; VII – non-planted 6 EDTA; VIII – planted 6 EDTA; IX – non-planted 1+1+1 EDTA; X – planted 1+1+1 EDTA; XI – non-planted 3+3+3 EDTA; XII – planted 3+3+3 EDTA; XIII – non-planted 6+6+6 EDTA; XIV – planted 6+6+6 EDTA.

Annually ground and plant's (shoots and roots) samples were collected from the vessels after harvest and analyzed for concentrations of metals Cd, Cu and Zn using atomic absorption spectrophotometer «Perkin-Elmer».

Statistical analyses of experimental results were carried out using MS Excel.

3 Results and discussions

3.1 Influence of EDTA on productivity of plants

EDTA in small rates 1 and 3 mmol/kg of ground (variants IV and VI) rendered stimulating effect on the plants.

Decrease in weight of plants and chlorosis on leaves of plants were registered at the EDTA rate 6mmol/kg of ground, especially at its annual application (variant XIV).

3.2 Influence of EDTA on metal mobilization in ground and on phytoextraction capability

The analysis of ground has shown that phytoavailability of metals Cd, Cu and Zn in substratum increases at increase in rates of EDTA and multiplicity of its applications. The concentrations of plant-available metals in rhizosphere-ground were higher than in bulk-ground. The EDTA stimulates root exudation and enhances accumulation of metal-EDTA complexes in rhizosphere (Wenzel, 2003).

Increasing application rates and multiplicity of applications of EDTA considerably enhance accumulation of all investigated metals by plants. Increase of metals' accumulation by plants under the influence of EDTA confirmed by (Wenzel, 2003, Avtukhovich, 2010).

In conditions of our experiment Cd and Zn accumulated mainly in shoots, while Cu – in roots of safflower plants (Figure 1).

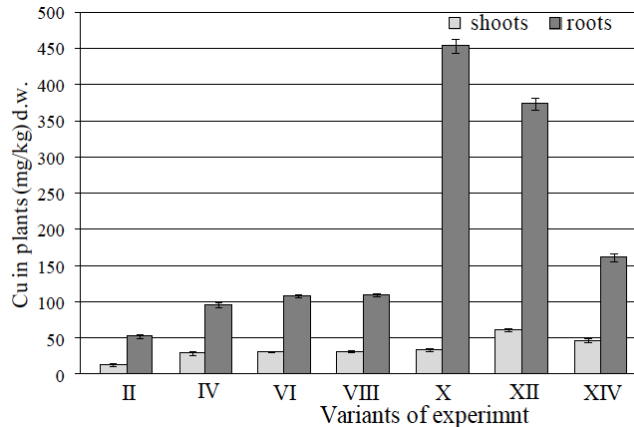


Fig. 1 – Influence of EDTA application to ground on Cu concentrations in shoots and roots of (*Carthamus tinctorius L.*) in 2012.

Variants X and XII - with annual application of EDTA in rates 1 and 3 mmol/kg of ground appeared the most effective considering phytoextraction capacity of safflower plants. In these variants the highest uptake and accumulation by plants of Cd, Cu (Figure 1) and Zn were registered.

Conclusion.

EDTA increases bioavailability of metals in the ground, considerably raises accumulation and uptake of pollutants by plants as well as improves parameters of plants' productivity in certain application rates.

References

Avtukhovich I.E. (2010). Inducirovannaya phytoextrakciya kak extensivnyi metod vosstanovleniya zagryaznennykh pochv i gruntov [Induced phytoextraction as an extensive method of remediation polluted soils and grounds] // *Agrochemical Herald*. 2, pp. 39-40.

Wenzel W.W. (2003) Chelate-assisted phytoextraction using canola (*Brassica napus L.*) in outdoors pot and lysimeter experiments// *Plant and Soil*. 249, pp. 83-96.

Zubko A.A., Shtonda Y.I. (2010). Obezvozhivanie osadkov gorodskikh stochnykh vod na peredvizhnykh kompleksakh [Dewatering of municipal sewage sludge on compact mobile complexes]// *Water Supply and Sanitary Equipment*. 9. pp. 14-17.

POLLUTION

STUDY OF ADSORPTION OF METHYLENE BLUE ONTO COFFEE GROUND

Conflict of Interest

None declared.

Mahdi Karima^{1,*}, **Benrachedi Khaled**^{2,*}

^{1,2}Laboratory of Food Technology, University of Boumerdes

*To whom correspondence should be addressed.

Associate editor: Alautdin Aliev

Received on 13 March 2017, revised on 20 March 2017, accepted on 31 March 2017.

Abstract

In this work, we study the elimination of an organic dye to use intensively in textile industry (Methylene blue BM) by adsorption on the coffee ground. The adsorbent was characterized beforehand. The physical characterization (porosity and surface) was determined by electronic scan microscopy MEB revealed the presence of a mesopore area. The chemical characterization was carried out by the pH at the point of zero load (pHPZC), confirmed the character neutral of material. Several parameters are studied in order to optimize the ideal conditions for a good adsorption of the pollutant study; in particular, the kinetics of adsorption, mass of adsorbent, the effect of the pH of the solution examined the effect the stirring velocity, the effect of salts and the temperature. The results were adapted to the kinetic models and the isotherms of adsorption. The whole of the got results watch that the isotherms of adsorption of the systems adsorbing/adsorbed studied are described satisfactorily by the mathematical model of Freundlich. The pH of the solution as well as the presence of salts affects the output of discoloration. In addition, the thermodynamic study revealed that adsorption is spontaneous and endothermic. Therefore, one can conclude that this study showed that the coffee marc can be used like new natural adsorbent for the water treatment contaminated by the textile dyes.

Keywords: adsorption, methylene blue, coffee ground

Contact: mahdi.karima1988@gmail.com, benrachedik@yahoo.fr

1 Introduction

Nowadays, the adsorbent material increasing demand for processes of environmental protection causes a complementary research in the manufacturing of the activated carbons starting from unclassical matters, in particular starting from the vegetation wastes. The raw materials being used as precursors are varied origins: lignocellulosic derivatives (wood, coconut hulls, almond hulls of hazelnuts and of walnut, apricot cores, apple pulp, cores of peaches thus that olive cores, date cores, the marc of the coffee, polymeric, as well as mineral coals. Quantities large of marc of the coffee are generated each year and constitute a significant source of agricultural waste. Such by-products corresponding to this loss are however likely to be of a considerable economic interest. It proves, thus, important to develop such waste. To work out adsorbent materials starting from agricultural waste makes it possible on the one hand to eliminate them and on the other hand to optimize the output and the manufacturing costs of the exploitations.

The use of the coffee ground in the water treatment polluted by the industrial wastes of textile such as the organic compounds (dyes) perhaps an interesting way of valorization of these materials. Many industries, and

particularly those of the textile, reject into the rivers of the colored by-products. These organic compounds have a great influence on the level of the pH, and have a high toxicity; all these effects can involve serious ecological problems; these compounds are structurally very different the ones the others, from where a real difficulty to eliminate them by the classical methods of decontamination. Ozonization and oxidation by hypochlorite are the most effective methods of the colorless of water, but, they remain inadequate because of their high cost and the chlorinated residues which result from this. Many studies led to the clarification of processes of adsorption on adsorbent materials.

We proposed to make a study of adsorption of an organic dye used intensively in textile industry, the Methylene blue on a natural adsorbent which is the coffee ground which has a porous texture.

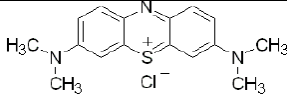
2 Experimental part

2.1 Equipment and methods

2.1.1 Studied dye

The studied dye is the methylene blue (BM) in cation matter. Its characteristics are presented in table 1

Table 1 – Characteristic of the studied dye

dye	λ_{\max}	molar mass g/mol	structure
« methylene bleu »	664 nm	373,9	

2.1.2 Adsorbent used

The coffee ground used is scented, soft and without bitterness. This waste abundantly is washed with distilled

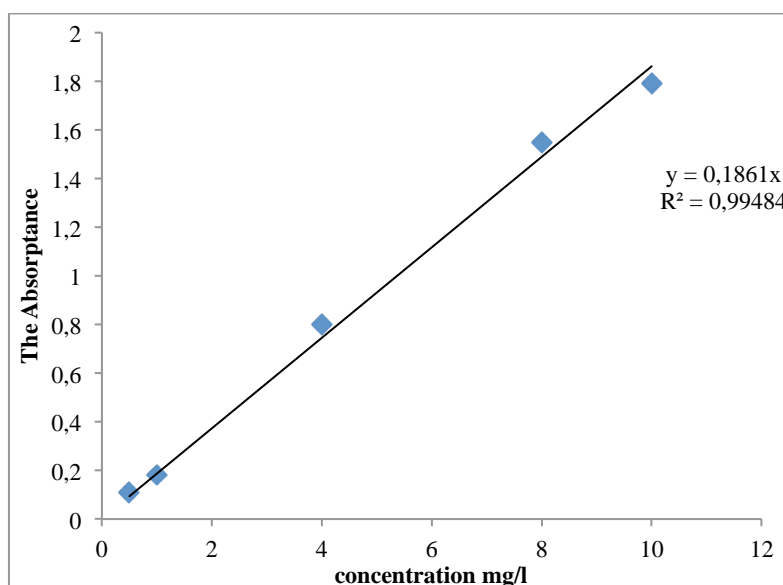
2.1.3 Adsorption tests of the methylene blue on coffee ground of the coffee in system “batch”

Establishment of the calibration curve:

After having prepared the various solutions of reagents, the spectra of adsorption into UV-Visible of the methylene

water then dried with drying oven (MELAG) with 110 °C during 24 hours. It is then filtered (sieve AFNOR) to retain the fraction higher than 500 micron.

blue was obtained by a sweeping spectral by using a UV/visible spectrophotometer of the type SHIMADZU UV-1800. entre [400 and 800] of a solution of dye with 10 mg/l to determine the wavelength of maximum adsorption; what enabled us to obtain the following wavelength: $\lambda_{\max} = 664$ nm.

**Fig. 1** – Calibration curve of the Methylene blue (BM)

2.2 Results and discussions

2.2.1 Physico-chemical properties of the coffee ground

The main features of the coffee ground used are presented on table 2:

Table 2 – Characterisation of the marc of the coffee used

Water content (%)	0,8
Apparent density	0,51
Iodine index (mg/g)	462
Phenol index (mg/g)	38
pH with 20 °C	6,3

Properties acido-basic of the coffee ground

The measures of pH are taken with a pH-meter (JENWAY). A mass of 1 gr. of coffee ground is introduced into 150 ml distilled water, the mixture is homogenized

using a regulated magnetic stirrer with 400 turn/times with room temperature. The graph obtained thus reveals stable kinetics in the neighbourhoods of pH= 6.3 our adsorbent is almost neutral.

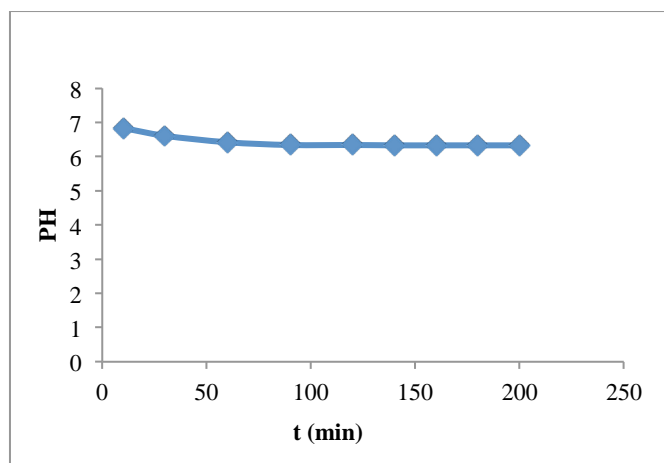


Fig. 2 – Evolution of the pH of coffee ground according to the time of contact

Technique of B.E.T

Specific area, the volume and the average diameter of the pores of our adsorbent (coffee ground) are determined by the technique of Brunauer, Emmett and Teller “BET” by using nitrogen to 7 K, the sample is subjected as a preliminary to a desorption with reduced pressure ($< 10^{-4}$ Torr), at temperature of degasification of 150°C during 12

hours. The device used is of type “Quantachrome Instruments”. The classification of the pores currently adopted by the International union of chemistry pure and applied (U.I.C.P.A) is founded on their sizes, three categories of pores were defined [2].

The results of measurement of the specific surface of coffee ground are gathered in table 3.

Table 3 – Determination of the specific surface of coffee ground by the method of (B.E.T)

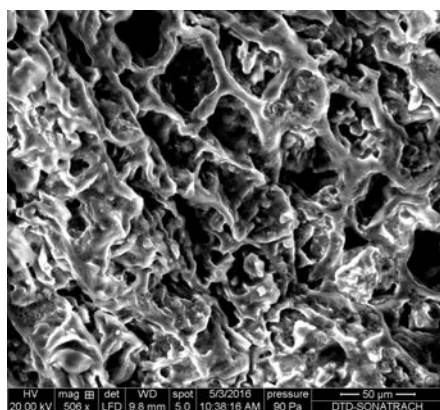
Specific surface ($m^2 \cdot g^{-1}$)	Average diameter (nm)	Average volume of the pores ($ml \cdot g^{-1}$)
0,58 (0,5-2 $m^2 \cdot g^{-1}$)	62 (>50 nm)	0,53 (0, 2-0,8 $cm^3 \cdot g^{-1}$)

These results enable us to conclude that our adsorbent (coffee ground) comprises primarily macropores.

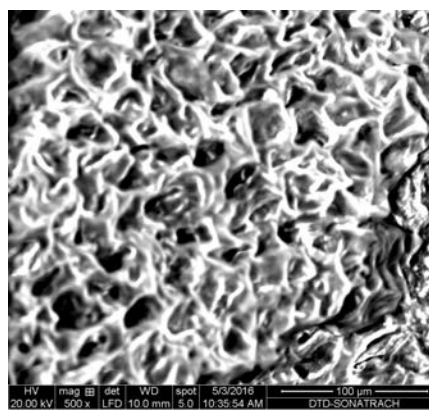
Porosity:

The determination of the porosity of our coffee ground was carried out via the electron microscope with sweeping (MEB) of brand (QUANTA 650) to see the form of the

pores and their respective diameters. The photographs (1 and 2) show the various states of porosity as well as the presence of cavities. It of form and diameter is varied primarily made up of macroporous, which is confirmed further by the type of isotherm obtained (type C).



PIX500 (50 μm)



P2X500 (100 μm)

Fig. 5 – Photographs with the M.E.B of the coffee ground

Analysis by x-ray fluorescence

The analyses of x-ray fluorescence were carried out on a spectrometer of x-ray fluorescence of brand PAMALYTICAL-AXIOS. The sample reduced out of

powder is subjected to a source of secondary X-radiation of fluorescence characteristic of its chemical composition.

The percentage of the elements obtained by x-ray fluorescence are consigned in table 4.

Table 4: Results of the analysis by x-ray fluorescence of the coffee ground

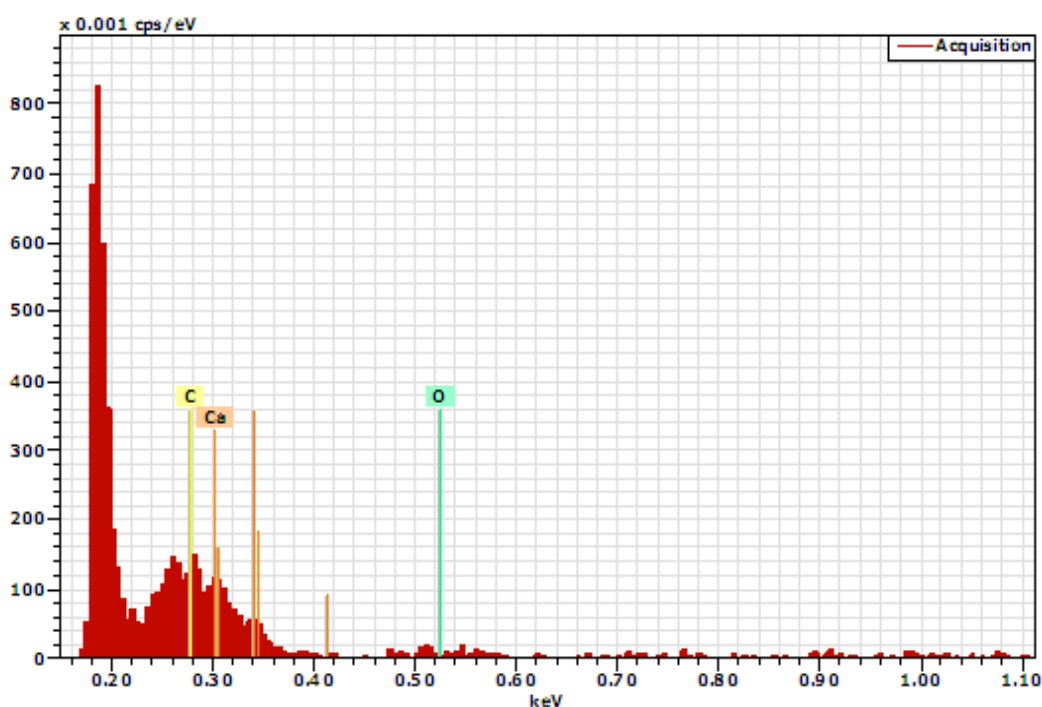
Elements	Pourcentage (%)	Elements	Pourcentage (%)
SiO ₂	0,73	MnO	0,03
Al ₂ O ₃	0,1	P ₂ O ₅	0,1
Fe ₂ O ₃	0,00	K ₂ O	0,01
CaO	1,11	Na ₂ O	0,00
TiO ₂	0,01	MgO	0,01
BaO	2,59	SrO	0,003
		(CO ₂)	95,3
		Total	99,993

Table 4 shows that the adsorbent is rich in biogenic salts. Among these elements quantified in the form of oxides we can quote: BaO, CAD, SiO₂, Al₂O₃, P₂O₅. The rest of the composition of the adsorbent represents the minor elements.

Elementary analysis

The MEB, assisted of an electronic microsunder (EDAX), as enabled us qualitatively to appreciate, the

majority elementary chemical composition of activated carbon. It should be noted as this probe detects only the elements whose content is higher than approximately 0.5%. The elements present in the coffee ground and their percentages are presented in table 5 and figure 6.

**Fig. 6** – Majority peaks of the elements present in coffee ground**Table 5** – Elementary analysis of coffee ground

Element	Percentage (%)
C	76,41
Ca	6,78
O	16,82
Total	100

It should be noted that this probe detects only the elements whose content is higher than approximately 0.5% and which the hydrogen content could not be given by this technique.

As one could expect it, the coffee ground is made up mainly of carbon (peak majority 76,4%), but also of much of oxygen certainly coming from the many oxygenated functions of surface.

Structural analysis by spectroscopy IRTF

The structural analysis by infra-red spectroscopy transformed furrier were carried out using a spectrometer

with transform of furrier of the type (Nicolet 560 FTIR) coupled to a digital calculator allowing the layout of the spectra between [4000 and 400 cm⁻¹]. The spectrum of analysis by will infrared of coffee ground is represented on Figure 7. The most intense bands are deferred in Table 6. The broad absorption band ranging between 3400-3200 cm⁻¹ corresponds to the vibrations of elongation of the hydrogen of the group hydroxyls O-H and adsorbed water. The spectra of IRTF show absorption bands ranging between 2930 and 2850cm⁻¹ resulting mainly from the vibrations of elongation of C-H of the aliphatic molecules.

The spectra also shows a band to 1450 cm⁻¹ due to the vibrations of elongation of connections C=C, the bands

ranging between 1000 and 1350cm⁻¹ is assigned vibrations of the connections CO [3].

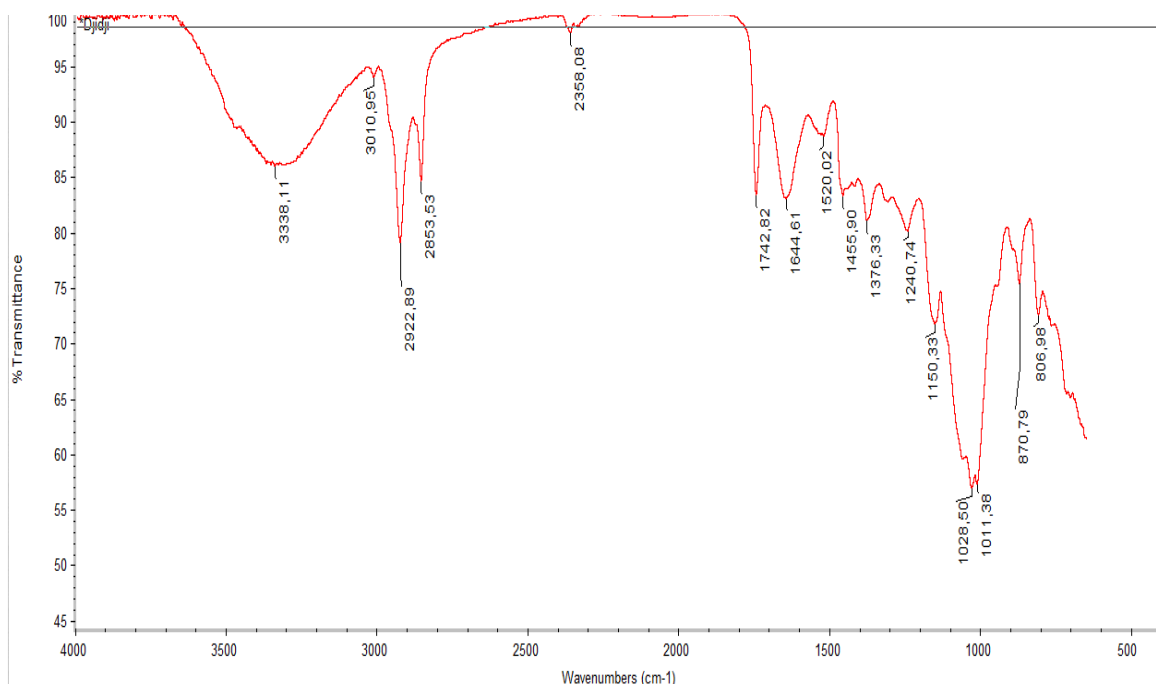


Fig. 7 – Spectrum IR of coffee ground

Table 6 – Result of the infra-red analysis of the coffee ground

Bands of vibration (cm ⁻¹)	Attribution
2922,89	C-H
1520,02	C-C/ C=O/ N-H
1455,9	C-H (CH ₃)
1028,5	C-OH
806,9	=C-H
3338,11	O-H bound
1455,9	C=C aromatic
1376,33	OH deformation in the plan
1240,74	CO

2.2.2 Tests of adsorption

The kinetics of adsorption (effect of the time of contact)

0.25 gr. of the coffee ground are put in contact with 100 ml of the colored solution. The mixture is agitated during 4 hours with room temperature and with a stirring velocity equal to 400 turns per minute. The taking away is collected with predetermined time intervals (10 min). The quantity (qt) of adsorbed dye is given by the following relation:

$$Q_t = (C_0 - C_r) \cdot V / m$$

Q_t: quantity of dye adsorbed per gram of adsorbent (mg/gr).

C₀: initial concentration of the dye (mg/l).

C_r: residual concentration at time t (mg/l).

V: volume of the solution (L).

m: mass of the adsorbent (gr.).

$$\% \text{ of colorless} = [(C_0 - C_r) / C_0] \cdot 100$$

The kinetic study of the elimination of dye by adsorbent material (coffee ground) shows an increase in percentage of colorless at with the increase in the time of contact. Indeed, after 100 minutes of contact the methylene blue output of colorless of the solution du reaches almost the 100% for the concentration of 5mg/l by dye. The results are presented in figure 8.

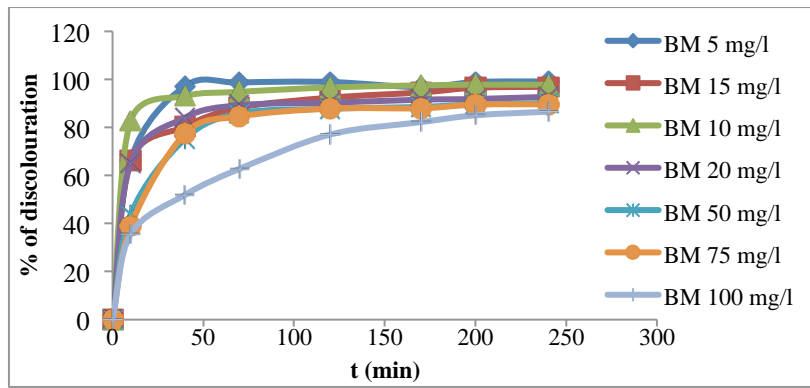


Fig. 8 –Effect of the time of contact on the percentage of colorless of the Methylene blue by the coffee ground (time of contact= 4:00; m =0,25 G; pH=6,4; Agitation = 400 tr/min; V =100 ml, T = 19 ±2°C)

Influence of the pH on discoloration

One adjusts the initial pH of the solutions colored by using solutions of NaOH (0,1N) and HCl (0,1N) for different the studied values of pH (2, 4, 6, 8 and 10) Figure 9, watch that with acid pH lower than 4, the adsorption of

the MB on the coffee ground is with its minimum whereas has pH higher than 4 adsorption is maximum with a percentage of colorless of 90% and remains constant until the limit of the study with pH 10.

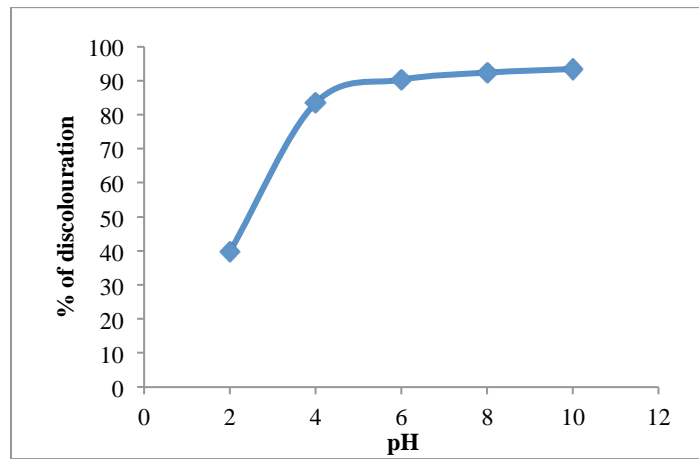


Fig. 9 – Effect of the pH on % of colorless of the Methylene blue by the coffee ground (time of contact= 4:00; m =0,25 G; C= 20mg/l; Agitation = 400 tr/min; V=100 ml, T=19 ±2°C).

For MB (pH free=6,4), the capacity of adsorption obtained of 40% with PH< 4 instead of 90% beyond this pH can be explained, by the fact why with pH< 4, the load of surface of coffee ground becomes positive in the presence of surplus of H⁺ ions in solution which return competing with the MB which is coloring cation. The adsorption of the BM is thus affected.

Influence of the mass of adsorbent on colorless

The masses of the coffee ground used are: 0.05 – 0.1 –

0.2 – 0.5 – 1 gr. As we can note it according to figure 10, the percentage of colorless of the methylene blue increases with the increase in the mass of the adsorbent used to stabilize itself with great values of this last. Indeed, the increase in the amount of the adsorbent makes grow the number of the sites available for the fixing of the dyes (increase in the free area of the adsorbent), which supports consequently the phenomenon of colorless [4].

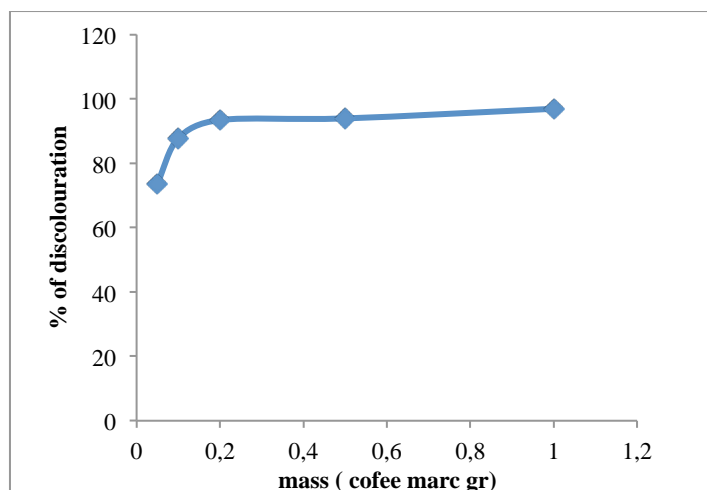


Fig. 10 – Effect of the mass of adsorbent (coffee grou) on % of colorless of the Methylene blue (time of contact= 100 min; pH = 6.4; C= 20mg/l; Agitation = 400 tr/min; V =100 ml, T 19= ±2°C)

Influence stirring velocity

The experiment is carried out in system batch, we mix 0.25 gr. of adsorbent with solutions of dyes (100ml), while varying the stirring velocity from 300 to 800 tr/min (300, 500,600,700, and 800). The results represented on figures 11, watch that the increase stirring velocity to 600

turns/times, makes increase the rate of colorless (93.8%). Beyond 600 tr/min the percentage of colorless decreases. We consider that it there is a stirring velocity optimal (600 turns/times), sufficient to support the contact between the particles of coffee ground and the molecules of dyes.

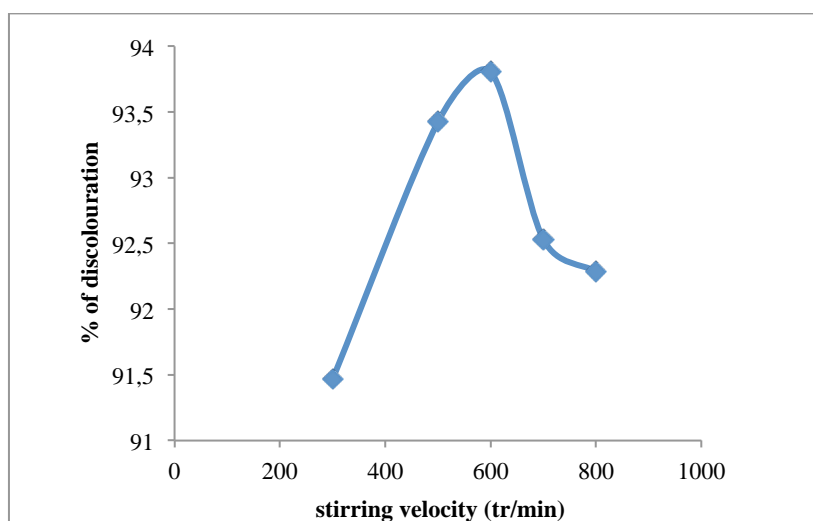


Fig. 11 – Effect of the temperature on % of discoloration of the Methylene blue (time of contact= 100MIN; pH = 6.4; C= 20mg/l; V =100 ml, mass of the coffee ground=0,25gr; T=20 ±2°C

Influence of temperature

The influence of the temperature is studied with solutions of concentrations equal to 20 mg/l, plunged in a bath MEMMERT to keep the constant studied temperature. We study following adsorption at the temperatures: 10, 20, 30, 40, 50, and 60°C. Figure 12 fact of appearing two

distinct parts:of 10°C until the 40°C, one notes that the rate of colorless remains almost constant by 40°C with 60°C, the percentage of colorless decreases in a remarkable way what leaves suppose that the fixing of the methylene blue on the coffee ground is carried out endothermicly.

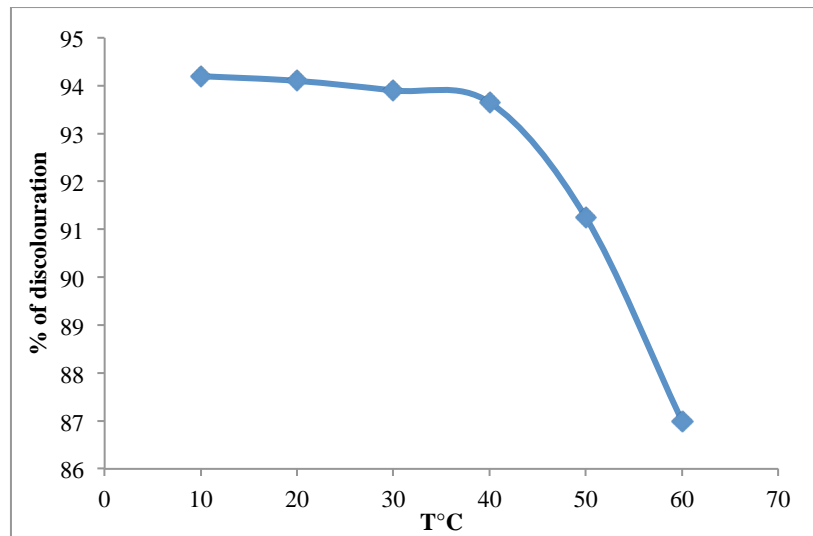


Fig. 12 – Effect of the temperature on % of colorless of the Methylene blue (time of contact= 100 min; pH= 6.4; C= 20mg/l; V =100 ml, mass of coffee ground=0,25gr; speed of agitation= 400 tr/min)

We can confirm this result by the notion of the enthalpy (ΔH). The value of the enthalpy of adsorption can be calculated according to the following expression:

$$\ln Q_{ads}(T_1) = \ln C - \Delta H/RT_1, \quad \ln Q_{ads}(T_2) = \ln C - \Delta H/RT_2$$

$$\Delta H = R \ln [Q_{ads}(T_2) / Q_{ads}(T_1)] / (1/T_1 - 1/T_2)$$

Temperature (°C)	10-40	40-60
Enthalpy (J/mol)	+107,046 > 0	-62,227 < 0
Nature of adsorption	endothermic	exothermic

With the increase in the temperature, results the rise in the mobility of dye in solution and the reduction of the attraction forces where of diffusion of dye on the surface of marc of the coffee. The capacities of adsorption of the methylene blue will be slowed down consequently.

Influence of salts

It is known that the waste water of textile contains, with variable concentrations, ions organic and inorganic, mainly of the cations and anions such as nitrates, chlorides, sulfates, carbonates and the carbonate hydrogen. Thus with an aim of better understanding the influence of these ions on the process of retention of the methylene blue by marc of the coffee, of the experiments were carried out while adding to each solution with 20 mg/L of dye and time $t=0$, a salt such as NaCl with (0,1M) and (1M). Pilot solutions were also agitated in presence and absence of the support

(marc of the coffee).

Figure 13 shows that, the NaCl addition, clearly increases the rate of colorless of the cation dye (methylene blue). And this adsorption will be still better when the content salt increases (NaCl 1M). In absence of the adsorbent (coffee marc), salt contributes slightly to the process of colorless. This phenomenon can be explained by the fact why salts support the bringing together-association of the particles by the formation of new sites of surface where the molecules and aggregate of dye would be trapped. We can also call on the theory of Gouy- Chapman on the dual-layer of diffusion which provides that the thickness of this layer would be low with the ionic force what facilitates the bringing together of the molecules of adsorbed and the particles of adsorbent [15].

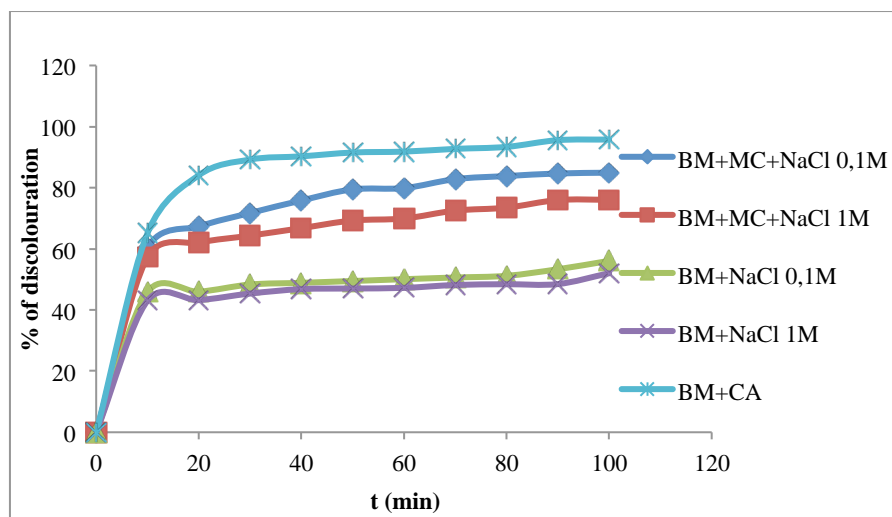


Fig. 13 – Influence of salts on the percentage of colorless of the BM by the coffee ground. (pH=6,4; m = 0.25 G; V = 100 ml; Time of contact = 100min; Agitation = 400 tr/min; C=20mg/l; T = 20 ±2°C)

Isotherm of adsorption

The isotherms of adsorption were studied by agitating a mass of the adsorbent 0.25 G in colored solutions of various concentrations going from 5 to 100 mg/L. The adsorbent and adsorbed it were put in contact during 100 minutes under an agitation of 400 tr/min. The results of the isotherms of adsorption of the dye on the coffee marc are presented on figure 14.

The isotherms show that there is a correlation between

the quantity adsorbed of dye to balance (Qe) and the concentration to balance.

According to the classification of the isotherms of adsorption of GILLES [6], the isotherms are of type C sub-group 1; they are in the form of straight lines what means that there is competition between solvent and the aqueous solution to occupy the sites, with always the same division (shares constant). They relate to flexible molecules being able to penetrate far in the pores to move solvents there.

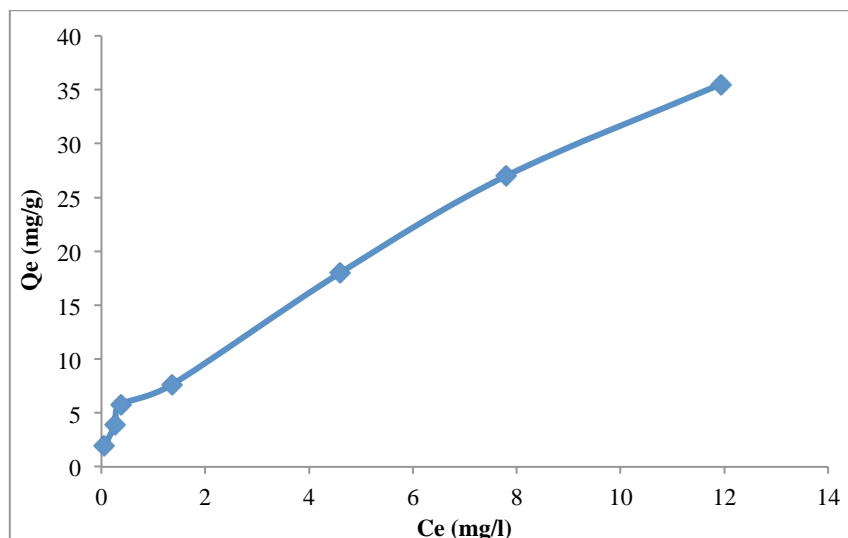


Fig. 14 – Isotherms of adsorption of methylene blue by the coffee ground (. (pH=6,4; m = 0.25 G; V = 100 ml; Time of contact = 100min; Agitation = 400 tr/min; T = 20 ±2°C).

Models of the isotherms of adsorption

Figures 15 and 16 represent the linear transforms of Langmuir and Freundlich respectively; according to these lines we deduced the values from the maximum capacities and the values of the constants of adsorption determined under the above mentioned experimental conditions.

1) **Model of Langmuir:**

$$\frac{x}{m} = Q_e = \frac{a \cdot b \cdot C_e}{1 + b \cdot C_e}$$

$$\frac{m}{x} = \frac{1}{Q_e} = \frac{1 + b \cdot C_e}{a \cdot b \cdot C_e} = \frac{1}{a \cdot b \cdot C_e} + \frac{1}{a}$$

$a = qm$ ultimate capacity

$\frac{1}{b}$ = Kd constant of dissociation of the adsorbent

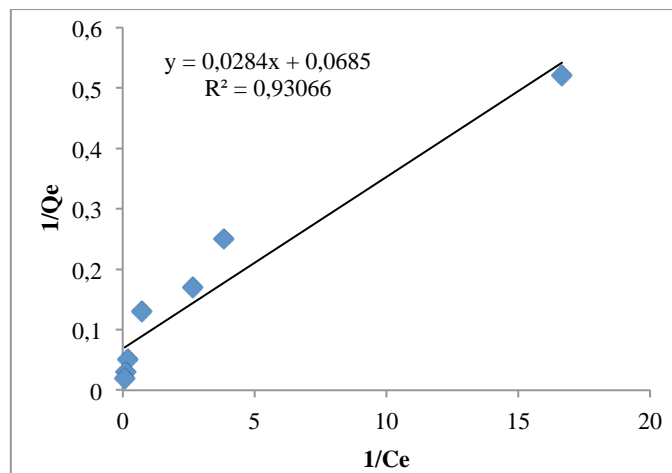


Fig. 15 – Linear transforms of the isotherms of adsorption of Langmuir.

2) Model of Freundlich

$$\frac{x}{m} = Q_e = k \cdot C_e^{1/n}$$

The linearization gives:

$$\text{Log } x/m = \text{Log } Q_e = \text{log } k + 1/n \text{ log } C_e$$

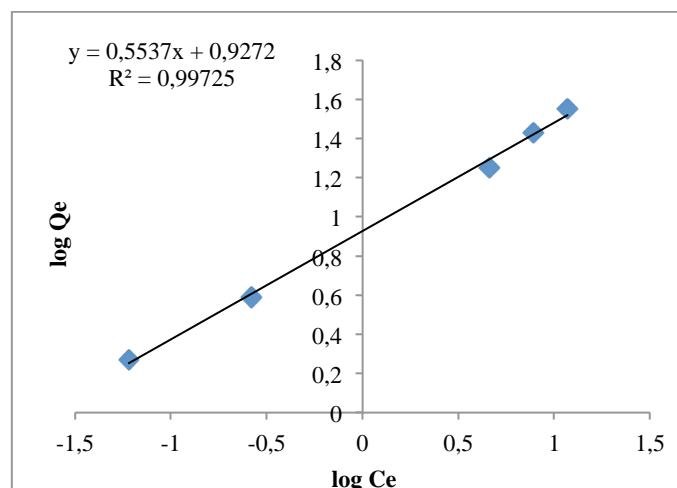


Fig. 16 – Linear transforms of the isotherms of adsorption of Freundlich

The linear representations of the experimental values this process of adsorption enabled us to determine the parameters of balance and the values of the constants of

Langmuir and Freundlich calculated by linear regression (Table 7).

Table 7 – Constant of the isotherms of adsorption of Langmuir and Freundlich of the methylene blue on the coffee ground

æ	n	1,8
	1/n	0,92
	K _F	2,52
	R ²	0,997
Langmuir	b	0,67
	q _m	23,09
	R ²	0,93
	K _d	1,49

The values of the coefficients of regression indicate that the process of adsorption, of Methylene blue by the coffee ground, is described in a favorable way by the isotherm of Freundlich (with excellent linear coefficients of regression R² which is very close to the unit).

The parameter of intensity, 1/n, indicates the deviation of the isotherm of adsorption of the linearity.

When 1/n=0, adsorption is linear, i.e. that the sites are homogeneous and that there is no interaction enters the

adsorbed species.

When 1/n<1, adsorption is favorable, the capacity of adsorption increases and again sites of adsorption appear.

When 1/n>1, adsorption is not favorable, the connections of adsorption become weak and the capacity of adsorption decreases.

3 Conclusion

The kinetic, thermodynamic studies and the isotherms of

adsorption were carried out to clear up the mode of fixing of the methylene blue on material tested. The experiments highlighted that the coffee marc is very effective for the colorless of water. The percentage of colorless is influenced by the variation of the pH, it can reach 98% for neutral values of pH, on the other hand it is influenced very little by the mass of adsorbent as well as the fixing of the methylene blue on the coffee marc is carried out endothermicly. The addition of salts (NaCl), clearly increases the rate of colorless of the cation dye (methylene blue). And this adsorption will be still better when the content salt increases (NaCl 1M).

The studies continue to seek other less expensive supports which will be combined with the coffee marc in order to in the case of improve the outputs of colorless for a possible use the rejections of textiles and other effluents charged in organic pollutants.

References

- Baccar, R., Sarra, M., Bouzid, J., Feki, M., Blanquez, P. (2012). Removal of pharmaceutical compounds by activated carbon prepared from agricultural by-product. *Chemical Engineering Journal*, 211, 310-317.
- Creangă, C. (2007). 'Procédé AD-OX d'élimination de polluants organiques non biodégradables (par adsorption puis oxydation catalytique)', mémoire de doctorat, Institut de Toulouse, 8.
- Kumar, R., Barakat, M. A. (2013). Decolourization of hazardous brilliant green from aqueous solution using binary oxidized cactus fruit peel. *Chemical Engineering Journal*, 226, 377-383.
- Abouzaid, A. (2001). Thèse de Doctorat, Faculté des Sciences, Université Chouaïb Doukkali, El Jadida, Maroc.
- Rashid, M. A, Buckley, D. E, Robertson, K. R. (1972). Interactions of a marine humic acid with clay minerals and a natural sediment. *Geoderma*, 8, 11-18.
- Limousin, G., Gaudet, J. P., Charlet, L., Szenknet, S., Barthèse, V., Krimissa, M. (2007). Sorption isotherms: a review on physical bases, modeling and measurement. *Applied Geochemistry*, 22, 294-275.