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FACULTY OF SCIENCE AND TECHNOLOGY

Synthesis, characterization and Batch adsorption analysis of spent coffee grounds, Chitosan and PVA composite beads for the removal of Cadmium and Lead from aqueous solutions.

THESIS TO OBTAIN THE MASTER'S DEGREE OF ENVIRONMENTAL ENGINEER IN WATER SCIENCE AND TECHNOLOGY

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Carolina Antonella Orquera Bugueño. June 15th. 2021

ABSTRACT

Adsorption of Cadmium and Lead in aqueous solutions by Spent coffee grounds/chitosan/PVA composite beads was studied.

An adsorption Batch experimental model was used to determine the Isotherms and kinetics of 4 different compositions of beads, it was developed according to the individual adsorption capacity of the constituents stated in the literature and assigned in 4 groups: Control bead (BC; containing only 4% chitosan), Bead 1 (B1; 1 gr of SCG, 4% chitosan and 7,5% of PVA), Bead 2 (B2; 2 gr of SCG, 4% chitosan and 7,5% PVA) and Bead 3 (B3; 3 gr of SCG, 4% chitosan, 10% PVA).

Morphological variables were measured using TGA, FTIR, BET, and SEM, and the adsorption capacity and removal efficiency were calculated.
The adsorption behavior was studied through non-linear and linear Isotherms and pseudo first and second order kinetic modeling. All beads presented a non-linear Langmuir and Temkin and a pseudo second order fit only for cadmium adsorption according to the R^2 correlation coefficients. Maximum values for adsorption capacity (qmax) were obtained for the adsorption of cadmium using the non-linear Langmuir model (B2 199,61 mg/g, B1 with 176,619 mg/g and B3 103,587 mg/g). B1 shown the highest value for lead adsorption among both approaches (263,16 mg/g).

These results could become a good contribution to the current knowledge along with a strong incentive to further research, about the valorization of waste and its important utilization in the synthesis of composites as remediators of contaminated water.

Key Words: **Spent coffee grounds, Chitosan, Polyvinyl alcohol, composite beads, Heavy metals, Water Treatment, Cadmium, Lead, waste valorization, non-linear isotherms, Linear isotherms, pseudo first-order, pseudo second-order, kinetics.**

LIST OF TERMS AND ABBREVIATION

K_F	Freundlich isotherm constant
K_T	Temkin isotherm constant
K_L	Langmuir isotherm constant
a_L	Langmuir isotherm constant
b_T	Temkin isotherm constant
C_e	Solution concentration at equilibrium
R^2	Statistical correlation coefficient
qmax	Maximum Adsorption capacity
q_e	Adsorption capacity at equilibrium
q_t	Adsorption capacity at time t
q_e exp.	Experimental adsorption capacity
q_e cal.	Calculated adsorption capacity
K_1	Pseudo first-order adsorption kinetic constant
K_2	Pseudo second-order adsorption kinetic constant
Ch	Chitosan
COS	Chitosan Oligomers
SCG	Spent Coffee Grounds
PVA	Polyvinyl Alcohol
SEM	Scanning Electron Microscopy
FT-IR	Fourier transform infrared spectroscopy
TGA	Thermal gravimetric analysis
BET	Brunauer–Emmett–Teller
Dm	Demineralization
Dp	Deproteinization
DAc	Deacetylation
FHI	Folkehelseinstituttet
SSB	Statistisk sentralbyrå
USGS	U.S Geological Survey
WHO	World Health Organization

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1 INTRODUCTION

Every year the awareness on how the development of populations leads to pollution has escalated quickly. The use of heavy metals in the expansion of technological applications can cause detrimental environmental effects which will affect human health due to its bio-accumulative and subsequently biomagnification ability through the food chain and transport through air and water. Therefore, various researchers have been trying to look for cheap and sustainable resources to develop new products to remediate contaminated water effluents with heavy metal content to avoid the pollution of the receiving water bodies.

Chitosan has been used since the ’70s as a cheap and environmentally friendly alternative for water treatment as a coagulant and flocculant but using this method to remove heavy metals will produce sludge that requires further treatment, instead, several studies have proposed the idea to not only produce chitosan bead but to combine this polymer with other components in order to enhance the adsorption of pollutants.

In this thesis, local low-cost alternatives derived from coffee collected from the cafeteria at the University of Stavanger and shrimp waste from fisketorget have being considered for the first extraction experiments. Nevertheless, since COVID-19 started the utilization of commercial chitosan was considered as a fast and easy access source of this polymer and the obtention of results.

Chitosan, spent coffee grounds, and polyvinyl alcohol (Ch-SCG-PVA) hydrogel beads were produced with different concentrations of the constituents (denominated B1, B2, B3, and BC) to adsorb heavy metals from aqueous solutions. Physical Characterization of the beads was done by scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR) to observe functional groups and any changes or degradation of the polymers before and after adsorption, Thermal gravimetric analysis (TGA), and Brunauer–Emmett–Teller (BET) to determine the weight loss, porosity, and surface area respectively.

Cadmium and lead were studied, at concentrations of 0.1 to 0.3 mg/L to determine the better fit to Isotherms such as Langmuir, Freundlich, and Temkin, as well as 0.15 mg/L for First and pseudo-second-order kinetic equations. The beads were compared with beads containing only 4% chitosan as control (BC) to determine the enhanced removal capacity along with the adsorption kinetics and isotherms in a single batch experimental model.

2 OBJECTIVES

Synthesize a new chitosan-spent coffee grounds-polyvinyl alcohol bead adsorbent to compare the adsorption effectiveness between beads enhanced extraction of toxic heavy metals in in a batch test.

2.1.1 Specific objectives

- Prepare and characterize four different composition beads BC, B1, B2 and B3.
- Determine the adsorption fit of the control bead BC with respect to B1, B2 and B3 composite beads using the linear and non-linear mathematical models of Freundlich, Langmuir and Temkin.
- Determine the reaction rate by adsorption kinetics of BC with respect to B1, B2 and B3
- Determine the removal capacity of Cadmium and Lead of all four Beads

2.1.2 Hypotheses

The addition of different components such as Chitosan, PVA and SCG will enhance the adsorption of cadmium and lead in comparison with only 4% chitosan beads

3 LITERATURE REVIEW

3.1 Water as a critical worldwide resource to life.

Water is one of the key resources to sustain life on earth, since it has no substitute, it becomes indispensable for the development and prosperity of any population and industry.

The bank Goldman-Sachs, in a Global Investment Research report in 2008, predicted that water would become the petroleum of the 21st century since its consumption will escalate at an unsustainable rate, due to population growth, industrial development, and environmental conditions.

The world's freshwater supply, which is composed of less than 1% of the whole water on earth (USGS, 2010), not including glaciers, icebergs, and groundwater, since it's not available for direct use. This small percentage is decreasing due to pollution, draining of underground aquifers, and climate change making it a precious resource that requires maximum attention to be taken.

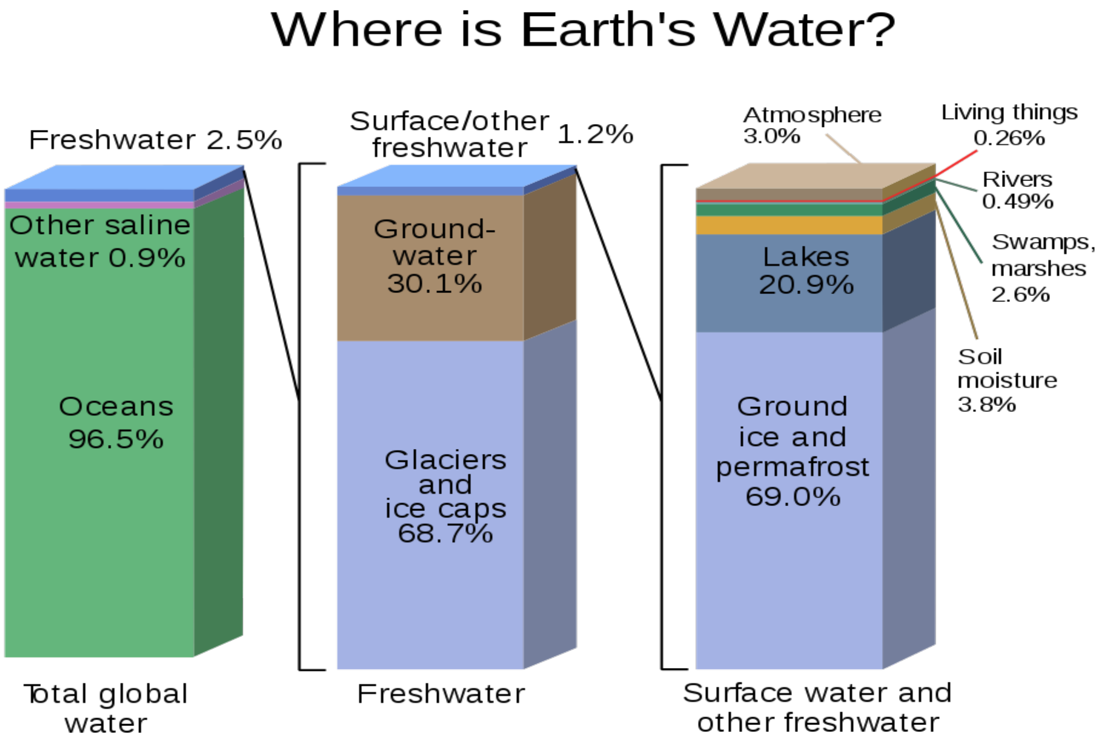
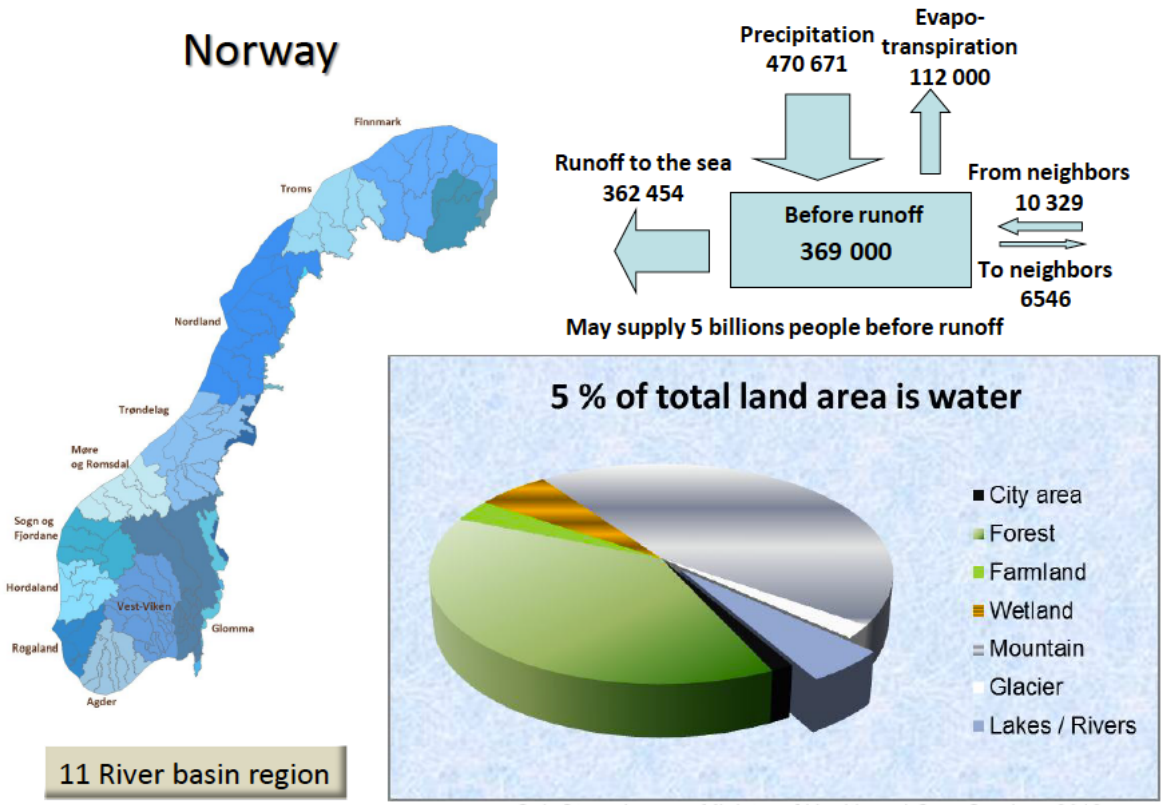


Figure 1.- *Distribution of water on whole Earth. Source: Where is Earth's Water, U.S. Geological Survey (unknown year)*

3.2 Fresh Water Resources in Norway

If we take in consideration the whole geography from Norway only 5% of the whole country correspond to surface water sources as lakes and rivers (Larsen, G.S. 2012), from which according to the updated information from the FHI, 10% of the drinking water supply derives from basins and the remaining 90% comes from lakes, ponds, streams, and brooks. From that 5% of available surface water around 34% are considered having a good status, 36% a moderate and around 29% is considered to have poor or bad status (Vann-nett.no)

This data is of sum importance, since despite the high precipitations in the country (up to 3000mm on the west coast), this resource is still limited and makes it even more precious than petroleum, since life depends on it.



Geir Stene-Larsen. Ministry of Health and Care Services 2012.

Figure 2.- *Sources of water and its distribution in Norway*

3.3 Heavy metals

The Store Norsk Leksikon, categorize a metal as heavy if they weigh more than 5 grams per cubic centimeter (g/cm3). Among these are cadmium, lead, mercury, and zinc, which are toxic persistent pollutants, and cause serious health damage.
Heavy metals are present as natural elements in soil and can be also present as contaminants in fertilizing materials. Cadmium and Lead are the most widely detected heavy metal in surface waters due to their toxicity. These two heavy metals when spread in the environment can have harmful effects along the whole food chain due to their bio-accumulative and biomagnification ability.

3.4 Cadmium

Cadmium (Cd) occurs in nature together with zinc, and is used in industry for welding and soldering, among other things. Rechargeable nickel-cadmium batteries used in mobile phones, tools and toys are an important source of pollution. Cd is easily absorbed by plants and can reach the grain via synthetic phosphate fertilizers (Haider, F. U. et al. 2021).

According to the WHO cadmium sources have changed during the development of populations, what before was only found in Ores associated with Zinc, Lead, and copper now it can be found in Air, soil, and water.

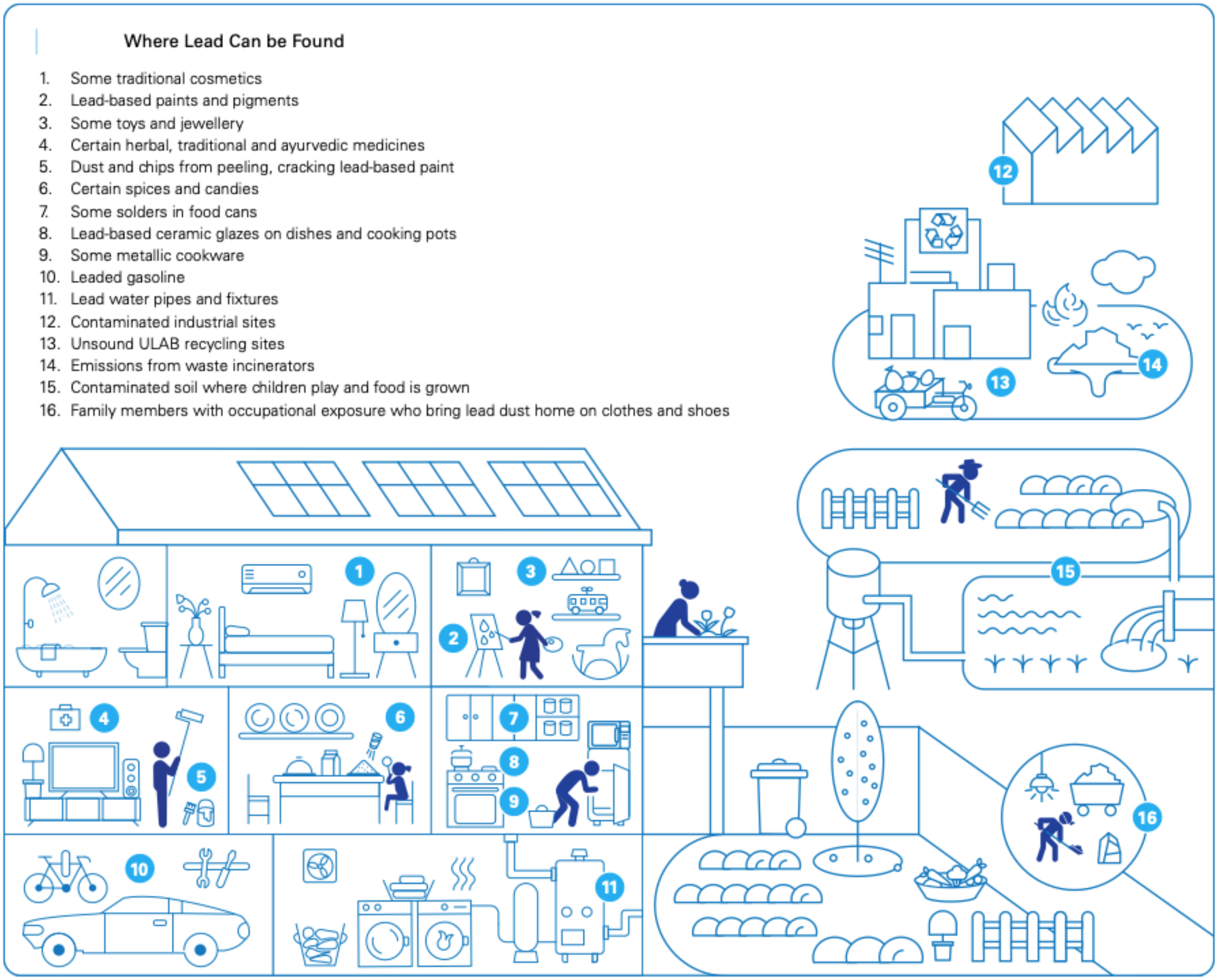
Due to the changes in its usage over the decades most of the cadmium is being transported through air emissions from anthropogenic sources, such as smelting and refining of metals, like occurs on northeast and some southern parts of Norway (Newman, H. R. 2004). Fossil fuel combustion, and municipal waste incineration are also a source of cadmium release to the environment (Krzyzanowski, M., & Cohen, 2008).

According to a 2018 updated report from the Folkehelseinstituttet (FHI) the limit values for cadmium should not surpass a concentration of 5 µg/L, this does not match with the European regulation established by the World Health Organization (WHO), who has stablished a health-based limit value for cadmium of 3 µg/L. Therefore, it is of great importance to monitor the release and accumulation of this pollutant and promote the utilization of new environmentally friendly techniques to remediate water bodies, sediments and soil that might contain this toxic heavy metal, to avoid its dispersion through the trophic chain.

3.5 Lead

Lead (Pb) is rarely found in nature in a metallic state, but as an ore bound to other substances, like in the case of galena (PbS). Lead compounds have been widely used in the 20th century, in oil industry, batteries, paint, radiation shields, and in the plastic industry (Acharya, S. 2013). Despite being consider a toxic metal, in the 21st century it has been still used as part of ammunition, cosmetics, toys, ceramics and cookware, transported over long distances by rainwater and runoff (Rees & Fuller, 2020) and several other sources as shown in Figure 3.
This heavy metal is a persistent contaminant in effluents at different pH values (Jin, L., & Bai, R. 2002) and thus gives opportunity for different types of adsorbents to be used for its removal.

Limit values for lead in drinking water in Norway should not be higher than 10µg/L, according to the FHI.



Where Lead Can be Found

1. Some traditional cosmetics
2. Lead-based paints and pigments
3. Some toys and jewellery
4. Certain herbal, traditional and ayurvedic medicines
5. Dust and chips from peeling, cracking lead-based paint
6. Certain spices and candies
7. Some solders in food cans
8. Lead-based ceramic glazes on dishes and cooking pots
9. Some metallic cookware
10. Leaded gasoline
11. Lead water pipes and fixtures
12. Contaminated industrial sites
13. Unsound ULAB recycling sites
14. Emissions from waste incinerators
15. Contaminated soil where children play and food is grown
16. Family members with occupational exposure who bring lead dust home on clothes and shoes

Figure 3.-infographic example of sources and lead exposure. Source: “The toxic truth” Rees & Fuller, 2020.

3.6 Effects of the exposure to heavy metals

For the general population, lead and cadmium exposure occurs mostly through food and water, and it can cause both acute and chronic symptoms of poisoning causing neurotoxic effects (Acharya,S 2013). In addition, the excretion of heavy metals from the body is slow and can be stored in the liver and kidneys causing critical damage to these organs. In the case for Cd exposure, this can cause osteoporosis (bone fragility), deformity of the skeleton, strong teratogenic and mutagenic effects, fertility, hormonal disruptions, serious effects on the mitochondria by the induction of oxidative stress (Genchi, G. et al. 2020).

An increase in the concentration of Pb in the blood stream will manifest as neuronal effects in the central nervous system such as cognitive performance. Pb also is a well-known carcinogenic and reason of cardiovascular, kidney, fertility, and hearing issues (Kumar, A. et al. 2020).

There is no cure for lead and cadmium poisoning, identifying local sources is a very important part of preventing exposure. In many cases, the population is exposed to more than one source without knowing, making the challenge even more complicated. (Demayo, A et al 1982)

3.7 Sources of contamination in Norway

In Norway most of the polluted water with heavy metals comes from different anthropogenic sources through run offs, especially close to roads (Baukhol Olsen, K. 2020; Grung, M. et al.2017). which according to a study conducted to determine the accumulation of heavy metals in road drainage (vegavrenning) receiving ponds, their sediments and biota around Ås-Rakkestad communes, observed that these two heavy metals reached concentrations above the limits stated by the WHO (Damsgård, 2011).

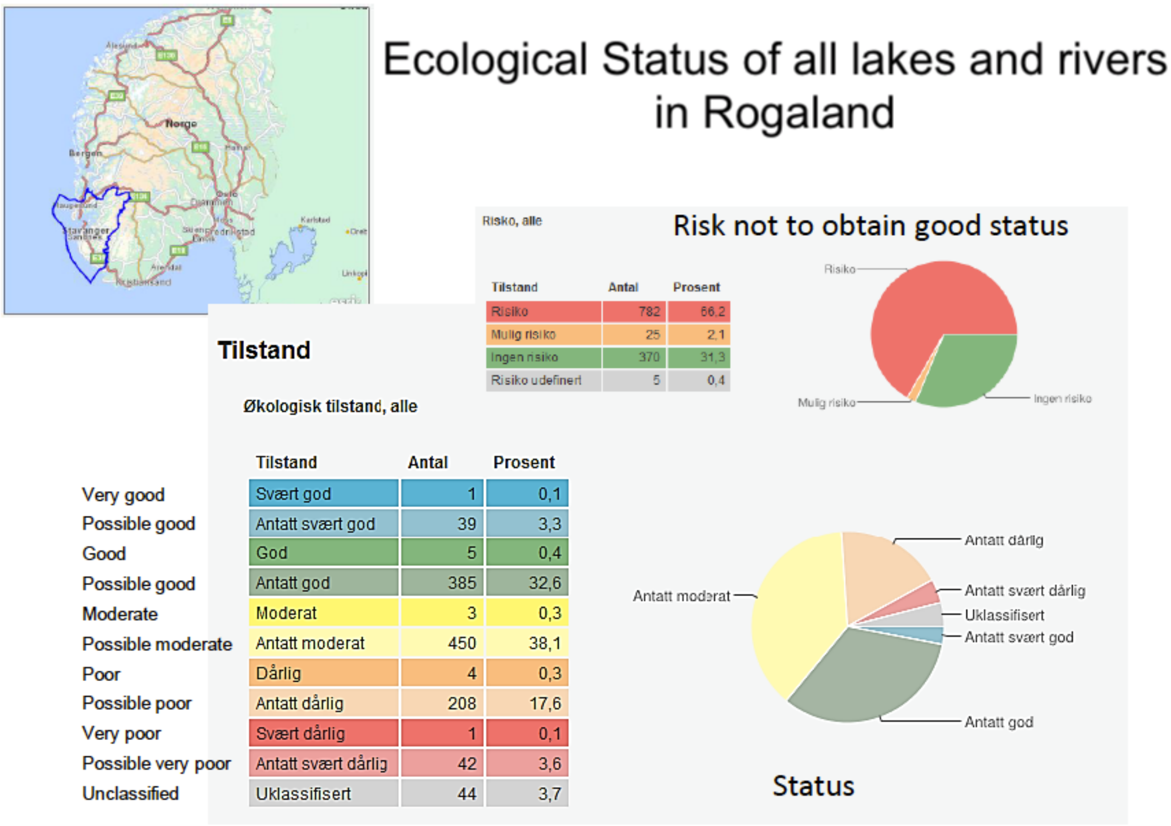
Other areas in which these metals can be found are the water bodies close to agricultural activity, this is due to soil contamination strictly related to the use of mineral fertilizers that contains trace amounts of heavy metals and that now a days are still being used.

Norway has a high agricultural activity and the use of fertilizers every season can result in an accumulation in soil that in conjunction with the heavy precipitations throughout the year will cause that the storm water gets combined with the sewers and thus increasing the discharges of polluted water, therefore, leading to noxious effects to the environment, crops, native plant species, animals and subsequently humans due to its bio-accumulative characteristic. (Gjengedal, E., et al.2015; Julshamn, K. et al.2013; Stene-Larsen, G. 2012; Airas, S. et al 2004; Julshamn, K. et al. 2001).

This not only affect the water bodies but also the biota present in them several studies have been conducted in the last years in mollusks such as blue mussels and cod, obtained from specific sources off the coast and fjords, indicating that fjords are the most endangered water bodies because they efficiently accumulate atmospheric pollutants and contaminants stemming from runoff far from point sources (Julshamn K. et al 2013; Berg V., et all 2000; Ugland KI. Et al 2000) as well as due to higher anthropogenic activity and weathering during summer season. (Breedveld, G. D. et al. 2021)

Norwegian water sources normally contain small amounts of lead, <1-5 µg/l (FHI). Nevertheless, there has been an enrichment of lead content in soil and lake sediments because of car emissions, industrial, and in southern Norway also from agricultural activity, anthropogenic factors as well as weathering and because of long-distance transported pollutants from other areas (Breedveld, G. D. et al.2021). In addition, it is also assumed that there will be an increased release of lead to water sources from local minerals due to acidification produced by environmental changes, since it can cause corrosion and release from wiring and fittings. In Norway, the use of lead-containing alloys in wiring, solder and fittings has been banned. Still traces of lead can be found in tap water since the old-fashioned piping system in Norway hasn't been fully changed even though over the last 30 years water treatment plants have improved their drinking water treatment practices (FHI, 2017)

Nonetheless, even though most of the data for heavy metals and the status of surface water (Figure4) from Norwegian waterworks are old few significant studies have been conducted recently since 2018 to determine the accumulation of this ones in water sources and sediments.



Ecological Status of all lakes and rivers in Rogaland

Risko, alle

Risk not to obtain good status

Tilstand	Antal	Prosent
Risiko	782	66,2
Mulig risiko	25	2,1
Ingen risiko	370	31,3
Risiko udefinert	5	0,4

Tilstand

Økologisk tilstand, alle

	Tilstand	Antal	Prosent
Very good	Svært god	1	0,1
Possible good	Antatt svært god	39	3,3
Good	God	5	0,4
Possible good	Antatt god	385	32,6
Moderate	Moderat	3	0,3
Possible moderate	Antatt moderat	450	38,1
Poor	Dårlig	4	0,3
Possible poor	Antatt dårlig	208	17,6
Very poor	Svært dårlig	1	0,1
Possible very poor	Antatt svært dårlig	42	3,6
Unclassified	Uklassifisert	44	3,7

Status

Geir Stene-Larsen. Ministry of Health and Care Services 2012.

Figure 4.- *Quality status of water bodies in Rogaland.*

One of the most recent studies conducted by the Norwegian Geotechnical Institute in 2020, found an accumulation of heavy metals in the Oslo Fjord, sediments and despite that the project manager Gøril Aasen Slinde stated that there is no danger associated with the pollution at the bottom of the fjord, this still represents a risk to the aquatic fauna, and subsequently the population. Thus, strict monitoring during a long-term period should be conducted in the surrounding water bodies, since the knowledge of specific sources for these pollutants are still limited, and the development of the metal accumulation is still unknown for other areas in Norway.

3.8 Food waste as a valuable adsorbent of pollutants in water

In Norway, there exist two highly produced food waste that can aid in the remediation of water effluents or later receiving aquatic environments.
The first under valuated waste is Spent coffee grounds, which according to SSB report from 2019, Norway imported around 40,000 tons of coffee every year for the last 10 years, which is equivalent to more than ten kilos per adult inhabitant or in other words 1,370 cups of coffee per inhabitant over 18 years of age, or almost four cups per day, conceding them the second place among the world's most coffee-thirsty nations. this waste currently ends up in the organic disposal bins and subsequently burned. The uses of SCG can be found in several areas nevertheless in this thesis it will only be address to the recently found ability as an adsorbent of pollutants.

The second most produced waste corresponds to shrimp shells. Worth notice that shrimp waste is highly consumed in Europe and worldwide, only in Norway, according to the Norwegian seafood council, the total household shrimp consumption reached a total of 9% in 2017 among all seafood consumption and predicts an increase in the upcoming years. Thus, the interest to give valorization to a large amount of waste that the consumption of this produces and it ends up being burned. Chitosan has been considered a promising material, because it is an abundant and can produce cost effective end products. The utilization of biopolymers such a chitosan has increased over the past decade, due to a better awareness and understanding of the advantages, as well as possible limitation of the use of petroleum resources and a partial substitution of petroleum-based products (Hassannia-Kolaee, M. et al. 2016.). As well as the interest in their affinity for certain characteristics as, chelating properties, biodegradability (Martínez-Macías, K. J. et al. 2020) and the fact that are non-toxic for the environment and its utilization will reduce de production of waste.

3.9 Spent Coffee Grounds

Coffee is one of the main agricultural commodities (Reis, K. C. et al .2015), and worldwide the processing generates significative amounts of residues, which account up to 50% of the total coffee produced (Aranguri-Llerena, G., & Reyes-Lázaro, W. 2019).

According to kaffe.no in Norway, the total consumption of raw coffee in 2019 was 47.089.678 kg. Due to this, large amounts of spent coffee grounds are being discarded since in Norway the organic waste gets burned and does not give any valorization to this waste.
Nevertheless, in the latest years, several studies have been conducted to determine the prospective uses of this waste. it has been reported that SCG poses a huge potential as an adsorbent of heavy metals due to its abundance in hydroxyl, amino, and carboxyl functional groups, and when combined with other polymers such as PVA and Chitosan, only enhances the adsorption capacity for pollutants and resulting in more efficient extraction of heavy metal from water effluents as reported by Hao, L., Wang, P., & Valiyaveettil, S. in 2017.

Spent coffee grounds uses can vary depending on its pre-treatment method. In the case of adsorption, the way this waste is treated will affect differently the affinity for a broad range of pollutants, making it a versatile adsorbent, that when combined with other type of adsorbents will only enhance the adsorption capacity of contaminants (Kim, M. S., & Kim, J. G. 2020; Aranguri-Llerena, G., & Reyes-Lázaro, W. 2019; Collazo-Bigliardi, S. et al 2019)

3.10 Chitosan

In Nature Chitosan is the second most abundant biopolymer after cellulose. In addition is also considered one of the most versatile and widely used polysaccharides in cosmetic, pharmaceutics, chemical, wine, beer, and medical industries. Its versatility has transcended these areas and reached remediation biotechnology to eliminate heavy metals and other pollutants through adsorption techniques.

Chitosan is the N-deacetylated form of chitin, a structural biopolymer found in the exoskeleton of several insects, crustaceans, and certain fungi.

Muhd, N. et al 2011, indicates that this polymer holds several peculiar physicals, chemical, and biological characteristics, that give this polymer a wide range of uses (figure 2) being one of them the ability to capture heavy metals due to its functional groups (Hydroxyl, Amino, acetamido).

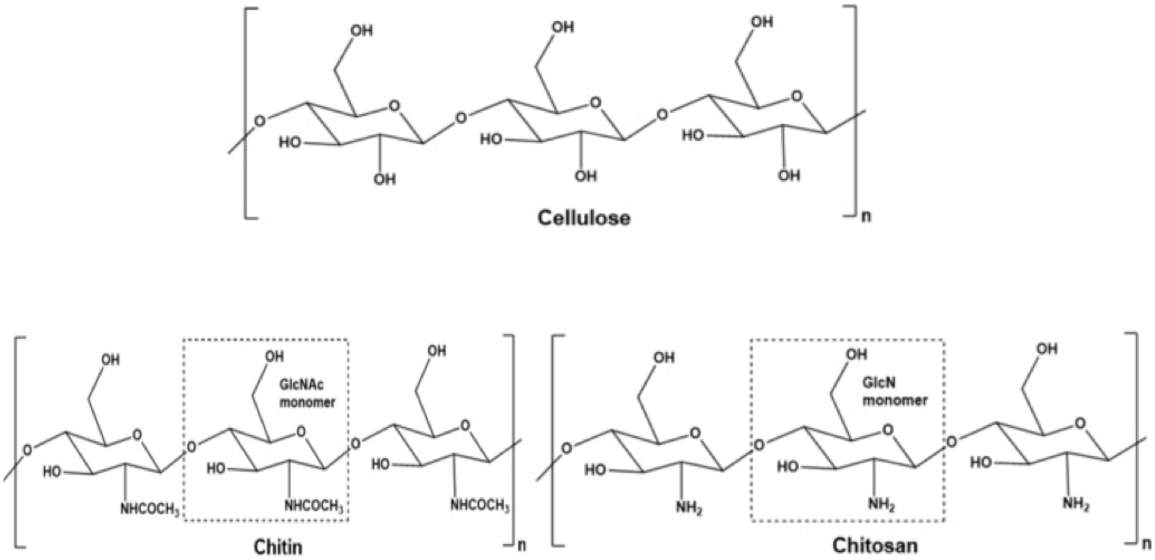


Figure 5.- *Chitin, chitosan and cellulose structures, the dotted squares indicate the main monomers linked which confers the difference between these 3 molecules and the beta linkage that gives them the similarity. (Extracted and modified from Schmitz, C et al.2019)*

Currently there exist two methodologies for the extraction and synthesis of chitosan. The chemical method, that include the procedures of demineralization (Dm), deproteinization (Dp) and deacetylation (DAc), the order of the technique for the first two steps can be changed to obtain different yields.

the second extraction method of chitin by biological means, involves the use of proteases secreted by bacteria such as *Bacillus licheniformis* serine endopeptidase, Alkalases, and the use of Lactic Acid producing bacteria suchlike *Lactobacillus sp*, among others. with the use of this type of bacteria demineralization and Deproteinization can be done in one step extraction, highly reducing the amount of time, resources and waste produced (Synowiecki & Al-Khateeb, 2000).

These methods are the most suitable procedure for the further use of chitin and chitosan in pharmaceutical, biomedical applications and has less environmental impact, moreover because unlike the chemical method, this doesn’t harm the physical, chemical (Younes & Rinaudo, 2015) and biological properties of chitin. Moreover, the Dp by enzymatic digestion of the waste allows the recovery of the protein hydrolyzed with a great proportion of amino acid, when the waste was previously Dm with HCl (Gortari & Hours, 2013; Rao et al., 2000).

Gortari & Hours, 2013 reported a summary of 21 publications in which lactic acid fermentation were used as the extraction process, showing the activity of 15 different microbial strain on different crustacean waste indicating that this procedure gives the best quality outcomes for Dp ranging between 45-99% quality and for Dm between 19-99%

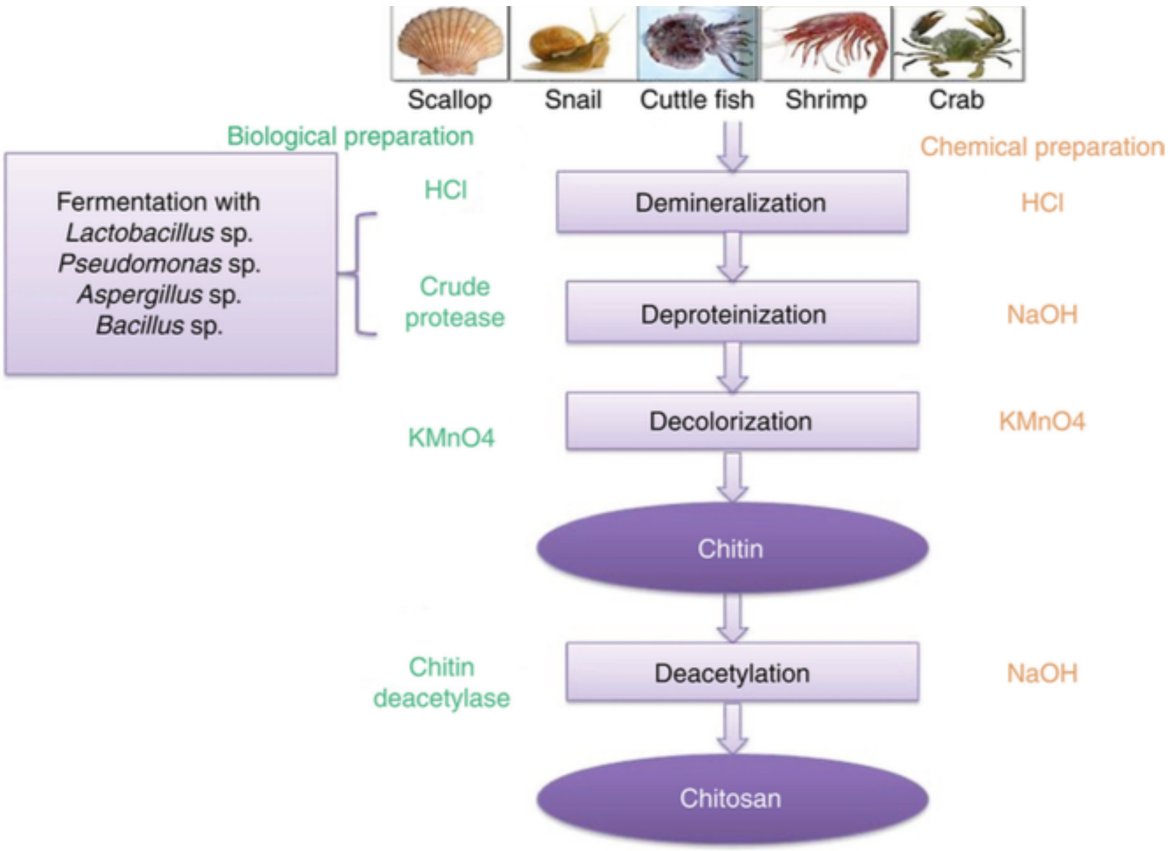


Figure 6.-*Extraction methods for Chitosan (Source: Hossain & Iqbal. 2014)*

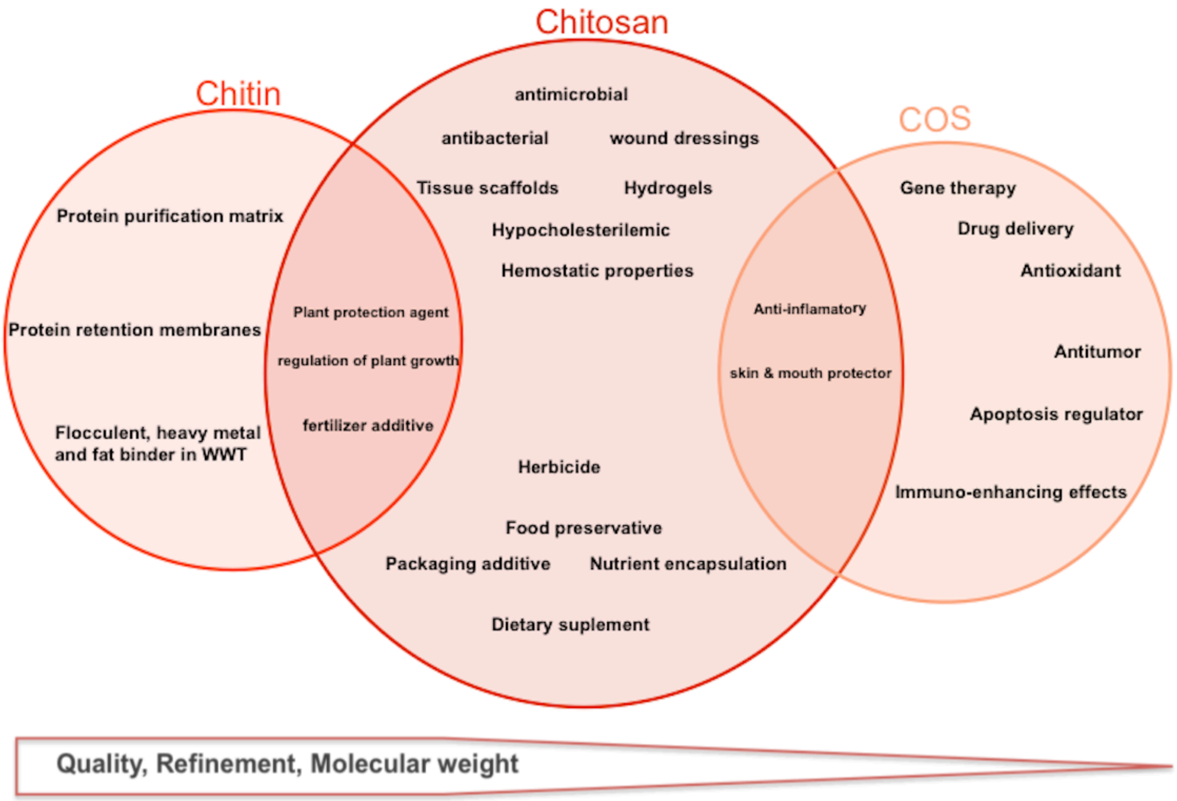
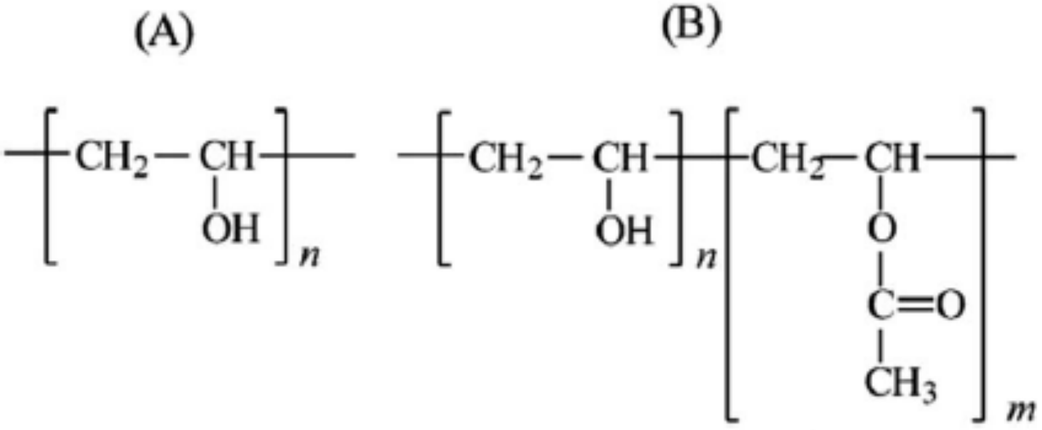


Figure 7.- *Applications of chitin, chitosan, and chitosan oligomers (COS) in different fields. *the size of the circle represents the market volume. the arrow shows the product quality and critical specifications needed in the final product. (Adapted from Schmit, C et al 2019)*

One of the most important characteristics of chitosan that encouraged its use in this study, correspond to its chelation properties. It has been stated by several authors that this natural cationic polysaccharide is capable to adsorb diverse heavy metals and pollutants at different pH, since its surface charge will change depending on the pH of the solution, and thus promoting the adsorption under different conditions, and even more interesting is that can be use in the remediation of contaminated soils (Martínez-Macías, K. et al 2020).

3.11 Polyvinyl alcohol

Polyvinyl alcohol (PVA) is a wide known cheap synthetic and nontoxic and biodegradable polymer with fair tensile strength and water solubility that depends on its degree of hydrolyzation (%DH) the higher hydrolyzation, less soluble in water this becomes. It has also been mentioned by Mok, C.F. et al 2020, that enhance the adsorption of chitosan by simple addition to the net content of hydroxyl groups in composite blends, since it contains large amounts of OH and around 14% residual acetate groups (after hydrolysis of polyvinyl acetate) in its polymeric structure (Wiśniewska, M., et al 2019; Halima, N. B. 2016). As well as improving the structural integrity of hydrogels (Agarwal, S. et al. 2016). Which will grant the final product the ability to be reused in multiple adsorption/desorption practices.



(Halima, N. B. 2016)

***Figure 8.-** Polyvinyl chemical structure. (A) fully hydrolyzed, (B)partially hydrolyzed*

3.12 Adsorption Isotherms

The most used models to describe and analyze the mechanisms of adsorption are Freundlich, Langmuir and Temkin (Ali, L. 2013; Ahmad *et al*. 2005). Non-linear and linear methods can be useful to fit the adsorption experimental data of metal ions in which the correlation of between adsorbed amount of any pollutant on adsorbent at equilibrium and given temperature will determine if whether fits a model.

Langmuir isotherm it is based in the hypothesis that all active adsorption centers are equivalent and the capacity of a molecule to adsorb to the surface is independent to the fact that if proximal positions are occupied or not. Moreover, the adsorption mechanism is restricted by the formation of a monolayer and there are not lateral interactions among de adsorbate molecules. (Penedo-Medina, M. et al. 2015; Lazo, J. C. et al. 2008; Mall, I. et al. 2005). For this the non-linear (Eq. 1) and linear (Eq. 2) equations are used to obtain the values of the main parameters, will determine the best fit for the data. q_e (mg/g) correspond to the equilibrium uptake by the adsorbent, Ce (mg/L) indicates the remained concentration of the pollutant in equilibrium, a_L and K_L (L/mg) are the Langmuir constants, K_L that will indicate the affinity between the adsorbent and adsorbate (Penedo-Medina, M. et al. 2015; Ho, Y. S. et al. 2002).

$$q_{\mathrm{e}} = \frac{K_{\mathrm{L}} C_{\mathrm{e}}}{1+a_{\mathrm{L}} C_{\mathrm{e}}}$$

Eq. [1]

$$\frac{1}{q_{\mathrm{e}}} = \frac{1}{K_{\mathrm{L}} C_{\mathrm{e}}} + \frac{a_{\mathrm{L}}}{K_{\mathrm{L}}}$$

Eq. [2]

$$R_L = \frac{1}{1 + (1 + K_L \, C_e)}$$

Eq. [3]

One of the major features of the Langmuir model is that incorporates the separation factor R_L. This parameter will determine if the fit is favorable or not for the experiment depending on its value. When $R_L = 0$ the isotherm is irreversible, $R_L = 1$; Linear isotherm, $R_L > 1$ denotes a non-favorable isotherm and lastly when the obtained value is in the range $0< R_L < 1$ indicates a favorable isotherm fit (Balarak, D. et al. 2017; Penedo-Medina, M. et al. 2015; Dada, A. O. et al 2012).

The Freundlich model, assumes that the surface of the adsorbent is energetically heterogeneous, conformed by adsorption sites of characteristic energy. Furthermore, it is considered that there are not lateral interactions in between the adsorbed molecules and that adsorption does not occurs on a monolayer surface. (López-Luna, J. et al. 2019; Penedo-Medina, M. et al. 2015; Imamoglu, M. & Tekir, O. 2008).

$$q_e = K_F C_e^{b_F}$$

Eq. [4]

$$\log q_e = b_F \log C_e + \log K_F$$

Eq. [5]

Non-linear (Eq. 4) and Linear (Eq. 5) Freundlich expressions are used to determine if the adsorption experiment fits either model. q_e(mg/g) correspond to the equilibrium uptake by the adsorbent, Ce (mg/L) is the final concentration in equilibrium, and K_F (mg/g) and b_F (also denoted as 1/n from some authors) are the empiric Freundlich constants that determine the adsorption capacity and intensity respectively. b_F is strictly related with the adsorption efficiency in which, similar to the Langmuir parameter R_L, will indicate if the adsorption is favorable ($0< b_F <1$) or not ($b_F >1$) (Penedo-Medina, M. et al. 2015)

The Temkin isotherm correspond to an adjusted equation of the Langmuir model, its linear form (Eq. 6) and non-linear (Eq.7) it's based on the assumption that an increase or decrease of enthalpy will depend on the adsorbed quantity of adsorbate. And should be linear rather than logarithmic (Shikuku, V. O. et al. 2018). Where B_T (L/mg) Corresponds to the Temkin constant K_T(L/mg) Corresponds to the equilibrium binding constant of adsorption heat, and b_T (kJ/mol) represents the variation in adsorption energy

$$q_e = B_T ln k_T + B_T ln C_e$$

Eq. [6]

$$q_e = \frac{RT}{b_T} \ln(K_T\ C_e)$$

Eq. [7]

The results can be easily obtained and interpreted by utilization of the equations and being the correlation coefficient R^2 a direct indicative to which model the data will fit best. Nevertheless, the use of the linear form of isotherms can alter the error, variance, and normality of the data (López-Luna, J. et al. 2019; Shikuku, V. O. et al. 2018) On the opposite, the use of Non-linear models could correct these issues by minimizing or maximizing the distribution from the calculated and experimental data While this type of single batch experimental procedures and adsorbents could fit the data in a satisfactory way for these models both forms of the isotherms were used in this study.

3.13 Adsorption kinetics

Suitable kinetic models are important to study to determine the residual contaminants water content in samples as well as the equilibrium and rate adsorption rates of pollutant adsorbed (Ahmad, et al. 2005). This data can be easily obtained by a conventional Batch test experiment using two of the most common methods equations, the pseudo first-order and pseudo second-order.

$$\ln(q_e - q_t) = \ln q_e - k_1 t$$

Eq. [8]

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$

Eq. [9]

In which K_1 (min -1) and K_2 (g/mg·min) correspond to the first and second order adsorption kinetic constant, q_e (mg/g) indicates the saturation adsorption capacity at equilibrium, and q_t (mg/g) indicates the adsorption amount of an adsorbate at a given time (t).

4 MATERIALS AND METHODS

4.1 Reagents

All reagents were purchased from VWR.no. Chitosan (Medium molecular weight, 85% deacetylated, Sigma Aldrich®) glacial acetic acid (≥99,7% ACS grade, VWR®) Cadmium nitrate tetrahydrate (99.97% ACS grade, Sigma Aldrich®) lead Nitrate (99.9% ACS grade Sigma Aldrich®) Nitric Acid (HNO3 65% ACS grade, Merk®), PVA (≥85% hydrolyzed, Merk®), Spent coffee grounds was recollected from UiS Kjolv Egeland hus cafeteria.

4.2 Stock and standard solutions

For the determination of the adsorption of trace heavy metals in aqueous solutions methods of the Swedish standards institute for water quality determination for trace elements handbook was followed to prepare the heavy metal stock and standard solutions used, ultra-pure water was used to prepare all solutions.

Three solutions of nitric acid were prepared, a concentrated solution at 15 mol/L(A) and two diluted ones at 0,5 mol/L (B) and 0.15 mol/L (C). This was done by adding the corresponding amount of nitric acid in a graduated flask and adjusting the total volume of 1L with ultra-pure water.

For the preparation of 1 g/l cadmium stock solution, 2.744 g of cadmium nitrate tetrahydrate, was dissolved in 1 liter of the diluted nitric acid solution B previously prepared. Subsequently, preparation of a cadmium standard solution at 1 mg/l was done, by taking 1ml of the cadmium stock solution and 999 ml of diluted nitric acid solution C in a graduated flask.

A 1g/l lead stock solution was made by previously dissolving 1g of lead in a mixture of 10 ml of nitric acid solution A and 10 ml of ultra-pure water, followed by diluting into 1L of ultra-pure water.

A lead standard solution of 1 mg/l was prepared by drawing 1 ml of the lead stock solution previously prepared into a graduated flask and 999 ml of nitric acid solution C was added.

Both standard solutions have a shelf-life of several months and they were used to prepare all the dilutions needed for the adsorption experiments

4.3 Synthesis of composite beads

The methodology conducted in this thesis is summarized in the Figure below.

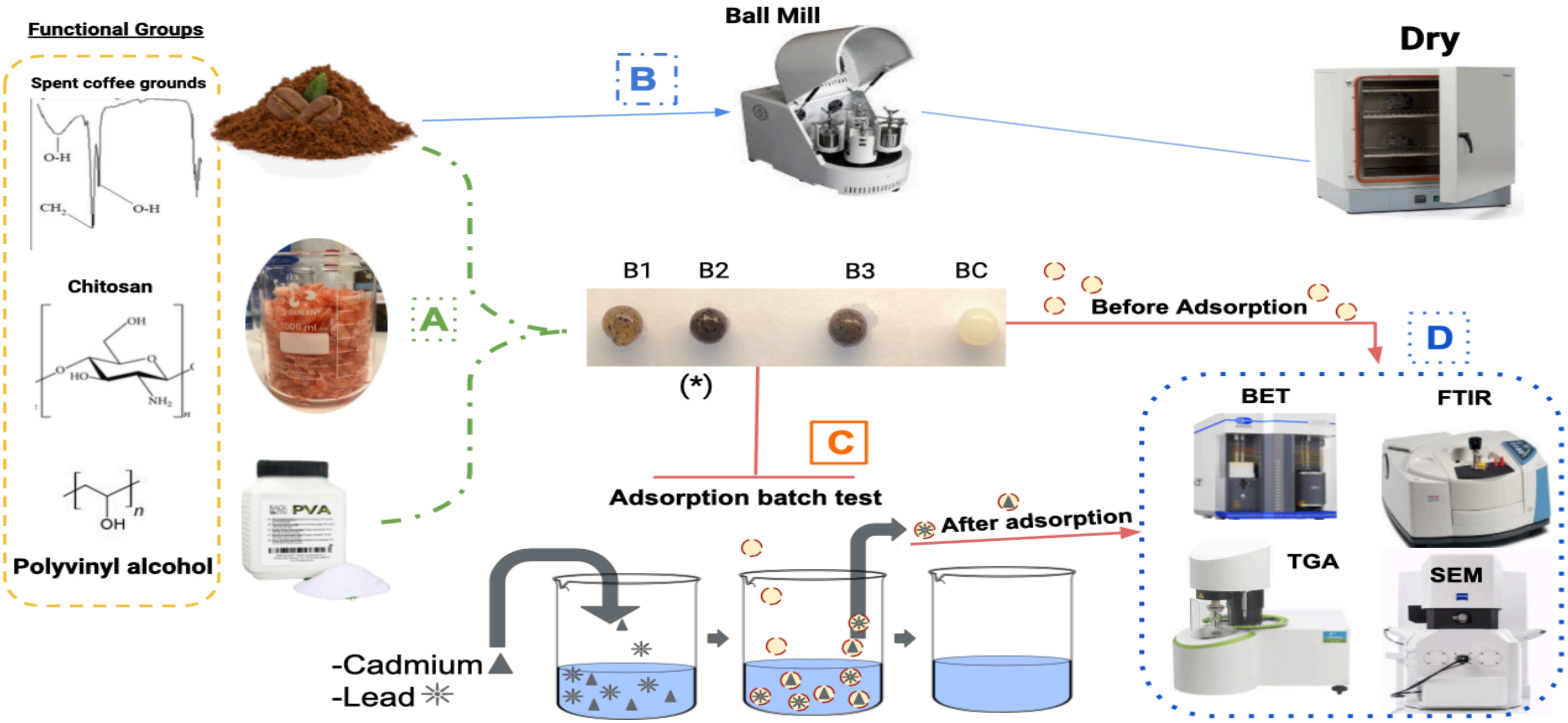


Figure 9.-*Flow chart methods conducted for production of composite beads to be used as an enhanced adsorbent of cadmium and lead in aqueous solutions.*

The left side of the scheme shows the functional groups for each adsorbent (yellow dotted line). According to the literature these groups endows them with the ability to sequester heavy metals from aqueous solutions by chelation, therefore its utilization in the remediation of several industrial processes and thus it becomes the main objective of this master thesis research, by using them in combination to enhance adsorption of two of the list of most known toxic heavy metals present in water effluents.

The central picture (*) exhibits the composite beads, in which different concentrations of chitosan, PVA, and untreated raw SCG (RSCG) were used (A) to determine the most suitable concentrations that will influence and determine the physical stability ("strength") of the beads when immersed in the solutions for the adsorption experiments performed with the aim to determine the reuse of these beads after several adsorption/desorption cycles.

In these first experimental procedures, it was possible to observe that the size of the SCG particles was too big to be dispersed homogeneously in each bead and while blending the mother solution, a lot of precipitation occurred, thus a new methodology was evaluated by using a ball mil (B) as proposed by Lee, H. K. et al. 2015. The parameters used are shown in Table 1, in order to produce a finer powder which will be distributed more homogeneously in the mixture.

Table 1.- *Ball mill parameters for raw spent coffee grounds used in the composite beads*

sample	Rotational speed (rpm)	time (min)	cooling pause (min)	repetitions	observation
RSCG1	750	10	1	6	very fine and pasty
RSCG2	750	10	2	3	fine powder less pasty

*RSCG: raw spent coffee grounds, meaning it's not treated in any way more than just dehydration at 65ªC in an oven to remove all traces of water.

4.4 Bead synthesis

Bead mixture was made by preparing a 4% w/v chitosan solution, dissolved in 1.4% acetic acid, PVA was dissolved in distilled water in two different concentrations 7,5% and 10% w/v, all solutions were stirred overnight to achieve maximum homogeneity. For the beads blend, a final solution of 25mL was made by mixing equal parts of chitosan and PVA, followed by the addition of SCG as shown in table 1, mixed overnight and sonicated for 1.5 hrs. in a Branson® 2510 ultrasonic bath, to achieve maximum homogenic dispersion of the SCG particles in the viscous solution and removal of any bubbles that could damage the extrusion and integrity of the bead.

Table 2.- *Composition of all beads used in this research.*

Bead	SCG (gr)	Chitosan (%)	PVA (%)
B1	1	4	7,5
B2	2	4	7,5
B3	3	4	10
BC	0	4	0

After obtaining a homogenous mixture, each bead solution was taken with a syringe and added dropwise to a solution of 1N NaOH at room temperature and stirred until the beads were stable and fully coagulated. Later the beads were strained and rinsed with distilled water until the rinsed solution reached pH 7, after this the beads can be stored in distilled water until use or used immediately (Figure 10).

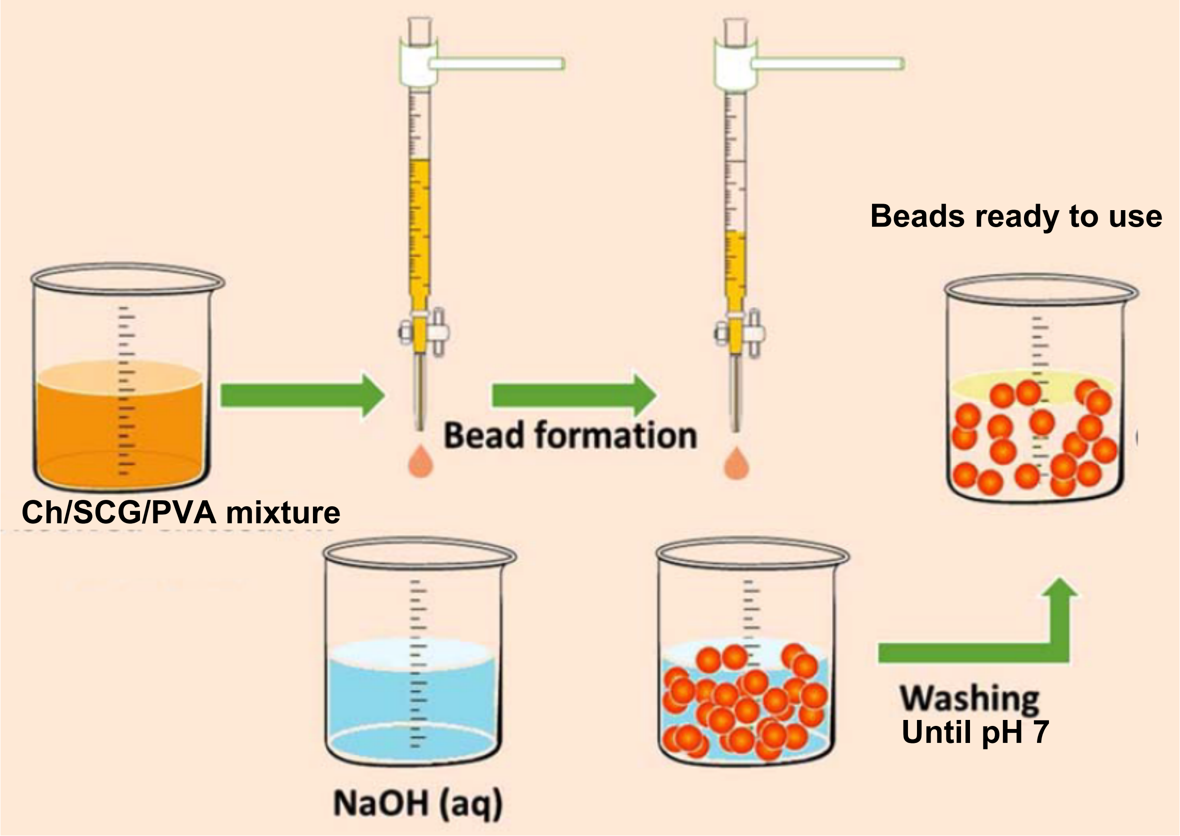


Figure 10.-synthesis of beads. Extracted and modified from Mahaninia, M. H., & Wilson, L. D. (2015)

Lastly, after the preparation of beads, adsorption studies in batch tests (C section of Figure 9) were conducted to confirm and discern which kinetic and isotherm models will fit best, and to determine the rate of adsorption, removal capacity and the relation between the amount of adsorbate (cadmium and lead) for each bead composition respectively.

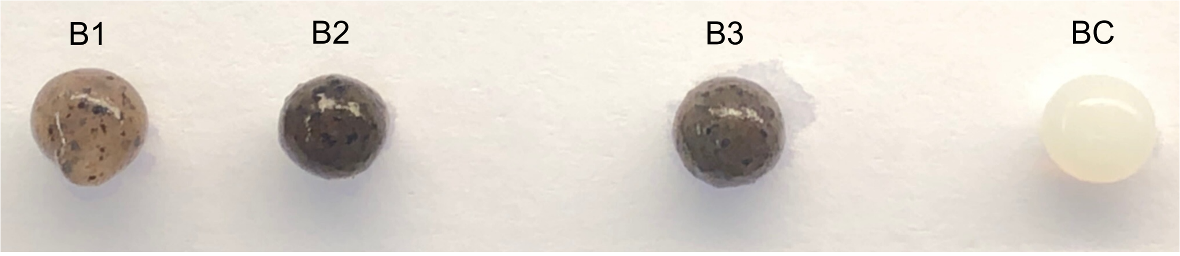


Figure 11.- *Visual aspect of all beads after spherification and before adsorption.*

4.5 Bead characterization.

In addition to all of the above SEM, BET and FTIR techniques (Figure 9 D) has been taken in consideration as a part of the methods for this thesis, with the aim to obtain an insight of the physical characteristics of the beads such as the thermal gravimetric analysis (TGA), surface topography (SEM), surface area and porosity (BET) and the availability or modification of functional groups that are responsible for the binding of the adsorbate (FTIR) of the composite bead before and after adsorption.

4.5.1 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis was performed in the petroleum department, using a simultaneous thermal analyzer (TA) (NETZSCH STA 449 F3 Jupiter).
Samples were dried overnight at 30ºC, and 1 mg was used to be analyzed under a helium atmosphere (gas flow 20 $mL.min^{-1}$), withing a temperature interval from 30 °C to 1000°C at a 10 °C min^{-1} heating rate. The weight loss data obtained was standardized and analyzed using the statistical software Origin lab version 9.65 to determine significant differences of each bead before adsorption of heavy metals.

4.5.2 Fourier Transform Infrared Spectroscopy (FT-IR)

For the FTIR analysis, was performed for the pure compounds in powder form (Ch, SGC, PVA) as reference and each set of beads (BC, B1, B2, B3) obtaining a total of 15 samples to be analyzed before, as well as after adsorption of cadmium and lead to determine if there are any changes of the peaks due to the adsorption of the compounds.
All beads were dried over night at 30°C together with the pure compounds. Each bead was crushed, and placed over the clean crystal at room temperature, followed by the measurement of the adsorption spectra in an Agilent Cary 630 ® FITR spectrometer with 1-Bounce Diamond ATR sampling module.
Infra-red radiation propagated through the crystal and sample to obtain the correspondent infrared adsorption operating over the spectral range of 4000 to 550

cm^{-1}. Major vibration bands were identified to determine the functional groups for all compounds as well as for each bead.

4.5.3 Determination of Surface area (BET)

To determine the surface area and porosity of beads an amount of approximately 1 gram of dry beads were degassed in vacuum at 30ºC overnight into BET quartz cells to ensure the removal of water and desorption of any other impurity on a Micromeritics VacPrep ® 061 sample degas system, followed by the physisorption analysis on a Micromeritics TriStar ® II 3020 with nitrogen as the adsorbate gas.

4.5.4 Scanning Electron Microscopy (SEM)

SEM was performed using a Transmission Electron Microscopy, JEOL JEM-2100Plus. The beads were analyzed to observe the topography of the surface. attached to aluminum supports and coated with gold at 25 °C.

4.6 Adsorption Analysis

Adsorption experiments were carried out by batch process at room temperature. The amount of adsorbent was weighed and placed in an Erlenmeyer flask containing 50 ml of a solution with either cadmium or lead previously adjusted to pH 5.

The mixture was stirred on a magnetic shaker at 150 rpm. At the end of the adsorption process, a filtered solution was taken from each flask and the concentration of cadmium and lead left was determined photometrically in a spectroquant ® using the spectroquant ® cadmium and lead cell test. The Removal Percentage (% R) and adsorption capacity (q_e) was determined by applying the following equations:

$$\%R = \frac{C_0 - C_e}{C_0} \times 100$$

Eq. [10]

$$q_e = \frac{(C_0 - C_e)V}{m}$$

Eq. [11]

Where Co (mg/L) corresponds to the initial concentration of cadmium or lead, and Ce(mg/L) is the final concentration of the heavy metal left in the liquid after reaching equilibrium, m (g) indicates the total mass of the adsorbent utilized and V (mL) the total volume of the solution containing the metal.

4.6.1 Determination of kinetics

For the determination of the kinetic model, a 0.15 mg/L of cadmium or lead solution was prepared from a 1 mg/L standard solution, and 50 ml was distributed in 10 separate 100ml Erlenmeyer flasks labeled at 0 min, 5min, 10 min, 20 min,30min,40min, 50min, 60min, 70min and 80min. Before adding 1 gram of the corresponding bead, the solution was adjusted to pH 5 with either 0.1N of HCl or 0.1N of NaOH. Subsequently each flask was positioned in the shaker at 150 rpm and removed after completion of each time, followed by the filtration of 10 ml of the sample solution with a 0.2µm Whatman® syringe filter.

Later the treated sample was added into a cadmium or lead spectroquant® reaction cell and followed the instructions of each kit for later measurement in a UV/VIS spectrophotometer (spectroquant® prove 300). All the date was noted and used to calculate the kinetic parameters, with equation 8 and 9 using the software OriginPro® 2019b.

4.6.2 Determination of isotherms

Linear and non-linear least squares method were applied to fit the experimental data of cadmium and lead adsorption for all different beads.

For the study of the Langmuir and Freundlich and Temkin isotherm models, 50ml of five solutions in a range of 0.1 to 0.3 mg/L was prepared from a 1 mg/L standard solution of either cadmium or lead and added into a 100 ml Erlenmeyer flask labeled correspondently, followed by the addition of with 0.1N of HCl or 0.1N of NaOH to adjust at pH 5. Later 2 grams of beads were added to the solution and stirred for 2 hours on a magnetic shaker at room temperature to achieve equilibrium.

After the time was concluded, 10 ml of sample were drawn out with a 0.2µm Whatman® syringe filter and transferred to a cadmium or lead spectroquant® reaction cell to be further analyzed in a UV/VIS spectrophotometer (spectroquant® prove 300). The measured final concentration was noted and used to calculate the Isotherm parameters with non-linear (Eq. 1, 4, and 7) and linear (Eq. 2, 5, and 6) equations for each bead and heavy metal using the software OriginPro® 2019b.

5 RESULTS & DISCUSSION

5.1 Thermogravimetric analysis (TGA)

According to the TGA analysis performed, it was not possible to observe a distinct different pattern between beads BC, B1, and B2, all three curves were significantly similar. Nevertheless It is possible to discern three-weight loss matching interval areas for BC, B1 and B2 in comparison with B3 which contains four.

The first decrease corresponds to the residual content water loss in the beads, which was 13,5% for BC, B1, and B2, and 7,9% for B3 in the temperature range of 23ºC to 250ºC approx. A second major interval of weight loss of 36,2% for BC, 36% for B1, 35,9% for B2 can be seen at a temperature interval of 250ºC to 350ºC, which for B3 divides into 2 drop intervals of 23,2% and 29,3% at a temperature range of 200ºC and 400ºC approx. this could indicate that since B3 has the highest concentration of PVA (10%) and SCG (3 g) resulted in better thermal stability due to the lignocellulosic content of the SCG, which can withstand temperatures up to 500ºC (Reis, K. C., et al.2015). In addition, this can indicate that B3 can retain higher amounts of water due to new hydrophilic areas created in composite beads since PVA has a high affinity with water and thus made the composite prone to retain more water in its structure (Nazarudin, M. F., et al. 2011; Yang, H., et al. 2017).

The final interval of weight loss corresponds to the full degradation of the beads (all carbon and oxygen get depleted to their maximum in this area of the graph). Again values were very similar for beads BC, B1, and B2 (19,7%, 20,1%, and 20,4% respectively) on the temperature range of 350ºC to 600ºC in contrast with B3, which displays a slight deviation in the degradation temperature line between the range 400ºC and 800ºC, in which lost 15,9% of the total weight. Implying that is more tolerant to higher temperature changes, since it reached full degradation at 800ºC in difference with 600ºC for BC, B1, and B2.

Noteworthy that according to literature chitosan only presents two main degradation steps which one of them can be almost perceptible in B1, B2, and B3 graphs (red arrow) at lower than 100 °C (due to water evaporation) and the second small deviation at around 300 °C (red arrow) when the polysaccharide started to degrade (Fan, C., Li, et al 2016)

The obtained results suggest that higher concentrations of PVA and SCG in the composite grants a better stability to extreme processing temperatures.

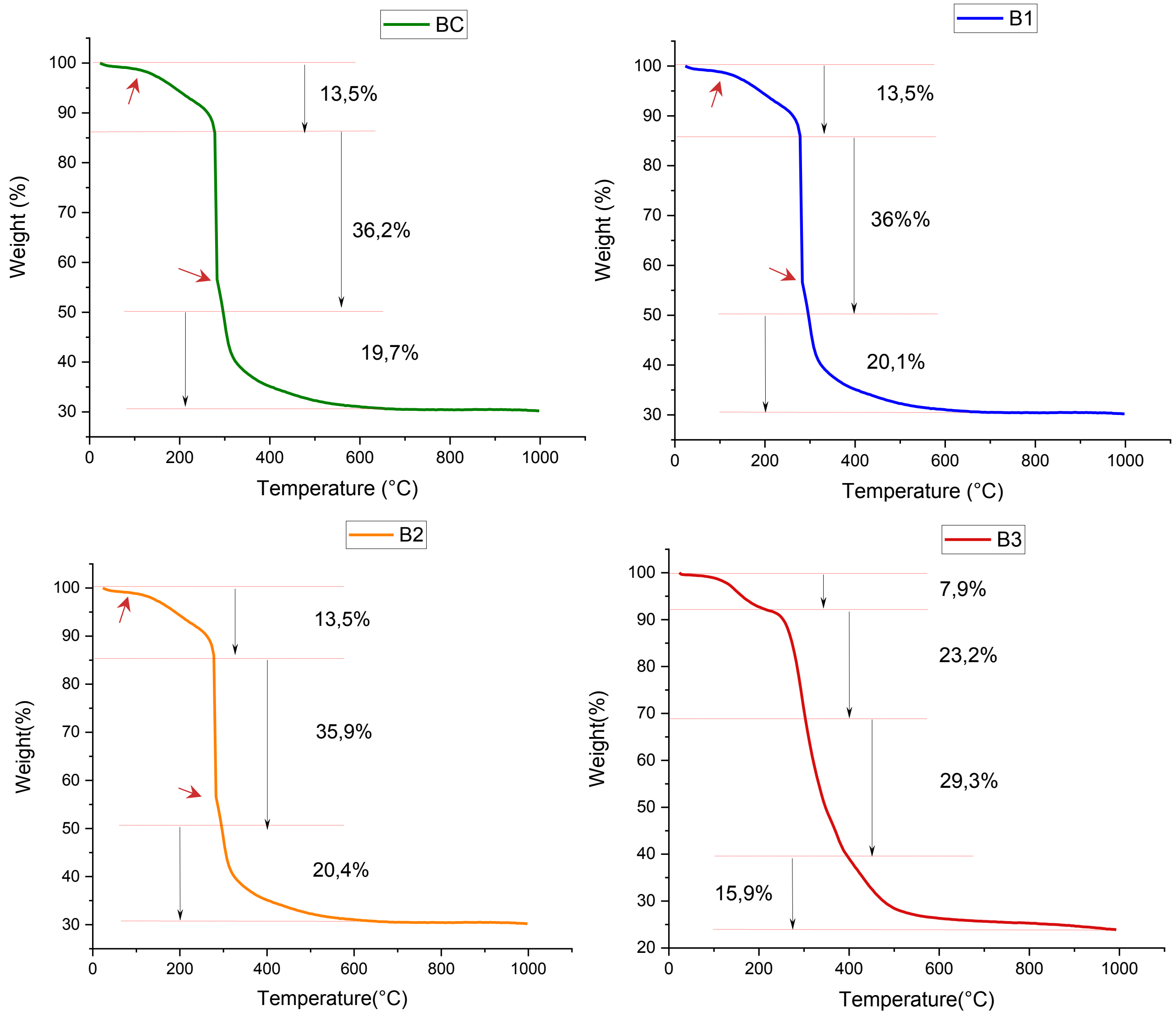


Figure 12.- *Thermogravimetric analysis of all four composite and their weight loss percentages.*

5.1 Fourier Transform Infrared Spectroscopy (FT-IR).

Figures 12 and 13 show infrared spectra of the pure components in powder form used in the bead blend mixture, and all beads used in this study before and after adsorption of heavy metals.

A peak with high of strong transmittance indicates few bonds available, indicating an interaction of heavy metals with each functional group. Conversely, a low or weak transmittance denotes a high presence of bonds (Nahm, S. 2015). In addition, any deviation of the peaks on the x axis (cm $^{-1}$) and changes in its transmittance denotes an interaction between the crosslink of the main components in the mixture as well as adsorption of the pollutants of interest (Mansur, H. S. et al 2008).

Pure PVA spectra (Figure 12a blue) depict all the major peaks for this pure element. A broad band was observed at 3308 cm^{-1}, corresponding to an OH-stretching typical for PVA, followed by two sharp peaks at 2939-2900 cm which correspond to a C-H stretching from an alkene. The fourth peak noted, was a weak broad signal at 2101 cm^{-1} indicating a C≡O stretching of an alkyne monosubstituted. The final major peak obtained was a weak peak at 1731 cm^{-1} that correspond to a C=O stretching from the remaining acetate groups after hydrolyzation, which correspond to the high dehydrolyzation percentage of the used PVA (85%) (Kharazmi, A., et al 2015; Agarwal, S. et al 2016).

Untreated SGC infrared spectra are shown in brown in Figure 12 (a), which have a characteristic transmittance profile typical of lignocellulosic materials. It is possible to observe a broad OH-stretching vibration at 3344 cm-1 that could be associated with moisture from the remanent water in the sample (Amir et al. 2011), followed by two sharp peaks at 2923- 2849 cm^{-1} that correspond to an alkane C-H stretching, possibly associated to a methyl group from the caffeine molecule. These peaks accord with the wavelength range suggested by Ballesteros, L.F. et al 2014, and several other authors from the same publication.

The fourth peak was encountered at 2101 cm $^{-1}$, being a weak C≡H stretching vibration like PVA, and chitosan (orange spectral line) as can be seen below. Nevertheless, for coffee, this peak is related to carbohydrates, proteins, and chlorogenic acids present in coffee (Barrios-Rodríguez, Y. et al 2021). Finally, three major peaks were found. A strong C=O stretching at 1748 cm -1, a medium C=C stretching from a conjugated alkene at 1652 cm-1, and lastly a strong N-O stretching at 1522 cm^{-1}, which according to Dos Santos, et al. 2021; and El-Abassy R.M et al 2011 could also correspond to lipid and CGA content in different types of coffee.

The infrared spectra for chitosan used in this study (Deacetylation degree 85%) is shown in Figure 12 (a) in orange. The spectra show a medium broad N-H stretching at 3299 cm-1 which according to several authors corresponds to a typical primary aliphatic amine from this polymer, which also has been attributed to an O-H stretching. The second and third peaks correspond to a C-H stretching alkane, and a C=H stretching alkyne mono substituted at 2866 cm-1 and 2090 cm-1 respectively. The subsequent peaks found show the characteristic amides of chitosan. at 1652 cm-1 in can be appreciated a C=O stretching that is part of a primary associated amide, followed by a to N-H bending secondary amide prolyl from residual N-acetyl groups at 1585 cm-1 and finally a C-N stretching of a tertiary amide in the range of 1320 cm-1. (Ranjbari, S. et al 2020; Rossainz-Castro, L. G. et al 2018; Fan, C. et al 2016; Nazarudin, M. F., et al 2011).

Figure 12 (b) shows the major peaks for bead BC (4% chitosan) before (control) and after adsorption of Pb and Cd respectively. The control bead BC shows similar spectra to chitosan powder with some minor deviation as well as after adsorption of the metals in the study. It is possible to appreciate an overlap of a O-H and a N-H stretching of primary amine (Mahaninia, M. H., & Wilson, L. D. 2015) at 3322 cm-1 and the C=O stretching, N-H bending and C-N stretching of primary, secondary, and tertiary amide peaks at 1650, 1586, and 1320 cm-1 respectively, these ones are situated in the same wavelength range even before and after adsorption. However, a transmittance variation is noticeable after adsorption for both heavy metals in the range of the tertiary amide (1320 cm-1) and as well as the N-H stretching of the primary aliphatic amine (3322 cm-1) after the adsorption of lead. These changes in transmittance can indicate that the major adsorption mechanism for this bead corresponds to an anionic exchange between these two major functional groups due to their chelating properties as well as the affinity that heavy metals poses for this kind of functional groups (Martínez-Macías, K. et al 2020).

Figure 13 (c, d, e) shows the IR spectra of beads B1, B2, and B3 before and after adsorption respectively. All beads presented 9 similar major peaks (Table 3) with some slight deviation in their wavelengths and some suggestive changes in their transmittance after adsorption within each other.

Table 3.- *Mayor characteristically functional groups and their wavelength observed for all beads in study*

	Peak wavelength (cm-1)			
Functional group	BC	B1	B2	B3
N-H stretching aliphatic primary amine/ O-H stretching *	3322	3327	3322	3327
C-H stretching (I)	2930	2923	2917	2922
C-H stretching (II)	2867	2849	2853	2850
C≡H stretching	2093	2107	2107	2107
C=O stretching	1747	1750	1752	1747
C=O stretching associated primary amide	1650	1660	1651	1645
N-H bending secondary amide	1586	1578	1574	1581
N-O stretching	(-)	1540	1536	1531
C-N stretching tertiary amide	1320	1320	1320	1320

(-) Peak is not present in this bead; (*) this two groups tend to overlap mostly since chitosan and PVA are combined (Jin, L., & Bai, R. 2002).

For bead B1, it is possible to differentiate four distinctive changes in transmittance after adsorption of both heavy metals (Figure 13 c) in comparison with the control bead before adsorption.

After the adsorption of lead and cadmium, B1 had a significant increase in the peak intensity in the wavelengths 2917-2853 cm-1 for lead, and a slight decrease in the intensity after the adsorption of cadmium. This followed by a sharp increase of the peak at 1750 cm-1 for lead, and into a minor degree for cadmium. A decrease in 1578 cm-1 and 1540 cm-1 might indicate that lead bonded or have more affinity with the last two functional groups in contrary as cadmium, which noticeable has been bounded with the first three functional groups.

When it comes to bead B2 (Figure 13 d) a decrease in the peak sharpness could be noticed after the adsorption of lead as well as for cadmium in the transmittance of the peaks at 1574cm-1, 1536 cm-1, this is a clear indicator that the N-H bending of the secondary amide and the N-O stretching was the functional groups responsible for the adsorption of the heavy metals. A final increase in sharpness of the peak at 1320cm-1 indicates a higher availability of C-N stretching functional groups.

For bead B3 (figure 13 e) different transmittance changes were observed.
After the adsorption of lead, there was a slight increase in the transmittance of the sharp peaks at 2922-2850 cm-1 followed by a noticeable reduction of the C=O stretching at 1747 cm-1, indicating that lead must have a higher affinity for this type of functional groups (high transmittance few bonds available). It is also possible to observe a change in the transmittance of the peaks at 1582 cm-1 and 1531 cm-1 showing more availability of the N-H bending secondary amide groups after the adsorption of lead.

On the other hand, the spectra obtained after the adsorption of cadmium show an opposite pattern in which the sharp peaks at 2922-2850 cm-1 and 1747 cm-1 developed a reduction of the transmittance or said in other words a high presence of C-H stretching bonds and thus denoting that cadmium is not binding to this functional groups, but maybe to the amides present in the ranges within 1645 to 1320 cm-1.

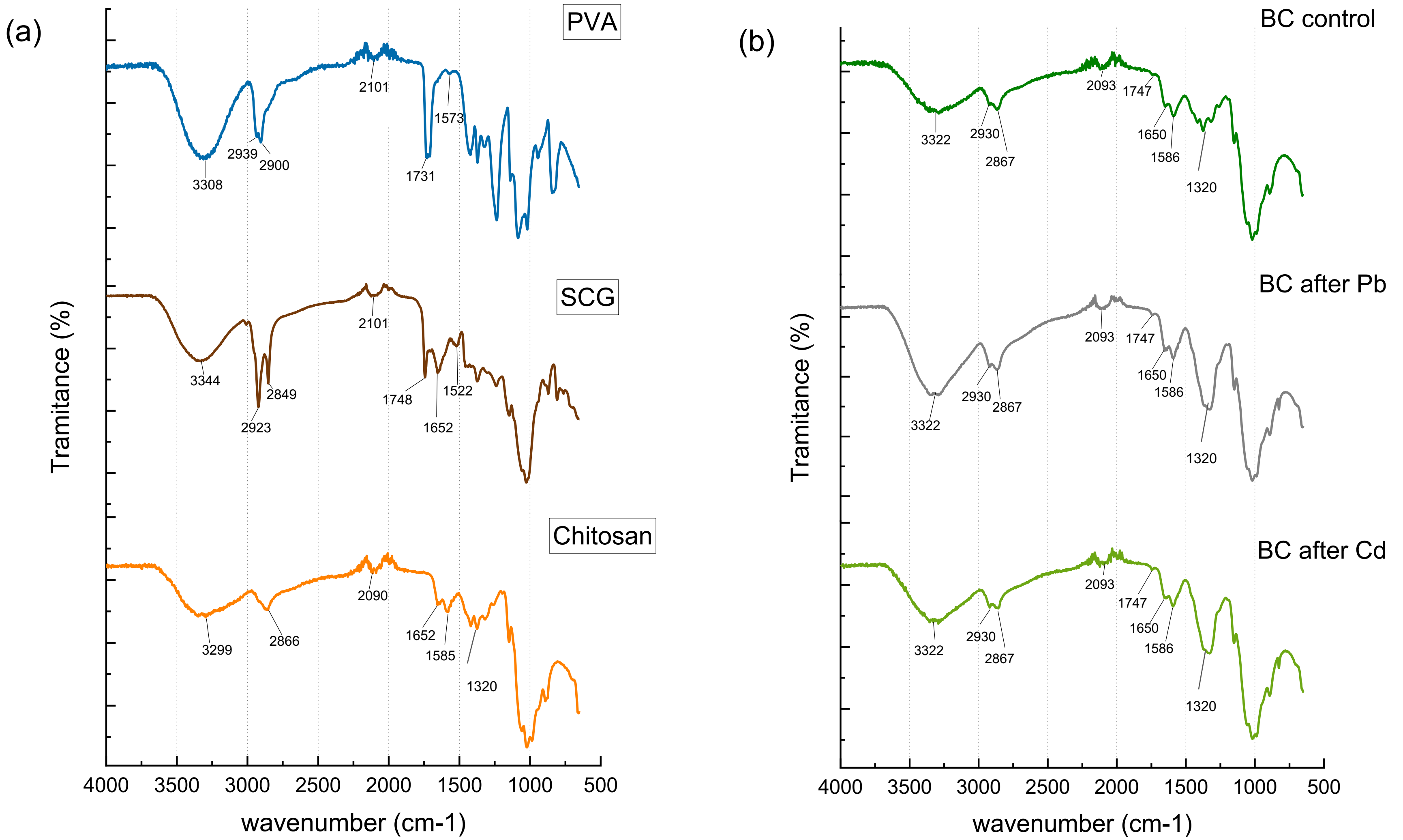


Figure 13.- *Fourier Transform Infrared spectroscopy of each component alone (a) and control bead (b) before and after adsorption of Lead (Pb) and Cadmium (Cd).*

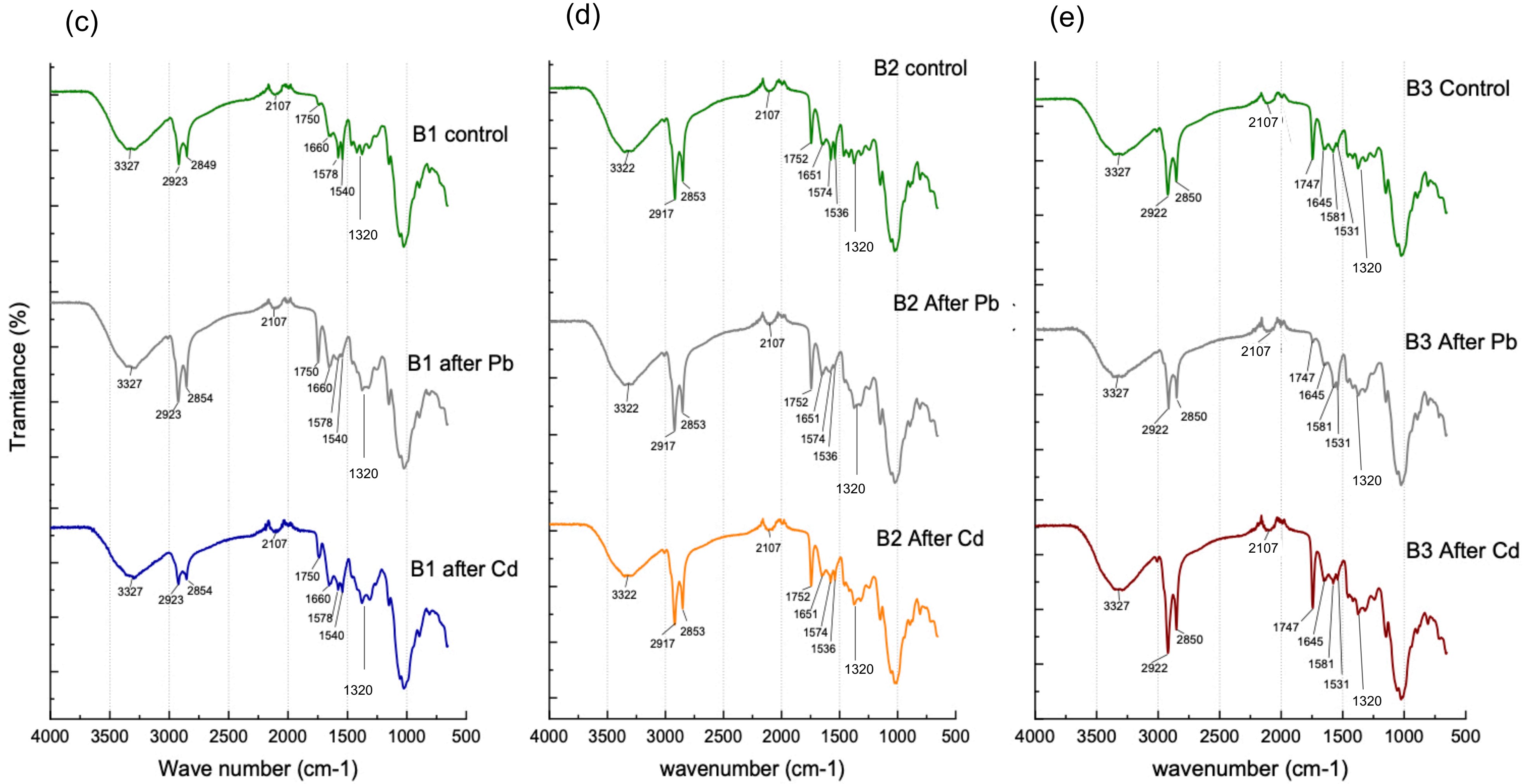


Figure 14.- *Infrared spectra of beads B1 (c) B2(d) and B3 (e) before and after adsorption of Lead (Pb) and Cadmium (Cd*

5.2 Determination of surface area (BET)

The BET Surface area for all beads in the study are shown in Table 4. Despite the fact the surface area values are very low in general the range is narrow, and distinctive of non-porous materials (Taborda-Acevedo, E. A., et al 2016), which can be corroborated by the SEM images in figure 15.

This characteristic didn't affect the removal of heavy metals, as shown in the removal efficiency results, the removal of heavy metals was enhanced for the beads with less surface area such as B2 Cd and B3 Cd (0,257 and 0,250 m²/g respectively). However, some significant changes in surface area can be perceived when comparing the before and after adsorption values of beads B1, B2 and B3

B1 was the bead that showed the more drastic changes in its final surface area after adsorption. Posterior to the adsorption of lead, there was a significant decrease from 0,503 to 0,317 m²/g, and an opposite change after cadmium adsorption, in which the surface area had an increase to 0,669 m²/g.

When it comes to B2, the changes after adsorption are not as drastic as B1 and opposite. In this case after the adsorption of lead is possible to observe a slight increase from 0,307 to 0,396 m²/g and after cadmium adsorption a decrease to 0,257.

For the last bead in study (B3) it showed a continuous decrease in the surface area after lead and cadmium from 0,375 m²/g to 0,283 and 0,250 m²/g respectively.

These results signals that the mechanism responsible for the adsorption of cadmium and lead in the beads is through surface anionic exchange, due to when crosslinking chitosan, some modifications on the surface will occur by incorporation of new functional groups from the additional components in the mixture (Mahaninia, M. H., & Wilson, L. D. 2015; Jin, L., & Bai, R. 2002) and thus independent of their surface area. Another plausible explanation could be technical issues related with the degassing time and temperatures of the beads prior to measurements of the surface area, in which the author had limited time to perform these experiments and thus only one repetition was possible to perform.

Table 4.-*Surface area obtained before and after adsorption of lead and cadmium.*

Sample	BET surface area (m^2/g)
BC BC Pb BC Cd	0,437 0,461 0,422
B1 B1 Pb B1 Cd	0,503 0,317 0,669
B2 B2 Pb B2 Cd	0,307 0,396 0,257
B3 B3 Pb B3 Cd	0,375 0,283 0,250

5.3 Scanning Electron Microscopy (SEM)

The Surface morphology at different magnifications (Figure 14) of only one bead was obtained in this study due to technical issues. However, it can be seen from the pictures that the bead (B2) shows a rough surface due to the incorporation of SCG in the blend, yet in some areas it looks smooth due to the crosslink of chitosan with PVA (Li, J. et al 2017; Zhu, Y. et al 2014) this smooth surface area wasn't a problem for the adsorption of metals since this bead was among the highest in the removal efficiency rate (Figure 16-17) as well as in second and fifth smallest surface area range of all beads. Nevertheless, these hypotheses could be corroborated by performing elemental analysis of the beads after adsorption, which leaves an open door to continue with further research of this type of composites.

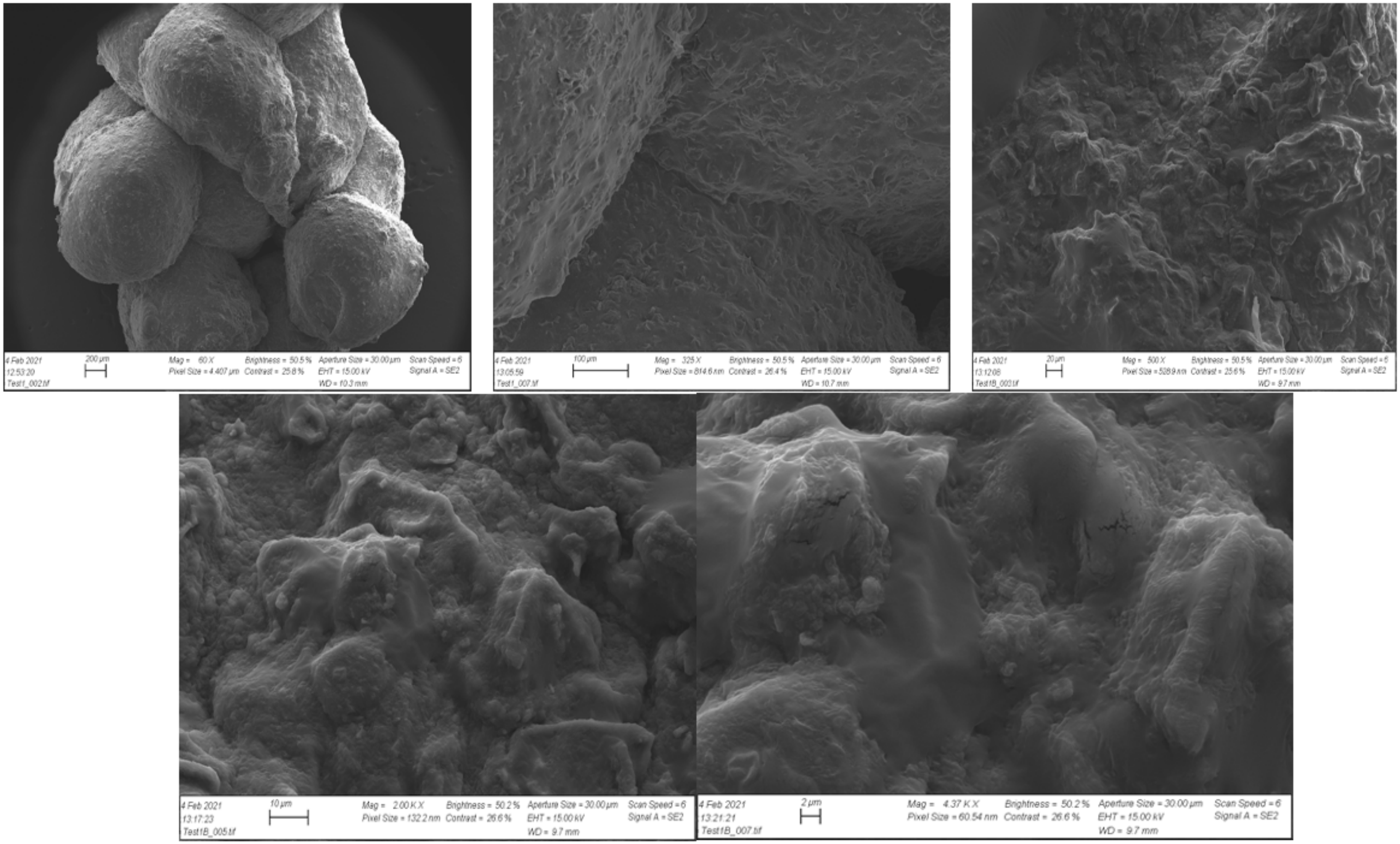


Figure 15.- *Scanning electron images of bead B2.*

5.4 Adsorption Models Studied.

5.4.1 Removal efficiency

The removal efficiency of all beads was obtained after the kinetic adsorption studies, unfortunately due to technical issues there is no data available for bead B1 after the adsorption of lead.

It is possible to observe that the highest removal was achieved by B3 for both heavy metals (72,7% for Cd and 69,1% for Pb). Noteworthy that this bead contained the highest amount of SGC and PVA, matching with the hypothesis proposed as well as literature, in which Lavecchia, R. et al. 2016, describe that only the use of untreated SCG was able to absorb up to 85% of lead in water. Consequently, the removal efficient decreased for B2 as expected. However, B1 presented a lower value than the control bead BC for cadmium, these values weren't projected since it was hypothesized that the addition of SCG and PVA would enhance gradually the removal of Pb and Cd from the solutions.

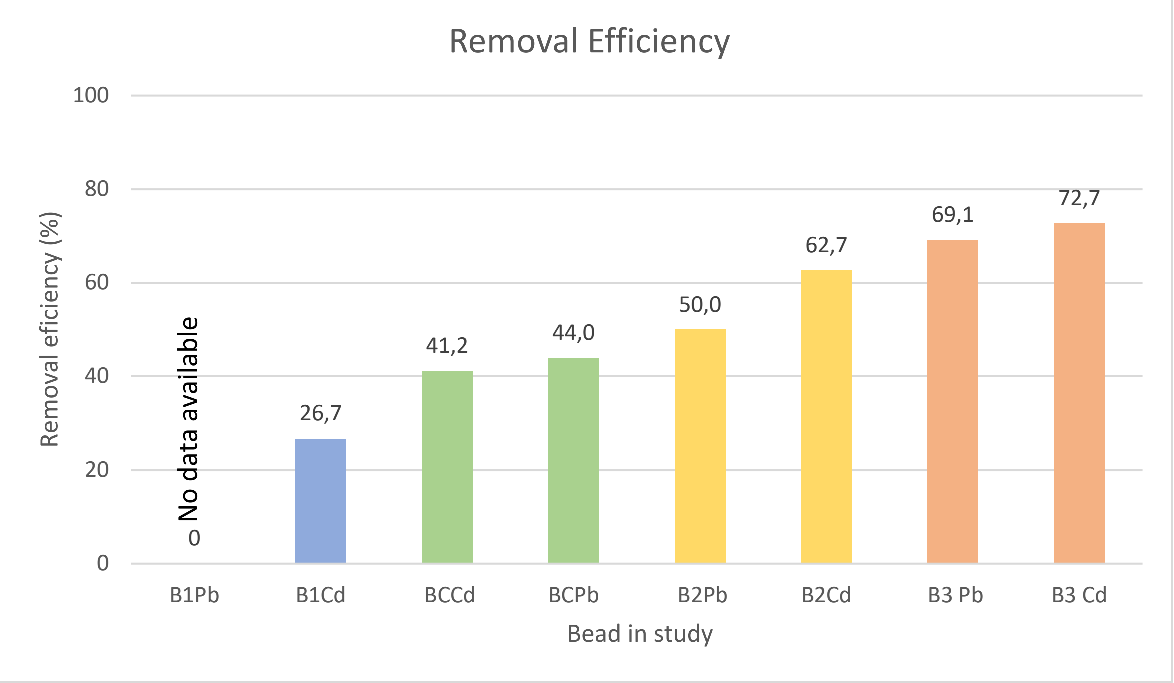


Figure 16.- *Removal efficiency of lead and cadmium for each bead studied.*

5.4.2 Linear and Non-linear Isotherm Adsorption

Table 5 and 6 shows the most important parameters obtained for linear and non-linear expression of the isotherms used in this study.

According to the linear expression, it’s possible to determine that the correlation coefficient (R^2) was low, implying that errors during experimental manipulation, the narrow concentration rate used 0,1-0,3 mg/l (Ho, Y. S. et al. 2002), and the fact that only one batch repetition per bead was performed could have occurred, as well as that the use of linear expressions of isotherm models might increase the bias and thus errors of the data that will not be representative of the regression coefficients, as stated before by López-Luna, J. et al. 2019. Conversely, it was possible to obtain some positive values in which the Non-linear expression of the three isotherm models fitted for certain beads, however a percentage of the correlation coefficients were inconsistent and even negative for Freundlich and Temkin isotherms of both heavy metals.

Further analysis of the data revealed that the correlation coefficient R^2 for non-linear Langmuir and Temkin model poses a better fit for the adsorption of cadmium instead of lead (Table 6), in which only B2 was close to obtain a R^2 value that could be accepted as valid for the adsorption of lead (0,941). Nevertheless, when analyzing the R_L (adsorption nature constant) and b_F (adsorption intensity constant) of Langmuir and Freundlich isotherms (respectively), both parameters show values within 0 and 1 indicating a favorable adsorption for both metals, as well as for the linear and non-linear expressions even though the R^2 values weren’t homogeneously distributed.

For the linear expression, the R^2 values obtained, only B1 and B2 presented a fit for Langmuir isotherm in the adsorption of cadmium (0,983 and 0,979 respectively). Indicating again that this form of the equation could not be reliable when calculating the adsorption behavior for this kind of composite beads and the experimental conditions used.

Furthermore, the maximum adsorption capacity values (q_{max}), was more consistent when applying the non-linear expression approach, in which all values were positive and B2 obtained the highest adsorption capacity for cadmium 199,61 mg/g, followed by the adsorption of lead by B1 with 176,619 mg/g and B3 103,587 mg/g. However, B1 obtained the highest value for lead adsorption among both approaches (263,16 mg/g). This only corroborates the hypothesis that the linear approach only increases the errors for the final data.

Table 5.- *Adsorption parameters of Linear isotherms for all beads.*

Isotherm	Parameters	Lead (Pb)				Cadmium (Cd)			
		B1	B2	B3	BC	B1	B2	B3	BC
Langmuir	q_{max}(mg/g)	263,16	-39,53	-36,36	-57,47	0,01	0,01	-0,01	0,01
	K_L (L/mg)	-1,55E-03	7,61E-03	8,22E-03	5,79E-03	557,21	173,48	-9,49	21,10
	R_L	1,000	0,999	0,998	0,998	0,010	0,032	2,981	0,210
	R^2	0,088	0,879	0,266	0,344	0,983	0,980	0,180	0,576
Freundlich	K_F	0,003	0,003	0,011	0,005	32946,80	524,32	0,46	41,00
	b_F	0,009	0,083	0,324	0,114	2,961	1,686	0,441	1,075
	R^2	0,018	0,049	0,409	0,067	0,865	0.1023	0,063	0,545
Temkin	B_T	-3,99E-04	-4,09E-03	1,25E-02	4,53E-03	1,32E-02	1,75E-03	5,37E-02	1,37E-02
	K_T	1,89E-31	4,04E-04	7,65E+02	2,05E+05	1,03E+04	1,16E+12	5,39E+01	1,18E+02
	R^2	0,004	0,116	0,481	0,085	0,018	0,058	0,741	0,393

Table 6.- *Adsorption parameters of Non-Linear isotherms for all beads.*

Isotherm	Parameters	Lead (Pb)				Cadmium (Cd)			
		B1	B2	B3	BC	B1	B2	B3	BC
Langmuir	q_{max} (mg/g)	176,619	0,059	103,587	0,110	40,16	199,61	0,04	0,08
	K_L (L/mg)	0,000	0,178	0,178	0,073	1,59E-04	2,73E-05	1,34E+06	-1,23E+05
	R_L	1,000	0,974	1,000	0,989	1,00	0,999996	4,96E-06	-5,40E-05
	R^2	0,802	0,941	0,476	0,647	0,944	0,951	0,999	0,999
Freundlich	K_F	1	0,065701	1	1	1,00	1,00	1,00	1,00
	b_F	1	1,00171	1	1	1,00	1,00	1,00	1,00
	R^2	-7,439	-5,172	-8,542	-7,429	0,673	-0,003	-13,467	-17,701
Temkin	B_T	2,41E-02	0	1,26034	1,2618	3,56002	2,12005	2,96121	1,07523
	K_T	1,78E-31	0	17,42942	0,066936	45,5814	100,96707	33,54625	31,61803
	R^2	-0,339	-4,985	0,212	-0,245	0,999	0,999	0,819	0,393

5.4.3 Adsorption Kinetics

Table 7 show the parameters for the kinetic parameters obtained in this study. The data shows that the R^2 values of cadmium adsorption follows a pseudo second order kinetics for B2 (0,982), B3(0,991) and BC (0,982). Demonstrating that this model is the one who represent better the adsorption of cadmium for this type of composites. These beads also presented the highest adsorption rates (K2) for cadmium adsorption, indicating high affinity for this metal to the beads in special with BC. Contrary the K2 value for lead revealed low and even negative data. One exception was bead B1, which even though its correlation value was neglectable (0,448) the adsorption rate was the highest among all (K2= 547,43 g/mg·min) which according to Choi, H. J. 2019, who studied the adsorbing behavior of a similar type of composites with lead, showed a high adsorption capacity for this heavy metal whit better pseudo second order fit.

When analyzing pseudo first order parameters data, neither lead nor cadmium showed a fit for this model, as well as low magnitude values of K1 for lead and negative for cadmium, which according to Lopez-Luna, J. et al. 2019, this could suggest a deprived or repulsion adsorption behavior between these beads and heavy metals. In addition, despite the adsorption capacity data was low, the calculated (q_e cal) and experimental (q_e exp) values weren't much diverse.

***Table 7.**-Adsorption kinetics parameters for all beads in study.*

Kinetics	Parameters	Lead (Pb)				Cadmium (Cd)			
		B1	B2	B3	BC	B1	B2	B3	BC
Pseudo 1st Order	q_e exp. (mg/g)	0,0023	0,0038	0,0035	0,0023	N.A	0,0038	0,0031	0,0024
	q_e cal. (mg/g)	0,0002	0,0064	0,1732	0,2006	N.A	0,0020	0,0013	0,0016
	K1 (min-1)	0,0014	0,0011	0,0004	0,0004	N.A	-0,0025	-0,0035	-0,0044
	R^2	0,746	0,531	0,109	0,109	N.A	0,819	0,000	0,783
Pseudo 2nd Order	q_e exp. (mg/g)	0,0023	0,0038	0,0035	0,0023	N.A	0,0038	0,0031	0,0024
	q_e cal. (mg/g)	0,0029	0,0077	0,0044	0,0056	N.A	0,0067	0,0072	0,0044
	K2 (g/mg· min)	547,43	6,08	51,14	-99,53	N.A	20,097	23,008	32,054
	R^2	0,448	0,595	0,904	0,959	N.A	0,982	0,991	0,982
Removal efficiency	% average	26,7	50,0	44,0	72,7	N.A	62,7	69,1	41,2

NA= no data available

6 FUTURE PERSPECTIVES

In order to have a full understanding on how these beads works, multiple additional studies should be conducted, which could lead to uncountable options. Nevertheless, studies about improving the adsorption efficiency must be the first of this list.

It has been proposed to carry on with a packed-bed or plug flow reactor, that could be a good application for these beads after comparison to batch results obtained. There are many advantages such as scalability, more retention and contact time, easier analysis of sorption and desorption experiments, that might result into high efficiency removal of heavy metals, since in batch experiments, the way is carried out can affect the capacity of a particular type of adsorbent to chelate metals and certain variables cannot be controlled such as flow rate, it would be more precise to conduct this in a packed column in which by controlling this parameter it will result in a fast an highly effective removal of pollutants. (Lu, Y., He, J., & Luo, G. 2013; Popuri, S. R et al. 2009).

Other important parameter that was not studied in this research correspond to the zeta-potential of the beads, and how changes in pH could affect the pKa values of all the multiple functional groups from chitosan/SCG and PVA present in the composites.

7 TECHNICAL ISSUES

This thesis was performed with some important limitations since it was executed from the beginning of the COVID-19 shutdown period in Norway. All these shortcomings delayed the delivery of essential kits, reactants, and the fact that some of the equipment was out of service in the university laboratories with no local availability of entitled technical personnel to fix them expeditiously.

The initial focus was changed several times to work with what we had to our reach in conjunction with the help of the petroleum and material department personnel who delivered practical training in precise time to use equipment or just performed the experiments by themselves and posterior delivery of the results to be analyzed by the student.

Nonetheless, the outcome is expected to give a general view of the proficiency for this type of "waste composites" to adsorb heavy metals and to possibly become a feasible solution for water remediation with an environmental and circular economy approach.

8 CONCLUSIONS

According to the TGA analysis. B3 is somewhat more tolerant the temperature changes in contrast with BC, B1 and B2, indicating that higher amounts of SCG and higher concentration of PVA, grants more thermal stability to the composite.

FTIR analysis corroborated that ion exchange might be the dominant mechanism for adsorption of these beads, due to the presence of carboxyl, amine, amide, nitrogenous and hydroxyl functional groups. This can as well be supported by the low range surface area values obtained though BET.

The combination of Ch/SGC/PVA adds reinforcement and a smoother surface area, despite of the addition of coffee grounds into the mixture, due to the crosslink capacity of PVA and Ch.

According to the removal efficiency values obtained for B3, it is possible to accept the hypothesis in which the higher the concentration of SCG and PVA enhanced the chelation and thus remotion of both heavy metals in solution. The main advantage of Ch-SCG-PVA beads (B1, B2, B3) over only Ch bead (BC) is that the adsorption sites of Ch-SCG-PVA showed higher removal efficiency.

The utilization of the non-linear isotherms, is a good approach to determine the adsorption behavior of this kind of composites, reducing the bias and obtaining better correlation (R^2) and q_{max} values.

So far this mixture of composites hasn't been found in literature, only mixtures of two component at the time have been studied, such as PVA/SCG, Ch/PVA and SCG/Ch. Thus, it turns them into a novel utilization of the literature and could become cost-effective because the inexpensiveness of the raw materials and the potential recycle, which is very significant in terms of the continuous circulation of resources, and a good competitor with other absorbent composites, opening new doors for the utilization of waste as useful nontoxic bio-sorbents.

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