

Chicken Eggshell as a Potential Eco-friendly, Low-cost Sorbent: A Mini Review

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Abstract

Water and soil are the basic needs of human being. Urbanization and industrialization activities are growing day by day, as we know mining, smelting, agriculture, and other industrial enterprises etc. are playing a vital role in any country's economic growth. But these anthropogenic activities create a somber environmental pollution. For the sustainability of green environment, many studies have reviewed for the removal of toxic heavy metal i.e. ion exchange, reverse osmosis, chemical precipitation, flocculation, electrolysis, coagulation etc. however, these methods have several disadvantages such as unpredictable metal ion removal, toxic sludge generation, requirement of huge amount of reagents etc. Adsorption is a very easy, cost-effective process that has become a best-preferred technique for the removal of toxic heavy metal contamination in soil and water. Cost is the important factor for the selection of adsorbent material and the expense of individual adsorbent varies depending upon its local availability and the degree of processing. Several natural adsorbent materials are available in the world. This paper reviews the use of highly efficient, cheap and readily accessible kitchen waste eggshell. Eggshell is one of the most environmental friendly and cost effective sorbent, due to high CaCO₃ concentration, which helps to restrain heavy metals, fluoride, phenol, and petrol etc. from contaminated soil and water, due to its physiochemical properties eggshell has many applications in the field of bioremediation, material, and metallurgical sciences. This sorbent is being proved to be a more useful and environmental friendly.

Keywords: Adsorption, Anthropogenic, Eggshell, Heavy metals contamination, Low-cost sorbent.

1. Introduction

Heavy metal contamination in soil and water are the main issue of global concern, Anthropogenic sources like mining, mineral processing, coal burning, sanitary landfilling, lather effluents, chemical industries, military operations, small and medium-sized industries are the major sources of heavy metal pollution in soil and water bodies, they create a harmful effects on human health and ecosystem (Wang *et al.*, 2005; Khan S *et al.*, 2008; Zhang MK *et al.*, 2010).

There are many procedures for to overcome the problem of heavy metals in soil and wastewater such as ion-exchange, ozonation, chemical precipitation, photochemical method, adsorption etc. (Atkinson BW *et al.*, 1998; Patterson JW, 1985; Ok YS *et al.*, 2007). But generally, the most procedure required a second step for to finish the process, Adsorption is the technique which is frequently used for the removal of heavy metal from several small and medium-size industrial effluents (US EPA, 1997; Farrell M *et al.*, 2010; Gottipati R *et al.*, 2012). In this method an inexpensive and cost-effective exterior agent used to fix the toxic metals. Adsorption is the best technique for the toxic metal removal, especially when the metal concentration is in range of 1-100ppm (Volesky B, 2001; Ruttens A *et al.*, 2010; Houben D *et al.*, 2012). Nowadays there is the main concern is to find out best cost-effective sorbent i.e. eggshell, is a low-priced sorbent which is used to consider as a kitchen waste. (Tsai WT *et al.*, 2006; Benaissa H, 2008; Ok YS *et al.*, 2010).

The egg is the secondary diet product worldwide, the utilization of egg as a food in Korea is 540,542 tons annually, and they are gradually increasing. Mostly all over the world Chicken eggshell disposed of in landfills annually as a waste (Clesceri LS, 1998; Ahmad R *et al.*, 2012). Eggshells are mainly rich in calcium carbonate, as compare to other lime materials, it is an ideal sorbent for the treatment of heavy metals in contaminated soil and water (OK YS *et al.*, 2007). It is used as an alkaline compound and also used as a bio-remediate tool for petrol contaminated soil, due to its physiochemical properties eggshell have many applications in the field of bioremediation, material and metallurgical sciences (Park HJ *et al.*, 2007; Arunlertaree C *et al.*, 2007; Pundir CS *et al.*, 2009). For pre-treatment process of contaminated soil and water, use of eggshell is a "green" approach because of its biodegradability and environmental friendly nature (Chojnacka K, 2005). As we know there are three main points of "green" industrial processing, number one is the recovery of heavy and precious metal, number two is minimized harmful waste, and the last one is maximized regeneration of useful and valuable energy and waste. So, in the term of eggshell, we should recycle and reuse this waste to minimize toxic metal ion contamination (Arami M *et al.*, 2006).

1.1 Overview of heavy metal contamination around the world

Global development of recent eras creates many environmental problems throughout the world. In Pakistan all metropolitan cities affected by messy and unplanned expansions due to the migration from rural to urban areas. Random urban crowding is the main reason of maximum utilization of natural resources, the lack of funding and unavailability of fresh water many peoples constraint to use contaminated water for domestic use (WWF, 2007; PCRWR, 2010). Groundwater is the main source of water in major big cities of Pakistan. Research disclosed that many industrial activities like textile manufacturing, mining, fertilizer, petrochemical production are the main source of the contamination of groundwater (PCRWR, 2010). Because of rapid development of urbanization and industrialization of past 20 years, chronic effects due to the pollution of heavy metal in their urban soil are seen in China (Wei B and Yang L, 2010). There are several published studies that have highlighted the heavy metal contaminated areas in many cities of China such as Xuzhou (Wang XS and Qin Y, 2006), Nanjing (Lu Y *et al.*, 2003), Guangzhou (Lu Y *et al.*, 2007), Changchun (Guo P *et al.*, 2005), Honking (Luo X *et al.*, 2011), Shanghai (Shi G *et al.*, 2008), Hangzhou (Zhang M and Ke Z, 2004), Beijing (Zheng Y *et al.*, 2008) Shenyang (Li F *et al.*, 2009).

According to ENS 2006 news report, Linfen city of China affected maximum load of pollution, Mailuu-Suu city of Kyrgyzstan is faced radioactive uranium contamination from mines, Pristan suffers lead contamination from local mines, lead and cadmium mining is widespread in Zambia. According to (Dembitsky, 2003; WHO, 2006) coastal areas has been threatening by mining activities, they release a lot of harmful substance and playing a vibrant role to pollute our environment. Sea animals affected by such kind of activities and they create a toxic effect on living organisms, some traces of heavy metal found in 31 coastal areas of China (Lion GN and Olowoyo JO, 2013). Previous data showed that due to heavy metal pollution ecological and agricultural environment are threatened and approximate 10 million hector of Chinese land is being contaminated (Chen L, 2009; Chen X, 2009; Zhao Q *et al.*, 2014). In Baiyin city China some villages are adulterated with toxic heavy metal, they create a possible health risk for the residential population of the area (Li Y *et al.*, 2006). Dabaoshane Mine, Guangdong province China is facing a serious toxic element contamination of their soil, and potential health risk is increasing day by day (Zhou J *et al.*, 2007). Export Processing Zone Dhaka is one of the biggest industrial sector of Bangladesh, in this sector there are many industrial units like leather goods, fertilizers, chemicals, metal production, garments, textile, and others many manufacturing units which are unambiguously a major source of pollution in Dhaka city (Khan MK *et al.*, 2011; Khanam D *et al.*, 2011). Massawippi and Saint-François rivers Canada are being affected by industrial and urban waste. Eustic mine disposed site also creates a harmful effect of Massawippi river basin (Berryman D and Pelletier L, 2001). Sulfurous mine waste is a major issue of Eustic creek Canada (St-Laurent J *et al.*, 2009). Eustic creek is highly contaminated by toxic heavy metal, there are some illegal hydrocarbon discharge spots along the river bank site of Drummondville and Massawippi rivers (St-Laurent J *et al.*, 2009). Jajmau, Kanpur India has suffering from tannery waste. The soil of Uttar Pradesh contaminated with Cu, Zn, Pb etc. (Sinha S *et al.*, 2014). Agricultural land of Agia (Greece) and Hong Kong affected by the chronic concentration of lead (Muramatsu Y and Wedephol KH, 1998; Alghobar MA, Suresha S, 2017). Some specific areas of Saudi Arabia and Africa where agricultural land irrigated by sewage wastewater have a potential risk of heavy metal contamination (Jiangming MO J *et al.*, 2008; Alghobar MA, Suresha S, 2017).

1.2 Poisonous effect of toxic elements

Heavy metals are lead, chromium, mercury, uranium, selenium, zinc, arsenic, cadmium, silver, gold, nickel, fluoride etc. The specific gravity of heavy metal is approx. 5.0, and atomic weight is between from 63.5 to 200.6, typically heavy metals are perilous and harmful for human health and ecosystem (Ahalya N *et al.*, 2003). Around 30 chemical elements that they are possibly a chronic part in various physiological disease in human body and ability to bio-accumulate in human life. Indications highlight the results of poisoning effect of heavy metals comprise mental illness of adults, hormonal disability of children, kidney and liver disease, nervous system breakdown and vision disturbance (Flora SJS, Mittal M and Mehta A, 2008; Jan AT, Ali A and Haq QMR, 2011). Many studies show that high concentration of heavy metal have an adverse effect on human body they affect human metabolism, nervous system and create hormonal changes of growing age children (Kumar A *et al.*, 1998; Tripathi RM *et al.*, 2001; Gasana J *et al.*, 2006). Additional intake of these trace elements through food and other sources are profound destructive effect of pathological disease, deposition of redox active metals, iron oxides create Parkinson's, cancer, allergies, birth defects, psychosis, autism, kidney damage, dyslexia, muscular weakness, weight loss, hyperactivity, paralysis, brain damage, and even death (Papanikolaou NC *et al.*, 2005; Candelaria M *et al.*, 2006; Umanzor J *et al.*, 2006; Elst P *et al.*, 2007 Mudgal V, Madaan N and Mudgal A. 2010). Sources and health effects of heavy metals are defined in Table I.

2. Eggshell as a green adsorbent for heavy metal removal

Local geology and eco-system play a vigorous role of water and soil quality of any specific area, as we know soil

and water bodies are a universal sink for human use (Johnson DL *et al.*, 1997). Currently, they endure with a huge amount of environmental toxic waste.

2.1 Soil

By the definition of soil contamination, it is stated that accumulation of toxic elements in soil such as disease-causing agents, chemicals, radioactive material creates chronic effect of human health, animals and plant growth (Okrent D, 1999). Consider foods are grown in healthy soil. The soil is the mixture of inorganic and organic material, the inorganic portion is the combination of broken rocks fragments these rock fragments formed due to the activities of natural, physical and chemical weathering, while organic portion derived from the decay and disintegration of animals and plants (Belluck DA *et al.*, 2003).

According to Swartjes FA, 1999, the source of soil pollution can be categorized into two types and agricultural source and the second one is non-agriculture source, where soil becomes polluted from seepage of solid waste, discharge of industrial effluent from pesticides, petroleum, hydrocarbon, textile, leather, chemical and metallurgical industries etc.

There are three mechanisms to restrain the heavy metals in contaminated soil. These methods are as follows complexation, precipitation, and coprecipitation. These toxic metals immobilization methods could be improved by adding the mixture of organic and inorganic alteration in soil (Farrell *et al.*, 2010; Park JK *et al.*, 2011). There is a large quantity of cheap and easily available industrial waste, and natural material such as lime-based material like the eggshell that they help immobilization of toxic metals in soil (Guo G *et al.*, 2006; Gadepalle VP *et al.*, 2007; Ruttens A *et al.*, 2010).

To remediate a toxic metal in soil, an alternative source of lime-based material is the eggshell, the best choice for immobilization (Ok YS *et al.*, 2011; Lee SS *et al.*, 2013). According to Ok YS *et al.*, 2011 five extractants were used to evaluate the extractability of heavy metal in contaminated soil after eggshell treatment. He found EDTA and CH₃COOH are a good extractants, and study concluded that for the immobilization of cadmium and lead eggshell can be used as an alternate of calcium carbonate. Another study has conducted by Mehrnaz A *et al.*, 2015 to evaluate the eggshell immobilization strength against heavy metal, her result indicated that eggshell sharply decreased the concentration of cadmium and zinc in leachate.

2.2 Water

Environmental water quality is also known as ambient water quality which relates such as an ocean, river, ponds, and lakes. Due to different environmental condition and human uses surface water quality standards vary from site to site. Many human activities like swimming, irrigation, industrial and mining activity pollute water bodies in the sense of toxic substance, and due to high population growth of chronic microorganism, increase of population growth and industrial development clean and fresh drinking water demands are increasing day by day. Because of toxicity and non-biodegradability inorganic pollutant like toxic heavy metal is the major issue in the marine environment (Pan B. *et al.*, 2006). There are several toxic elements removal techniques for the removal of heavy metal from aquatic system, but due to low operating cost, eco-friendly and highly efficient sorption process immobilization found a best result as compared to others conventional system (Villaescasa I *et al.*, 2004; Fiol N *et al.*, 2006; Ahmady-Asbchin S *et al.*, 2009). Numerous research discussed the adsorption capacity of eggshell powder for adsorption of Cu⁺² and Fe⁺² (Yeddou N *et al.*, 2007; Ennil Kose TE and Betul kivance, 2011; Ahmad R *et al.*, 2012). Eggshell contain (80-95%) of calcium carbonate many studies proved that the chicken eggshell has been applied as a toxic heavy metal sorbent in the process of wastewater treatment (Suyama K *et al.*, 1994; Park HJ *et al.*, 2007; OK YS *et al.*, 2010). Hydroxylapatite (CHAP) is a good and effective adsorbent, it has an ability to immobilization of heavy metal (Ma QY *et al.*, 1995; Laperche V *et al.*, 1997), according to Weizheng *et al.*, 2007, eggshell derived CHAP gives the best results for removal of Cd and Cu in aqueous solution. Phenol toxicity is a concern because it is found in gasoline, pharmaceutical, fertilizer and rubber industries (Calace N *et al.*, 2002). Jou-Husuan Ho *et al.*, 2014, He concludes this concept that as a "green" adsorbent material derivatives of eggshell have a great potential for the treatment of silver and nickel contaminated wastewater, eggshell membrane is an excellent adsorbent to maximize the adsorption process to reach its standard discharge value. Eggshell gives paramount results for adsorption of phenol in aqueous solution (Yeddou N *et al.*, 2007; Boukhelifi F *et al.*, 2013). As we know that fluorine is an electronegative element, it is a globally present as a fluoride on earth (Kugali NM and Yadawe MS, 2010). Water bodies are the main source of fluoride contamination and its intake of human bodies (WHO, 2006). Chronic effects of fluoride are irredeemable damage of skeletal fluorosis and loss of calcium in human bodies (Emamjomeh MM, *et al.*, 2005). Studies show that role of the chicken eggshell is suitable for the removal of F⁻ from aqueous solution, thermodynamic studies propose the removal of fluoride from aqueous solution is an exothermic and spontaneous reaction, eggshell is an effective sorbent for removing of fluoride from wastewater (Bhaumik R *et al.*, 2012).

2.3 Eggshell towards textile dyes

Present record shows that textile dyes waste effluent is a major source for creating the toxic and carcinogenic effect of marine life (Crini, 2006; Mahmoodi *et al.*, 2006). Kannan and Sundaram, 2001; Meshko *et al.*, 2001, said that because of low cost and easy availability of raw material sorbent eggshell, adsorption through eggshell is an excellent practice for treating textile effluent. As eggshell membrane contains polypeptides and polysaccharide present in their inner surface (Allen *et al.*, 2000). Study of Scanning Electron Microscope shows that Eggshell membrane has a valuable amount of pores this is a good ability to trapped dyes and absorbed into their pores (Mokhtar Arami *et al.*, 2006).

2.4 Removal of Phosphate

Agriculture and industrial effluent is a source of the pollution of phosphate in water bodies (Huang X *et al.*, 2009). According to standard if phosphate concentration is more than 2um it assumes to be a dangerous and alarming situation, an excessive amount of phosphate reduces the oxygen level in water bodies and is harmful for the aquatic environment (Mustufa S *et al.*, 2008). Adsorption through low-cost sorbent is very popular treatment method for phosphate removal (Li Y *et al.*, 2006; Krishnan KA *et al.*, 2008; Jeon DJ *et al.*, 2009). According to (Ennil Kose T *et al.*, 2011), Eggshell is an effective adsorbent for the removal of phosphate from aqueous solution, the adsorption capacity of a calcined waste eggshell is approx. 99% with pH range from 2 to 10. The descriptive study indicated that after adsorption, the bond between phosphate and adsorbent is very strong and due to its high nutrition contain it should be used as a fertilizer or soil conditioning agent.

3. Characterization of eggshell

Eggshell made by three-layered named are cuticle on the outer surface, the spongy (calcareous) in the center and lamellar in the inner part, these all layers consist of ceramic material (Stadelman, 2000). There are two shell membrane around the eggshell a thin membrane and a thick membrane (Nakano T *et al.*, 2003). Eggshell membrane owns water-insoluble fibers, intricate lattice network and also has a high surface area for many application like adsorbent (Tsai WT *et al.*, 2006). Chicken eggshell has assessed approximately 7000 to 17000 pores in their shell, this pores nature considered as a valuable and cheap adsorbent material (William JS, Owen JC, 1995). According to the figure, I result of IR spectrum are 711.68, 871.35, 1394.62, 1794.86 and 3245.48 cm^{-1} (Erika Zamora- Villafranco *et al.*, 2014) this above result is accord as witoon T, 2011 research. Presence of C=O stretching shows in IR peak 1795 cm^{-1} , CO group indicated in IR peak 1397 cm^{-1} these both results are the property of calcium carbonate, scanning electron microscope result shows the little porous structure is attached to its membrane, such like structure is responsible the adsorption capacity of eggshell, similarly in figure II shows the X-ray Diffraction result shows the crystal structure containing calcite type of CaCO_3 (Erika Zamora-villafranco *et al.*, 2014). Chicken eggshell should be a best and valuable sorbent due to its cellulosic structure, small amounts of MgCO_3 , $\text{Ca}_3(\text{PO}_4)_2$ and contains amino acids and a mucopolysaccharide protein (Kalyani G *et al.*, 2009).

4. Adsorption properties of eggshell

Due to its high absorbent ability, they remove pesticides, heavy metal and phenolic compounds from wastewater and contaminated soil (Carvalho J *et al.*, 2011). PH concentration, micro-precipitation, and Ion exchange are the most suitable mechanism for metal removal from the initial solution (Mudhoo A *et al.*, 2012). According to Pettinato M *et al.*, 2015, there is no need to activation surface pretreatment because shell of chicken egg is very naturally porous structure and rich in fibrous protein, due to its typical chemical composition such as 2% of organic and 98% of inorganic compounds material they have the ability to permits gaseous exchange. Ultimate analysis of eggshell shown in Table II.

5. Adsorption kinetics

Adsorption Equilibrium and kinetics studies are the main factors for the fabrication of adsorption plant, for large-scale adsorption, this study is one of the significant parameters to plan and development of any project (Karaca S *et al.*, 2005). Langmuir, Redlich- Peter son isotherm and Freundlich isotherm are the famous models to estimate the adsorption features of eggshell (Vecchio A *et al.*, 1998; Gazc3, 2001; Acar FN & Malkov E, 2004). Eggshell membrane obeys the Redlich- Peter son isotherm (Mokhtar Arami *et al.*, 2006). Langmuir isotherm provides a significant model for the adsorption ranging from 0.83 to 0.990 (Ayodele RI *et al.*, 2014). For beneficial adsorption "n" value of Freundlich isotherm must between 1 to 10. According to Ayodele RI *et al.*, 2014, n value of Freundlich isotherm ranged between 1.41 and 2.89 this values indicated the beneficial metal ion adsorption through the eggshell.

Pseudo-first order model does not describe the adsorption process of eggshell, most cases, the pseudo-first-order equation for sorption process does not suitable for the whole range of contact time (Rao HJ, *et al.*, 2010), but the correlation coefficients ranged between 0.999 and 1.000 of pseudo-second-order model well designated

the kinetics of metal ions sorption, therefore it is stated that kinetics of the metal ions sorption is well best described by pseudo-second-order kinetic model rather than pseudo-first order. (Singha B *et al.*, 2011; Ayodele RI *et al.*, 2014).

6. De-sorption/reactivation of eggshell

Desorption study pH is a very important factor to support and assess the recovery and mechanism of adsorbent and adsorbate. Desorption process connected to the fact that, the number of negative charges increase by the increase in pH value. During electrostatic repulsion negative charges on the adsorbent favors desorption process, desorption study of eggshell proved that in alkaline pH condition result looks a high desorption rate of dyes which is ensured to recycle of the material in desired practice (Namasivayam C *et al.*, 2002; Yuzhu F *et al.*, 2002; Mokhtar Arami *et al.*, 2006).

Desorption efficiency improved with the increase of HNO₃ and NaOH concentration, this phenomenon might be credited to ion exchange interaction (Venkata *et al.*, 2002). Nitric and sodium hydroxide acids are sufficient to use for desorption process of metal ion from eggshell, desorption mechanism is sound suited with 3 mol L⁻¹ of sodium hydroxide (Ayodele RI *et al.*, 2014).

According to Alejandro Guijarro-Al daco *et al.*, 2011, an economical activated agent via modification of chicken eggshell surface chemistry to improve the adsorption capability of toxic heavy metal ions. This study shows that at high metal concentration the adsorption of heavy metal ion is affected by the co-ion competition and the range of metal reduction from 0.1% - 77%, this study provide the new vision and development of low-cost reagent for the removal of heavy metal in contaminated Soil and water.

7. Conclusion

Urbanization and industrialization are keys to growth, these activities generate a new type of environmental concern to our society, this drawback comprise worsening of our air quality, soil and water bodies and the outcome is that plants, animals, and human being are directly affected by these activities. Toxic elements like heavy metals gradually degrade and pollute our environment. To overcome this situation there is the urgent need for developing an efficient, easy, readily available and eco-friendly method for the remediation of this pollution. By using low-cost adsorbent, this process has a great potential for the removal of the toxic element from contaminated soil and water. This review concludes that due to high calcium carbonate, inexpensive easy and widely available chicken eggshell is found to be the most effective sorbent for the situ-immobilization of toxic elements. Adsorption through eggshell is proved to be a paramount option for this purpose. This practice should be implemented for to refurbish the quality of soil and water. For the green environment, more studies should be carried out for low-cost adsorption process to enhance the large-scale use of non-conventional adsorbents. Economical and abundantly available adsorbents should be used to minimize the cost and maximize the hazardous elements removal efficiency.

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Table I: Source and perilous effects of some typical heavy metals (Alluri HK *et al.*, 2007)

S.no.	Hazardous metal	Sources	Health effects	Permissible level (ppm)
1	Manganese	Smelting, welding, fuel mixing units etc.	Damage nerve impulses, cytoplasm, nucleus, and other organelles harming.	0.26
2	Cadmium	Fertilizer production units, metallurgical plants, woven and fabric industries.	Liver damage, lung cancer, kidney failure	0.06
3	Mercury	Paint, paper, rubber, battery and fertilizer industries	Mental illness, hair and teeth disease, pre-post-natal issues.	0.01
4	Zinc	Metal manufacturing, oil refineries,	Nervous system and skin disease.	15
5	Arsenic	Smelting, fungicides, fertilizer units	Mucous membrane and eczema disease.	0.02
6	Lead	Automobile, mining, paint industries.	Mental disorder, liver and kidney disease, muscular fatigue, effect during pregnancy,	0.1

Table II: Ultimate analysis of Eggshell Membrane (ESM) and eggshell particles (wt %). (Pettinato M *et al.*, 2015)

Samples	C	H	N	S	O
ESM	47.50	6.78	15.34	12.03	3.00
Eggshell	13.09	0.35	0.54	29.46	0.03

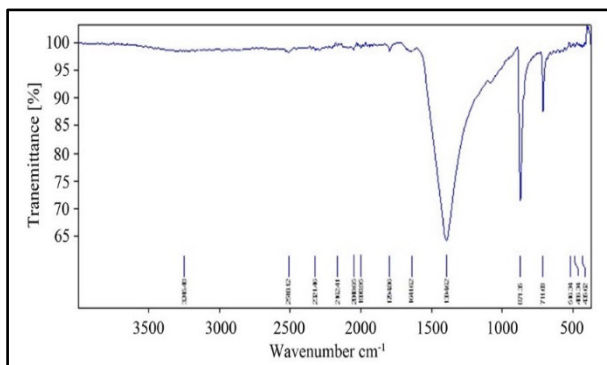


Figure Eggshell IR.

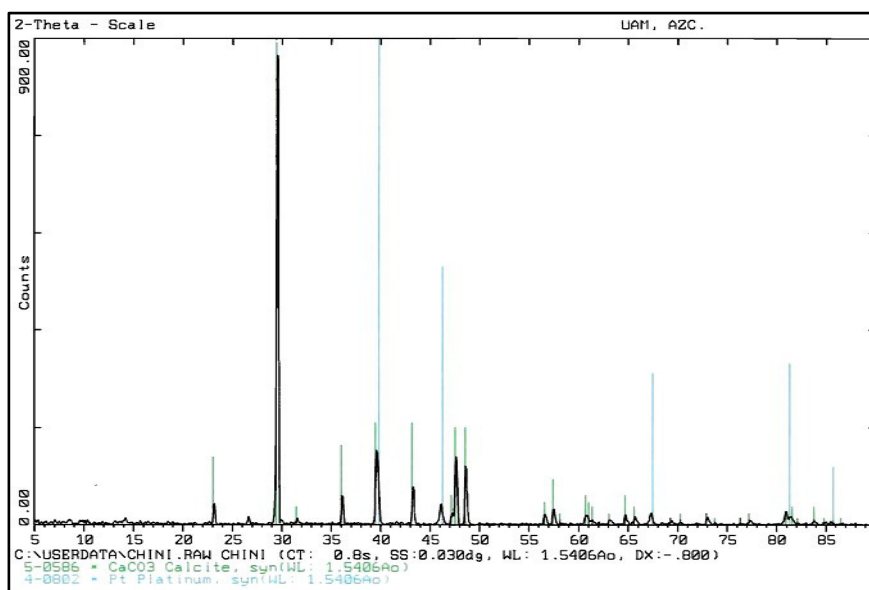


Figure II Eggshell RXD.